



KISII UNIVERSITY
UNIVERSITY EXAMINATIONS

FIRST YEAR EXAMINATION FOR THE AWARD OF THE DEGREE OF
DOCTOR OF PHILOSOPHY IN CHEMISTRY
SECOND SEMESTER 2022/2023
[MAY, 2023]

DPAP 921: ADVANCED ANALYTICAL TECHNIQUES

STREAM: Y1 S2

TIME: 3 HOURS

DAY: TUESDAY, 2:00 – 5:00 P.M.

DATE: 02/05/2023

INSTRUCTIONS

- 1. Do not write anything on this question paper.***
- 2. You should have the following for this examination;***
 - Answer booklet***
 - Scientific calculator.***
- 3. Attempt ANY SIX Questions (6) from the paper. ALL Questions carry the same marks.***

QUESTION ONE

- a) Using an illustration derive the wave number equation you can use in the teaching of IR Spectroscopy. (5marks)
- b) Use the equation derived in 11(a) above to calculate the following wave numbers
- C-C bond in ethane ($K = 4.5 \times 10^5$ dynes/cm)
 - C-C bond in benzene ($K = 7.6 \times 10^5$ dynes/cm)
 - Comment on the values obtained in b(i) and b (ii). (3marks)
- c) Discuss two sample preparation methods used in infrared analysis. (2marks)

QUESTION TWO

Fluoxetine is an antidepressant drug. The determination of fluoxetine and its metabolite norfluoxetine in serum is an essential part of monitoring its therapeutic use by BIOPHYCHEA research and consultancy firm. The analysis is complicated by the complex matrix of the serum samples. A solid phase extraction followed by HPLC analysis using a UV-visible detector provides the necessary selectivity and detection limits. An isocratic mobile phase mixture of water and acetonitrile is used to elute the sample using a column packed with C8-bonded stationary phase.

a) Define the following as used in HPLC;

- I) Selectivity
- II) Detection limit
- III) Isocratic elution
- IV) Resolution (3marks)

b) In HPLC analysis of fluoxetine and its metabolic norfluoxetine, you found that fluoxetine elutes with retention time of 7.63 minutes and norfluoxetine elutes at 5.68 minutes with a void volume of 0.31 minutes. Calculate

- i) The capacity factor for fluoxetine
- ii) The selectivity factor for fluoxetine and norfluoxetine
- iii) The resolution of the two components if their base widths are 1.46 and 1.65 minutes respectively. (3marks)

c) Explain the purpose of including an initial solid phase in the extraction process. (2marks)

d) if the peaks for fluoxetine and norfluoxetine are insufficiently resolved, describe how the mobile phase might be altered to improve their separation. (2marks)

QUESTION THREE

You have been employed as a county Chemist in your home county and a metal has been discovered in your county suspected to contain zinc. Prepare a report to be presented to the county assembly to convince the members on the viability of extracting the ore by first

- a) confirm the presence or absence of zinc in the ore using AAS. (7½ marks)
- b) Estimate the amount of zinc in the ore by the AAS (2½ marks)

QUESTION FOUR

- a) Supercritical fluid chromatography is a hybrid between gas capillary and chromatography. Explain this statement in terms of;
 - i) Separation (1mark)
 - ii) Instrumentation (3marks)
- b) Discuss the principle involved in micellar electrokinetic capillary chromatography (2marks)
- iii) Explain how the technique in b(i) above differs from zone electrophoresis. (2marks)

QUESTION FIVE

- a) An organometallic sample which was suspected to be toxic has been brought to your office as the principal government chemist for analysis. Discuss which method between thermal desorption and headspace techniques you can use in the analysis of the sample. (6marks)
- b) Cite the conditions for use of reversed phase HPLC as a method of analysis. (4marks)

QUESTION SIX

Discuss the radioisotope decay process with suitable illustrations as analytical methods of analysis. (10marks)

QUESTION SEVEN

Discuss in detail neutron activation method as an analytical method of analysis. (10marks)

QUESTION EIGHT

- a) Explain how the following works
- i) Chemical ionization
 - ii) Matrix assisted laser desorption in mass spectrometry (4marks)
- b) Discuss in detail any three procedures of mass spectrometry used in the analysis of mixtures. (6marks)

QUESTION NINE

When a magnetic sector instrument was operated with an accelerating voltage of 3000V, a field of 1350G was required to focus the CH₄ on to the detector.

- i) What range of fields of strength would be required to scan a mass of range 16 to 300 if the accelerating voltage was kept constant at 3000V? (4marks)
- ii) What range of voltage would be required to scan a mass of range 16 to 250, if the field was maintained at 1350G? (4Marks)
- iii) What resolution is required to resolve C₂H₄⁺(MW= 28.0313) and CO⁺(MW= 27.9949). (2marks)

QUESTION TEN

- a) A NMR instrument had a frequency of an isolated proton at 300 MHz. What is the strength of the magnet in that instrument? (2Marks)
- b) Explain the medical application of NMR spectroscopy (4marks)
- c) Explain two ways in which the magnetic field is kept constant throughout the sample during NMR analysis (2marks)
- d) Distinguish between spin-spin and spin-lattice relaxation. (2marks)