MACHAKOS UNIVERSITY

University Examinations 2022/2023 Academic year

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

SECOND YEAR SECOND SEMESTER EXAMINATION FOR

BACHELOR OF SCIENCE IN ANALYTICAL CHEMISTRY

SAN 200: SEPARATION, PURIFICATION AND DETECTION TECHNIQUES

DATE: 11/4/2023 **TIME: 8:30 – 10:30 AM**

INSTRUCTIONS:

- The paper consists of **two** sections.
- Section **A** is **compulsory**.
- Answer any **two** questions from section **B**.

SECTION A – COMPULSORY (30 MARKS)

QUESTION ONE (COMPULSORY) (30 MARKS)

a) Define the following terms. (5 marks)

i) Longitudinal diffusion

ii) Eddy diffusion

iii) Retention factor

iv) Selectivity factor

v) Plate height

b) List five variables that lead to increased zone broadening in chromatographic measurements. (5 marks)

c) List three variables that affect selectivity factor in chromatographic measurements. (3 marks)

d) Differentiate how retention factor is varied in gas chromatography and liquid chromatography. (3 marks)

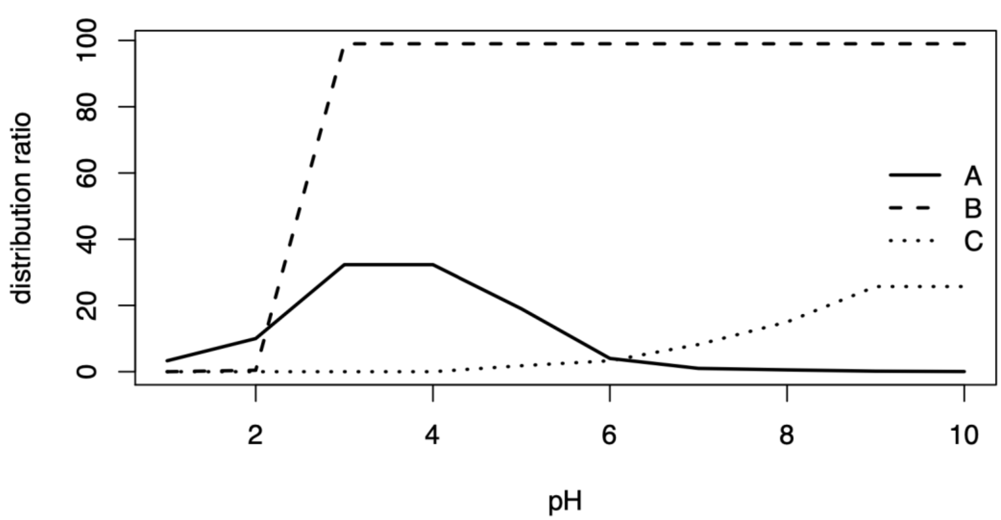
e) Explain the disadvantage in a chromatographic separation that can result from a decrease in particle size. (2 marks)

f) Consider the following chromatogram. The fast-eluting peaks and the slow-eluting peaks present a problem.

i) Describe the chromatographic nature of the problem. (3 marks)

ii) Devise a way in gas chromatography to eliminate the problem. (3 marks)

g) The figure below shows the distribution ratio for the aqueous solutes A, B, and C as a function of pH. Describe how you can separate these solutes from each other and from other inert species solely by adjusting the sample's pH and extracting with a non-polar organic solvent. (6 marks)



SECTION B

ANSWER ANY TWO QUESTIONS (EACH QUESTION IS 20 MARKS)

QUESTION TWO (20 MARKS)

a) List five variables that can improve band separation in chromatography. (5 marks)

b) The goal of an analytical separation is to remove either the analyte or the interferent from the sample's matrix. List and explain two factors that limit a separation's efficiency. (2 marks)

c) The data in the following table were extracted from the chromatogram of a two-component mixture of x and y. Calculate:

	Air	x	y
Retention time (s)	5	25	30
Peak width, FWHM, (s)	-	2.5	2.0

i) The capacity factors k' for x and y. (3 marks)

ii) The number of theoretical plates N for the column and the theoretical plate height H (assume a column 25 cm long). (4 marks)

iii) The separation factor α and explain if this is a reasonable value for achieving separation of the components. (3 marks)

iv) The resolution and explain if this is sufficient to obtain fully resolved peaks. (3 marks)

