



MACHAKOS UNIVERSITY

University Examinations 2023/2024

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

FOURTH YEAR SECOND YEAR EXAMINATIONS FOR THE DEGREE OF

BACHELOR OF SCIENCE IN ANALYTICAL CHEMISTRY

SAN 410: ADVANCES IN CHROMATOGRAPHY

DATE:

TIME:

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) Non chromatographic separation technique which is actually solvent-solvent extraction (partition) is one of the necessary steps in the analysis of an analyte in analytical techniques
- (i). State three purposes of solvent extraction. (3 marks)
- (ii). State clearly the principle underlying the solvent-solvent extraction. (2 marks)
- (iii). State Nernst distribution law in the solvent-solvent extraction defining each term in the equation. (2 marks)
- (iv). What is the difference between partition (distribution) coefficient and distribution ratio? (2 marks)
- (v). Define the separation factor for two solutes undergoing solvent-solvent extraction. (2 marks)

- b) Briefly explain the principles behind each of these methods of solvent extraction listed below:
- i. Chelate extraction. (4 marks)
 - ii. Extraction by solvation. (4 marks)
 - iii. Extraction by pair ion formation. (4 marks)
- c) Explain briefly the following steps in the solvent-solvent extraction procedure
- i. Stripping. (3 marks)
 - ii. Salting-out. (2 marks)
 - iii. Masking. (2 marks)

QUESTION TWO

- a) In chromatographic separations, there are normally two phases, stationary and mobile.

Unlike the solvent-solvent separation techniques, chromatography can also be used as an analytical technique for identification and quantitation.

- i. Differentiate between adsorption chromatography and partition chromatography with the help of chemical equations. (2 marks)
 - ii. Define retention time t_R as used in chromatography. (2 marks)
 - iii. Define retention volume V_R . (2 marks)
 - iv. Describe the meaning of height equivalent to a theoretical plate (HETP) in the efficiency of separation of components in a mixture by a chromatographic column. (2 marks)
- b) In gas chromatography the stationary phase is either a solid or a liquid adsorbed on a solid base.
- i. Explain why a solid phase stationary has limited use in gas chromatography (2 marks)
 - ii. The solid support in the gas liquid chromatography which supports the stationary liquid phase also causes tailing of peaks. Explain why tailing occurs. (2 marks)
 - iii. Explain how silanization helps in the prevention of the tailing of peaks mentioned in (b) ii. (3 marks)
 - iv. Differentiate between splitter flow and non-splitter flow in relation to the injection port as applied to gas chromatography. (3 marks)
 - v. Explain the properties of organic compounds which can be analyzed by gas Chromatography. (2 marks)

QUESTION THREE

- a) High performance liquid chromatography (HPLC) normally operates at a lower temperature than GC (between freezing point and boiling point) of the solvent. Two types of columns are normally incorporated in the HPLC, known respectively as normal phase and reverse phase.
- What kind of compounds can be separated by liquid chromatography? (3 marks)
 - Describe briefly and differentiate between normal phase and reverse phase columns in HPLC. (4 marks)
 - Differentiate between isocratic elution and gradient elution. (3 marks)
 - Explain why gradient elution is ideal in the separation of complex mixtures of compounds with a wide range of polarities. (2 marks)
- b) Describe briefly the ion-exchange chromatography. (4 marks)
- c) Describe briefly the Gel Permeation (Filtration) chromatography. (4 marks)

QUESTION FOUR

- a) Ion chromatography is considered more sensitive than the routine analysis of ions by traditional wet chemical methods such as titration, photometry or calorimetry.
- State the main challenges encountered in the wet chemical methods in the analytical determinations. (3 marks)
 - State the challenge in the ion chromatography and explain how the challenge can be overcome. (3 marks)
- b) The matrix of the resins used in the ion exchanger is made of copolymers of unsaturated styrene and divinyl benzene.
- Give the chemical composition of the functional group which exchanges with the cations. (2 marks)
 - Show chemically how the ions exchange occurs in the cationic ion exchanger. (2 marks)
 - Give the chemical composition of the functional group attached to the resin matrix of the anionic exchangers. (3 marks)
 - Describe briefly the detection methods such as conductivity and UV-VIS detections coupled with ion chromatography. (3 marks)
- c) Briefly describe how waste water is collected and treated before analysis by ion

QUESTION FIVE

- a) There are currently pollutants in the environment which have attracted the attention of researchers which hitherto remained undetected but now are being detected despite their low concentration levels in the environment.
- State the name given to this group of these chemicals. (1 mark)
 - Explain why this group of chemicals are currently of concern to the scientific community. (1 mark)
 - State clearly the major difference in behaviour between these chemicals and persistent organic pollutants (POPs). (2 marks)
 - What challenge is encountered in the analysis of these chemicals in both the aqueous phase and in biotic (biological samples)? (1 mark)
 - The per-fluorinated compounds (PFCs) which are members of CECs are said to be bio-accumulative. Explain clearly what bio- accumulative means. (1½ marks)
- b) (i). Describe briefly the procedure of samples extraction as part of the steps in the analytical determination of CEC in environmental samples. (2 marks)
- (ii). State the three reasons for samples clean up as a necessary step in the analytical determinations of these compounds. (1½ marks)
- c) State the principles behind the solid phase extraction (SPE) technique. (1 mark)
- d) State the uniqueness of molecularly imprinted polymers as SPE technique. (1 marks)
- e) Explain how solid phase microextractions (SPME) and liquid phase microextraction (LPME) have revolutionized the SPE cleanup steps. (2 marks)
- f) Gas chromatography (GC) is the technique preferred for separation of non-polar and volatile CEC.
- Explain why it is a necessary step to derivatize CECs that are polar before analysis by GC method. (1 marks)
 - State the major drawback in the derivatization process for polar CEC. (1 mark)
 - Explain the principle behind reverse phase columns for LC analyses. (1 mark)
 - State the major challenge in the use of LC-MS in the analysis of polar CEC.

- g) Explain clearly and with details how the development of ultra-high-performance LC (u-HPLC) coupled with MS utilizing Electrospray ionization (ESI) has overcome challenges in f(iv) above. (2 marks)