



MACHAKOS UNIVERSITY

University Examinations 2021/2022

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

FOURTH YEAR SECOND YEAR EXAMINATIONS FOR
BACHELOR OF SCIENCE IN ANALYTICAL CHEMISTRY

SAN 410: ADVANCES OF CHROMATOGRAPHY

DATE:

TIME: 2 Hrs

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) Highly sensitive instruments have been developed to deal with complex environmental issues arising from diverse pollutants from anthropogenic activities.
- i. Explain with examples what the chemicals of emerging concern (CEC).
(2 marks)
 - ii. Explain why this group of chemicals (CEC) are currently of concern to the scientific community.
(1 mark)
 - iii. State clearly the major difference in behaviour between these chemicals (CEC) and persistent organic pollutants (POPs) which are being phased out. (2 marks)

- iv. What challenge is encountered in the analysis of CEC in both the aqueous phase and in biotic (biological samples)? (1 mark)
 - v. The per-fluorinated compounds (PFCs) which are members of CECs are said to be bioaccumulative. Explain clearly what bio- accumulative means. (2 marks)
- (b)
- i. Describe briefly the procedure of samples extraction as part of the steps in the analytical determination of CEC in environmental samples. (1½ marks)
 - ii. State the three reasons for samples clean up as a necessary step in the analytical determinations of CEC. (1½ marks)
- (c) State the principles behind the solid phase extraction (SPE) technique. (1½ marks)
- (d) State the uniqueness of molecularly imprinted polymers as SPE technique. (1½ 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.
- i. State clearly the underlying principle for GC technique. (2 marks)
 - ii. Explain why it is a necessary step to derivatize CECs that are polar before analysis by GC method. (2 marks)
 - iii. State the major drawback in the derivatization process for polar CEC. (2 marks)
 - iv. Explain the principle behind reverse phase columns for LC analyses. (2½ marks)
 - v. State the major challenge in the use of LC-MS in the analysis of polar CEC. (2½ marks)
- (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? (3 marks)

QUESTION TWO (20 MARKS)

- (a) Ion chromatography is considered more sensitive than the routine analysis of ions by traditional wet chemical methods such as titration, photometry or calorimetry.
- i. State the main challenges encountered in the wet chemical methods in the analytical determinations. (3 marks)

- ii. State the challenge in the ion chromatography and explain how the challenge has been overcome. (3 marks)
- (b) The matrix of the resins used in the ion exchanger is made of copolymers of unsaturated styrene and divinyl benzene.
- i. Give the chemical composition of the functional group which exchanges with the cations. (2 marks)
- ii. Show chemically how the ions exchange occurs in the cationic ion exchanger. (2 marks)
- iii. Give the chemical composition of the functional group attached to the resin matrix of the anionic exchangers. (3 marks)
- iv. 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 chromatography. (4 marks)

QUESTION THREE (20 MARKS)

- (a) Polycyclic aromatic compounds (PAHs) have low solubility in water but are highly lipophilic.
- i. (Explain how the PAHs are generated into the environment. (3 marks)
- ii. Although there are many different PAHs, most of the studies have been made on BaP, What is the name of BaP in full and what is chemical formula (structure)? (2 marks)
- iii. Describe the effects of PAHs on living organisms. (3 marks)
- (b) PAHs are said to be highly hydrophobic with increase in their molecular weight resulting in decrease in water solubility and volatility.
- i. Why are PAHs regarded as priority pollutants? (3 marks)
- ii. Mention the available techniques which can be used to analyze PAHs in environmental samples. (3 marks)
- iii. Explain why both solid-phase microextraction (SPME) and liquid-liquid microextraction (LPME) are preferred to SPE and LLE in extraction and concentration of PAHs from environmental samples. (3 marks)
- iv. Explain why molecularly imprinted polymers (MIPs) have high extraction ability for PAHs from environmental samples. (3 marks)

QUESTION FOUR (20 MARKS)

You are presented with an organic analyte to determine in a solid sample. The sample has a lot of other analytes which may act as interferences with varying solubilities in different solvents which are best distinguished by the Eluotropic series. With the help of appropriate examples, describe the steps required to bring the sample into the state it is able to be determined of its identity and amount in the sample either by gas chromatography or Liquid chromatography under the following:

- i. Describe how it is brought to the solution state. (5 marks)
- ii. Cleaning the sample so that the interferences are removed. (5 marks)
- iii. Factors considered whether the analyte will be determined by GC or LC method. (5 marks)
- iv. Detailed description of the analysis and the type of data generated by your choice of the method selected in (iii). (5 marks)

QUESTION FIVE (20 MARKS)

(a) Non chromatographic separation technique which is actually solvent-solvent extraction (partition) is one of the necessary steps in the analysis in analytical techniques.

- i. State three purposes which solvent extraction serves. (3 marks)
- ii. State clearly the principles underlying the solvent-solvent extraction. (3 marks)
- iii. What state Nernst distribution law in the solvent-solvent extraction defining each term in the equation. (3 marks)
- iv. What is the difference between partition (distribution) coefficient and distribution ratio? (3 marks)
- v. Define the separation factor for two solutes undergoing solvent-solvent extraction. (3 marks)

(b) Effective removal of a solute from one phase to the other in the liquid-liquid extraction is called efficiency of extraction. The complete removal of 0.1g of iodine from 50 cm³ of aqueous solution of iodine and sodium chloride is carried out using CCl₄/H₂O; the value of D given as 85. Calculate the efficiency using;

- i. 25 cm³ of CCl₄ once. (2 marks)
- ii. Batch extraction three times. (3 marks)