QUESTION THREE (20 MARKS)

a) Determine the smallest distribution ratio for a solute, *S*, if you want to extract 99.9% of *S* from 50.0 mL of aqueous phase using two 25.0-mL portions of the organic solvent. (5 marks)

b) The amount of copper in a penny is determined by an analytical method in which zinc is an interferent. The selectivity coefficient, $K_{Cu,Zn}$, for the analytical method is 0.125. When a sample where $[Cu^{2+}]_o = 10 \times [Zn^{2+}]_o$ is carried through a separation to remove the zinc, the error in the analysis for copper is −2.42%. When a second sample where $[Cu^{2+}]_o = 0.1 \times [Zn^{2+}]_o$ is carried through the same analysis, the error is 5.88%. Knowing that the absolute error, E, is defined as:

$$E = (R_{Cu} - 1) + K_{Cu,Zn} \times \frac{Zn^{2+}}{Cu^{2+}} \times R_{Zn}$$

Determine the recoveries for Cu^{2+} and of Zn^{2+}. (5 marks)

c) An analytical method for determining Cu in an industrial plating bath gives poor results in the presence of Zn. To evaluate a method for separating the analyte from the interferent, samples with known concentrations of Cu or Zn were prepared and analyzed. When a sample of 128.6 ppm Cu was taken through the separation, the concentration of Cu that remained was 127.2 ppm. Taking a 134.9 ppm solution of Zn through the separation left behind a concentration of 4.3 ppm Zn. Calculate:

i) The recoveries for Cu and Zn. (3 marks)

ii) The separation factor. (2 marks)

d) Following the separation outlined in question 3 (c), an analysis is carried out to determine the concentration of Cu in an industrial plating bath. Analysis of standard solutions that contain either Cu or Zn give the following linear calibrations. Determine;

$$S_{Cu} = 1250\ ppm^{-1} \times C_{Cu}\ and\ S_{Zn} = 2310\ ppm^{-1} \times C_{Zn}$$

i) The relative error if we analyze a sample without removing the Zn. Assume the initial concentration ratio, Cu:Zn, is 7:1. (2.5 marks)

ii) The maximum acceptable recovery for Zn if the recovery for Cu is 1.00 and if the error due to the separation must be no greater than 0.10%. (2.5 marks)

QUESTION FOUR (20 MARKS)

a) Briefly explain:

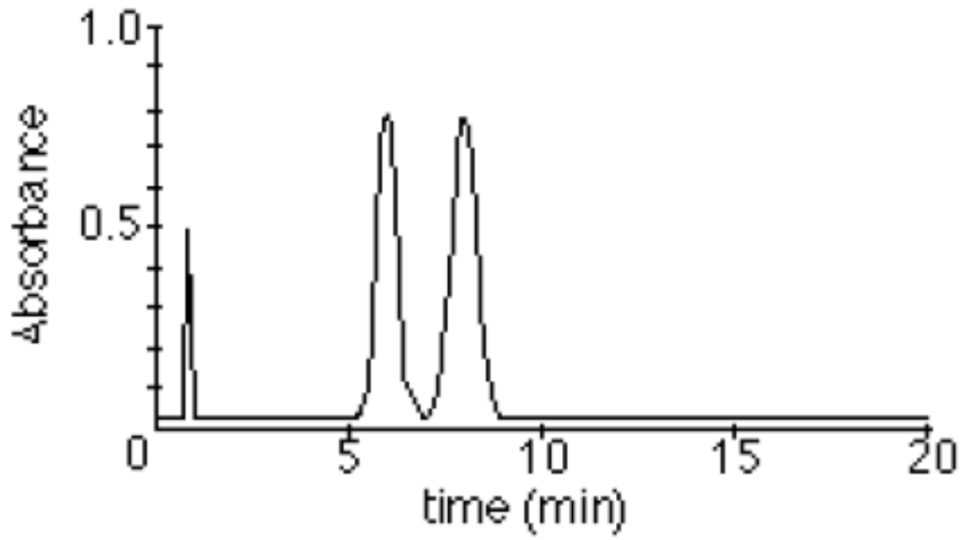
i) The principle of the following separation techniques.

1. Solid Phase Extraction (SPE). (4 marks)
2. Thin Layer chromatography. (4 marks)

ii) The advantages and disadvantages of SPE over liquid-liquid extraction.

