DATE: 26-10 -18

ST. JOSEPH'S COLLEGE (AUTONOMOUS), BENGALURU-27

M.Sc. CHEMISTRY: III SEMESTER

SEMESTER EXAMINATION: OCTOBER 2018

CH-9216 : SEPARATION AND ELECTROCHEMICAL TECHNIQUES

Supplementary candidates only.

Attach the question paper with the answer booklet

Note : (i) The question paper has **four printed pages** and **three parts**. All parts are compulsory.

(ii) **Graph sheets are provided.**

(iii) Answer any **SIX** out of eight questions from part – A, Any **FOUR** out of six questions αfrom part – B, and any **two** out of three questions from part – C.

Time : 2 ½ hrs Max .Marks : 70

PART A

1. Calculate the minimum value of the separation factor, α , for the extraction of 98% of A in organic phase while retaining 98 % B in aqueous phase.
2. What is the minimum value of K_D which would allow the extraction of 99% of a solute from 50 ml of water with two successive 25.0 ml portion of benzene?
3. A mixture of benzene , toluene and methane was injected into a gas chromatograph. Methane gave a sharp spike at 42 s, whereas benzene and toluene were eluted at 251s and 333 s respectively. Calculate the relative retention.
4. Write the formula to estimate the number of theoretical plates of an asymmetric peak. Draw a tailing peak and mark the parameters.
5. An analyte containing 10 compounds are separated using a non polar column in GC. The names of the analytes and their respective boiling points are given below. Plot a chromatogram showing the order of elution.

	Compound	Boiling point (°C)
1	Acetone	56
2	Pentane	36
3	Propanol	97
4	Methyl ethyl ketone	80
5	Hexane	69
6	Butanol	117
7	3-Pentanone	102
8	Heptane	98
9	Pentanol	138
10	Octane	126

6. Explain the order of elution in capillary electrophoretic separation.
7. Explain in brief any two modes of mass transport in voltammetry.
8. Write an expression for electroosmotic flow and explain the terms.

PART B

9. a) Determine the distribution of an analyte A in first two vessels after 4 transfers when V_s =3 ml , V_m = 6 ml and K_D = 6.0.

   b) A mixture of hydrocarbons were separated by gas chromatography with a capillary column of length 100.0 m long. The unretained peak eluted at 30 s and A and B at 250 s and 270 s respectively. The Calculate the following: (i)capacity factor for A (ii)the number of theoretical plates for this peak , given $W_{1/2}$ is 7 min. (iii)HETP for the peak A (iv) the resolution between peak A and B provided the base widths of A and B are 15 and 17 min respectively. (6+6)

10. (a)Answer the following with respect to gas chromatography:

    (i) Explain purge and trap method.

    (ii) What is the difference between wall coated and support coated open tubular columns? What is the advantage of latter?

    (iii) How does solvent trapping and cold trapping work in splitless injection?

    (iv) To which kind of analytes do the thermal conductivity detectors and electron capture detector respond?

    (v) Explain solid phase micro extraction (5 x 2 = 10)

    (b) Explain hydrophilic interaction chromatography. (2)

11. (a)Selecting a suitable solvent is very important step for a better resolution of all peaks in HPLC. THF , methanol and acetonitrile are the three important organic solvents for reverse phase system. Answer the following regarding the selection of a suitable solvent + buffer or solvent mixture + buffer for a reverse phase chromatography .

    (i) Which organic solvent + a buffer of suitable pH will you try first? Why?

    (ii) After selecting the organic solvent , how will you adjust the percentage of the composition of the mixture (solvent + buffer) if the early peaks are crowded and later eluting peaks are eluted after a long gap?

    (iii)If the organic solvent is not giving proper result, which solvent will be your next option?

    (iv) Finally, how will you find out the most suitable organic solvent for the separation of given mixture? (4)

    (b) How does evaporative light scattering detector function? (4)

    (c) A mixture contains 1% KCl particles and 99% KNO_3 particles. If 10^4 particles are taken, what is the expected number of the KCl particles? What is the standard deviation if the experiment is repeated many times? (2)

    (d) Predict the elution order of ortho, meta and para methyl anilines in a silica column (normal phase chromatography) (2)

10. (a) Explain the application of gel filtration chromatography in (i) studying the folding and unfolding conditions of protein molecules (ii) Determination of molecular mass of macromolecules. (4)

(b)Write a note on immobilised metal chelate affinity chromatography. (2)

(c)Explain suppressed ion anion chromatography. (4)

(d)Explain the functioning of quadrupole mass analyser in GC-MS (2)

11. a) i) What is alkaline error? What is the significance of selectivity coefficient? ii)What is asymmetric potential? What are the possible causes for it? iii) Explain electrical conductance across a glass membrane.

b) Discuss isoelectric focusing method of separation. (6 +6)

12. a) With the help of relevant plots explain how do you carry out an amperometric titration and get the equivalence point if the solute is electroactive and the reagent is electro-inactive.

b) Obtain an expression for the determination of equilibrium constant for coupled chemical reaction.

c) Discuss mechanism of response of CO_2 in a gas sensing probe (3+5+4)

Part C

13. a)The thermal conductivity (in J/(K.m.s) of some gases are given in brackets : H_2 (0.170); He (0.141) ; N_2 (0.0243) ; C_2H_4 (0.0170) ; C_3H_8 (0.0151) ; Ar (0.0162) : Answer the following: i) Why He is preferred as a carrier gas over nitrogen while TCD is used in GC? (ii)Can we use Ar as a carrier gas for the detection of ethene? Give reason/s.

(b)Two compounds A and B are separated using a non polar column in GC. The polarity of B > A. We used a Photoionisation detector with a UV lamp of 9.5V. The required physical data for the compounds are given in the following table. Plot the expected chromatogram showing the order of elution.

Compound	Boiling point (^{0}C)	Ionisation potential (eV)
A	80.1	9.24
B	82.5	10.15

(2+3)

14. A nitroglycerine patch (used in treating heart diseases) was dissolved in approximately 20 mL ethanol and then diluted to 100 mL. 10.0 mL of this solution was diluted again to 100 mL with water. 2 µL volumes of the diluted sample and 2 µL of each of the prepared standards of nitroglycerine were injected onto a 1.5 m chromatographic column and analysed using a nitrogen-specific detector.

Nitroglycerine standards	Peak area (mm^2)
Standard 5 mg/ mL	7.2
Standard 10 mg/ mL	14.6
Standard 15 mg/mL	22.0
Diluted sample solution	10.8

i) Construct a calibration curve and determine the concentration of nitroglycerine in the diluted sample.

ii) What mass of nitroglycerine was in the patch?

iii) The patch has a total mass of 8.0 g. What is the percentage concentration (w/w) of nitroglycerine in the patch? (5)

15. The following species undergo oxidation/reduction in the potential range +0.85V to -1.0V in pH 5: Cd^{+2}, nitrostyrene and methylene blue are to be reduced whereas ascorbic acid, Ferrocyanide are to be oxidized. You have been provided with the following solid electrodes Hg, Pt and gold. Answer the following questions: i) Identify and justify your choice of suitable electrode material to carry out above mentioned processes for the respective molecules. ii) If glassy carbon is given will you change your mind? (5)