RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (Honours) Degree in Chemistry
B.Sc. (General) Degree in Applied Sciences

B.Sc. Third year Semester II Examination – January/February 2023
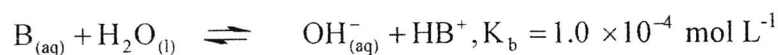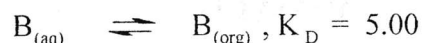
CHE 3311 – ADVANCED ANALYTICAL CHEMISTRY

Time: Three (03) hours.

Answer all questions.
The use of a non-programmable calculator is permitted.

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1. a) (i). Describe the terms distribution coefficient (K_D) and distribution ratio (D). Obtain the relationship between (K_D) and (D). State any assumption you have made and predict the extraction efficiency in both acidic and basic medium.

   (ii). List three disadvantages of liquid-liquid extraction method and three advantages of solid phase extraction method (SPE).

   (iii). Explain the three different types of interactions utilizing with extracting phases as solid phase extractants.

   (30 marks)

   b) Compute the smallest distribution ratio for a solute, S, to extract 99.9% of S from 50.0 mL of an aqueous phase using two 25.0 mL portions of the organic solvent?

   (30 marks)

   c) A solute has a K_D between water and chloroform is 5.00. If extract a 50.00 mL sample of a 0.050 M aqueous solution of the solute extracted using 15.00 mL of chloroform. Calculate the:

   (i). The separation's extraction efficiency.

   (ii). The volume of chloroform do you need to extract 99.9% of the solute.

   (40 marks)

2. a) The liquid–liquid extraction of the weak base, B is governed by the following equilibrium reactions:

$$B_{(aq)} \rightleftharpoons B_{(org)}, K_D = 5.00$$

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HB^+, K_b = 1.0 \times 10^{-4} \text{ mol L}^{-1}$$

Derive an equation for the distribution ratio, D and calculate the extraction efficiency if 25.0 mL of a 0.025 M solution of B, buffered to a pH of 9.00, is extracted with 50.0 mL of the organic solvent. Comment your result.

(40 marks)

b) (i). Briefly discuss the extraction of metals using liquid-liquid extractions.

(ii). A liquid–liquid extraction method was used to extract the divalent metal ion, M^{2+}. The partition coefficients for the ligand, $K_{D, HX}$, and for the metal-ligand complex, $K_{D,MX}$, were 1.0×10^4 and 7.0×10^4 respectively. The ligand's acid dissociation constant, K_a, is 5.0×10^{-5}, and the formation constant for the metal–ligand complex, K_f, is 2.5×10^{16}. What is the extraction efficiency if we extract 100.0 mL of a 1.0×10^{-6} M aqueous solution of M^{2+}, buffered to a pH of 1.00, with 10.00 mL of an organic solvent contains 0.1 mM of chelating agent? Repeat the calculation at a pH of 3.00. Derive the equation for distribution ratio for the metal complex. Predict the shape of the graph of extraction efficiency versus pH for the extraction of metal ion M^{2+}.

(60 marks)

3. a) Define the following terms:

(i). Retention time.
(ii). Selectivity factor.
(iii). Eddy diffusion.
(iv). Column resolution.

(16 marks)

b) Write down the van Deemter equation and define the terms. Explain with the use of van Deemter equation, how does the capillary column configuration achieve its advantages over the packed column setup in gas chromatography.

(30 marks)

c) Describe briefly with schematic diagrams of FID and ECD detectors used in gas chromatography. Give the types of analyte species which sensitive to FID and ECD. List one advantage and one disadvantage of each detector.
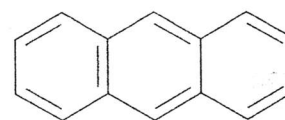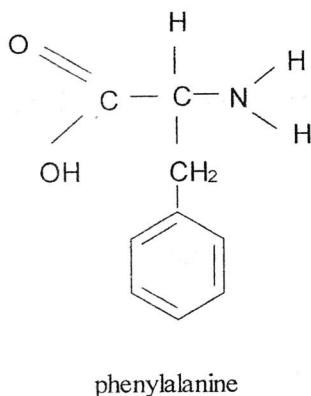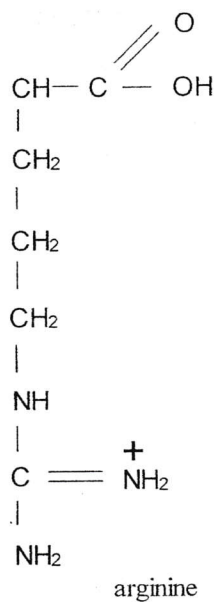
(30 marks)

d) Explain the terms the normal phase and the reverse phase techniques used in chromatography. Give the order of the elution times ranked in terms of shortest

to longest of the following species when used a very non-polar stationary phase in GC. Explain your answer.