(4 marks)

b) Given the following chromatogram for the separation of two solutes on a 25 cm long HPLC column. Assume that the exact retention time for the compound ***A*** (tR(A)) is 6.0 min and tR(B) = 7.8 min and that the width of the eluting peak at the baseline for compound **A** is 1.5 min and for compound ***B*** is 1.9 min. Also, the column yielding a *tm* = 0.9 min. Determine:



i) The H.E.T.P achieved under the operating conditions of the column using solute A values for calculations. (2 marks)

ii) The resolution achieved for solutes A and B. (2 marks)

iii) The capacity factors for solutes A and B. (2 marks)

iv) The linear velocity of the mobile phase in the column. (2 marks)

QUESTION FIVE (20 MARKS)

a) Differentiate between the following terms.

i) Recrystallization and distillation. (2 marks)

ii) Gravimetry and titrimetry. (2 marks)

b) Explain why it is impossible to completely purify a mixture using distillation. (2 marks)

c) Briefly explain how one can:

i) Determine the amount of copper in brass bearing in mind that brass is a complex matrix. (2 marks)

ii) Isolate aluminum from impure samples of bauxite, an ore of Al_2O_3. (2 marks)

iii) Determine the purity of the organic product. (2 marks)

d) A liquid–liquid extraction of the divalent metal ion, M^{2+}, uses the scheme outlined in Figure 1. The partition coefficients for the ligand, $K_{D,HL}$, and for the metal–ligand complex, $K_{D,c'}$, are $1x10^4$ and $7x10^4$, respectively. The ligand's acid dissociation constant, K_a, is $5.0x10^{-5}$, and the formation constant for the metal–ligand complex, β_2, is $2.5x10^{16}$.

i) Determine the extraction efficiency if we extract 100.0 mL of a $1.0x10^{-6}$ M aqueous solution of M^{2+}, buffered to a pH of 2.00, with 10.00 mL of an organic solvent that is 0.1 mM in the chelating agent. (4 marks)

ii) Repeat the calculation at a pH of 4.00. (3 marks)

iii) Comment on your answers. (1 mark)

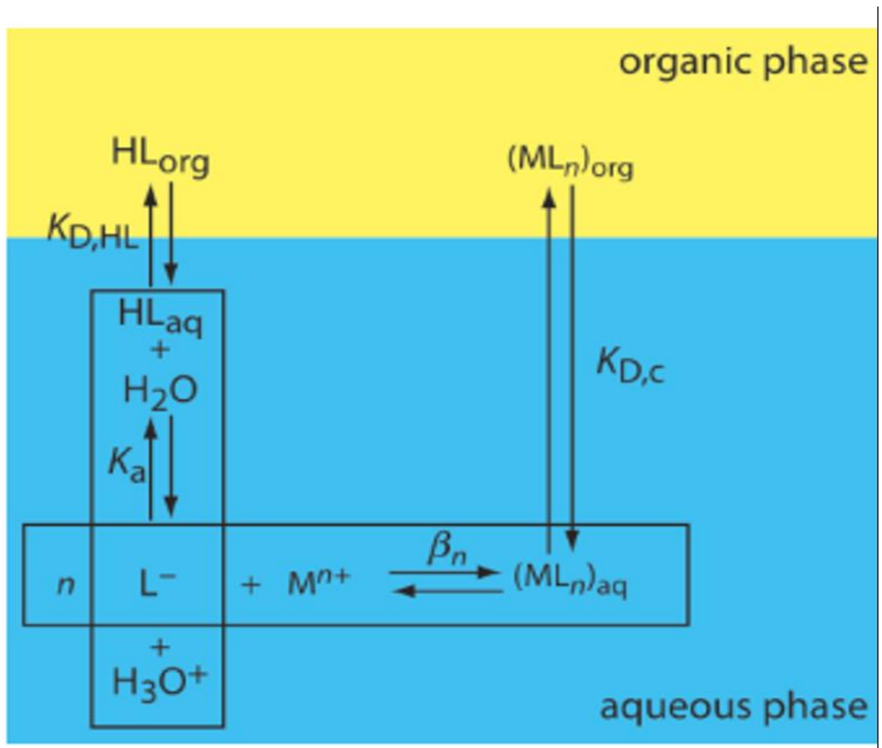


Fig 1. Liquid-liquid extraction of divalent metal ion