(I). Benzene   (II). Isopropanol   (III). Ethanol

(24 marks)

4. a) (i).   Explain the difference between gas liquid and gas solid chromatography.

    (ii).   Briefly explain how you would analyze the gas chromatogram for both qualitatively and quantitatively.

(20 marks)

   b) Describe the differences between an open tubular column and packed column. What are the advantages and disadvantages of each column?

(10 marks)

   c) Define the term temperature programming in gas chromatography. Why is it used and how does it gain an advantage over isothermal separations?

(10 marks)

   d) The following retention times were observed with a 1.75 m chromatographic column: An unreacted species passes through the column in 23.7 s, isopropylamine, 275.5 s, and n-propylamine, 294.6 s. Half peak widths ($W_{1/2}$) for isopropylamine and n-propylamine were 11.5 s and 13.2 s respectively. Calculate:

   (i).   Capacity factor for each amine.
   (ii).   Selectivity factor.
   (iii). An average number of theoretical plates in the column.
   (iv)   Plate height of the column.
   (v).   Resolution for the two amines.
   (vi).   Length of the column required to achieve a resolution of 1.5.
   (vii). Time required to achieve a resolution of 1.5. Comment your answer.

(60 marks)

5. a) (i).   What is meant by gradient elution and how does this differ from an isocratic one? What advantage does gradient elution have over isocratic separations?

(20 marks)

    (ii).   Predict and explain the elution order when arginine, phenylalanine and antracene are separated with reverse phase chromatography.

arginine

phenylalanine

anthracene

(20 marks)

b) (i) Explain with suitable diagrams of sample injection system in high-performance liquid chromatography (HPLC) and list four different types of detectors used in HPLC. Give one advantage of HPLC over GC.

(ii) HPLC was used to determine the sucrose concentration in a sample taken from a can of soft drink. Standard solutions were made up using pure sucrose and deionised water. A 1 mL sample of each standard solution was injected into the HPLC column and its peak area was recorded, as shown in the table below:

Concentration of sucrose / g L^{-1}	Peak area / mm^2
0.10	700
0.20	1000
0.40	2500
0.60	3300
0.80	4200

A 5.0 mL sample of the soft drink was diluted to 100 mL in a volumetric flask. A 10.0 mL aliquot of this solution was transferred to a 250 mL volumetric flask and filled up to the calibration mark using deionized water. A sample of this solution was injected into the HPLC column. The peak area of the sample solution at the same retention time and under the same conditions as those used to determine the calibration line was found to be 1900 mm^2.

(1). Determine the sucrose content of the sample tested in the HPLC, in g / L^{-1}, using a suitable calibration plot.

(2). Calculate the percentage mass/volume (% m/v) of sucrose in the 5.0 mL sample of soft drink.

(3). The can used to obtain the sample contained 330 mL of soft drink. Assuming that the only sugar in the soft drink is sucrose, calculate the mass of sucrose in the can of soft drink.

(60 marks)

6). a) Draw a block diagram of an atomic absorption (AAS) instrument and explain the radiation source used in AAS.

(20 marks)

b) (i). List three uses of colorimeter and give one advantage and one disadvantage of using calorimeter in chemical analysis.

(ii). A student prepared a calibration curve by measuring of the absorbance of five standard solutions of a compound at 300 nm. A cuvette with path length of 5 cm and the slope of the curve was 300 L mol^{-1}. Calculate the molar absorptivity of the compound.

(35 marks)

c) In the coulometric titration of U^{4+} in the presence of excess Ce^{3+}, it was found to require 652 s to reach the equivalence point using a constant current of 100.0 mA. How many moles of U^{4+} were present in the solution? (F = 96485 C mol^{-1}).
(Hint:- U^{4+} is reduced to UO$_2^{2+}$)

(20 marks)

d) (i). List two advantages and two disadvantages of dropping mercury electrode (DME).

(ii). Write down the Ilkovic equation and define the terms with appropriate units. The diffusion limiting current (i$_d$) at a dropping mercury electrode for an aqueous Mg(II) solution of concentration C (mol L^{-1}) is 300 μA. If C is increased by 0.1 mol L^{-1} the current increases to 900 μA. Calculate the value of C.

(Hint: $E_{1/2} = 0.05$ V, $i_{d.ave} = 1.81$ μA, rate of flow of the mercury = 2.00 ng/s, drop interval = 5 s and diffusion coefficient = 2.12×10^{-5} cm^2/s).

(25 marks)

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