UNIVERSITY OF SWAZILAND

Faculty of Science
Department of Chemistry
Final Examination 2014/2015

TITLES OF PAPER: Separation Methods & Environmental Analytical Techniques.

COURSE CODES: C611 & ERM642

TIME ALLOWED: 3 (THREE) HOURS

INSTRUCTIONS:
1) Answer any Four (4) questions
2) Each question is weighted 25 marks
3) Write neatly and clearly
4) A periodic table and other useful data have been provided with this paper.

REQUIREMENT: GRAPH PAPER

DO NOT OPEN THIS QUESTION PAPER UNTIL PERMISSION TO DO SO HAS BEEN GRANTED BY THE CHIEF INVIGILATOR

Question 1 (25 marks)

(a) (i) Supply the expression that relates retention volume and specific retention volume. Identify the factors that influence the value of the specific retention volume in a given solvent. (3)

(ii) Under ideal conditions, show how the retention time/volume is affected by enhanced temperature and volatility of the solutes. (3)

(b) (i) Explain the term 'resolution of chromatographic elution bands' Give an expression for the resolution factor in terms of N(number of theoretical plates), and the distribution coefficients of the solutes. Define all the terms in it. (4)

(ii) Summarize the specific effects of capacity factor, selectivity factor and N on the resolution of two solutes with adjacent peaks by a given column. (3)

(c) Two eluted solutes A and B have retention times of 8.26 and 8.43min. respectively on a 20-m column. The peak widths (at the bases), for A and B were 0.15 and 0.16min. respectively. The retention time for an unretained solute is 0.19min.

(i) Calculate the number of theoretical plates for each compound and the average number of theoretical plates.

(ii) Determine the average height of a theoretical plate.

(iii) Calculate the resolution and the capacity factors for A and B.

(iv) Compare the resolution obtained using Δt_r, with that obtained using the capacity factors.

(v) Estimate the column length required to achieve a resolution of 1.5. (12)

Question 2 (25 marks)

(a) (i) What is meant by the term 'band broadening' in GC analysis? (1)

(ii) Employing the Van Deemter equation, account for the contribution by each of the factors responsible for band broadening and column efficiency in terms of HETP. (8)

(b) By making use of the Van Deemter equation, predict the effect (increase, no effect, cannot determine), on the plate height, H, in each of the following conditions, with only one parameter varied at a time:

(i) Decreasing the particle size.

(ii) Increasing the column temperature.

(iii) Increasing the thickness of the liquid coating material.

(iv) Increasing the linear gas flow rate. (2)

(c) n-hexane was analyzed by injecting 2-μL samples unto a 3.00m GC column. The following table contains the data obtained:

Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Flow Rate (mL/s)	2.00	1.51	1.20	1.05	0.84	0.67	0.53	0.43
Retention time, t_r (s)	329.4	382.2	430.2	457.2	517.2	589.8	678.6	761.4
Peak Width, w (s)	21.0	23.4	25.8	28.2	32.4	40.8	48.6	57.0

(i) Prepare a van Deemter plot (i.e. plot HETP vs. flow rate). (8)

(ii) Obtain the optimum flow rate. (2)

(iii) Calculate N and H (HETP), at the optimum flow rate. (4)

Question 3 (25 marks)

(a) Give three specific applications of GC method of analysis in everyday life, giving local examples in each case. (6)

(b)

with regard to the E.C.D. – GC detector,

(i) Briefly discuss its advantages, limitations and working principles.

(ii) Give two examples of its usual applications in environmental analysis. (8)

(c) Summarize the basic features of a flame ionization detector of a GC. How does its sensitivity compare with that of a thermal conductivity detector? (5)

(d) During a GC determination of the %v/v of methyl salicylate in a rubbing alcohol, a set of standard additions was prepared by transferring 20.00mL of the rubbing alcohol to separate 25 – mL volumetric flasks and pipetting 0.00mL, 0.20mL and 0.50mL of methyl salicylate to the flasks. All three flasks were then diluted to volume using isopropanol. Analysis of the three samples gave peak heights of methyl salicylate of 57.00mm, 88.5mm, and 132.5mm respectively. Determine the %v/v methyl salicylate in the rubbing alcohol. (6)

Question 4 (25 marks)

(a) State three advantages and two disadvantages of HPLC when compared with GC as separation techniques. (5)

(b) Identify five desirable characteristics of a liquid to be employed as a mobile phase for HPLC analysis. (5)

©

(i) What is 'Polarity Index'? How is it's principles employed during HPLC analysis? (3)

(ii) During a reverse phase HPLC separation, a mobile phase mixture of 70%v/v water and 30%v/v methanol was used. Calculate the polarity index of the mobile phase. The polarity index of water is 10.2 while that of methanol is 5.1. (3)

(d) Given the following compounds: n-hexane, n-hexanol, benzene

Predict the order of their elution, using:

(i) A normal phase separation,

(ii) A reversed phase separation. (2)

(e) A multivitamin tablet was being analyzed for its contents using HPLC. A 5μL standard containing all the vitamins was first injected into the HPLC. The amount of the vitamins and their corresponding signals are tabulated below. Similarly, the unknown was treated and a 5μL sample injected into the HPLC. The corresponding signals are also shown in the lowest row of the same table. Determine the amount of each vitamin present in the sample in mg, given that the unknown tablet was dissolved in a 100mL volumetric flask. (7)

Vitamin	Vit.C	Niacin	Niacinamide	Pyridoxine	Thiamine	Folic Acid	Riboflavin
Conc. (ppm)	170	130	120	150	50	15	10
Signal (arb. Units)	0.22	1.35	0.90	1.37	0.82	0.36	0.29
Unknown (Arb Units)	0.87	0.00	1.40	0.22	0.19	0.11	0.44

Question 5 (25 marks)

(a) Define the following terms and discuss the factors that influence their values:

(i) electrophoretic mobility

(ii) Electroosmotic flow velocity. (6)

(b) Summarize the principles of capillary zone electrophoresis (CZE).
Identify its main limitation and explain how this aspect is overcome by the micelar electrokinetic chromatography(MEKC). (7)

© Briefly discuss the efficiency and solute resolution of capillary electrophoresis, indicating the parameters that influence them. (6)

(d) The CZE method was employed for the analysis of NO_3^- in aquarium water using IO_4^- as an internal standard. Standard solutions of 30.00ppm NO_3^- and 20.00 ppm of IO_4^- gave peak heights (arbitrary units), of 190.0 and 200.2 respectively. A 2.50 mL water sample from an aquarium was transferred into a 250.0 mL volumetric flask and then diluted to volume after adding sufficient internal standard to make its concentration 10.00 ppm. Analysis gave signals of 29.2 and105.8 NO_3^- and IO_4^- peak heights respectively. Estimate the concentration of the NO_3^- in the aquarium sample in ppm. (6)

Question 6 (25marks)

(a) Draw and label a schematic diagram of a HPLC. (4)

(b) Account for the basic structural features and requirements of HPLC columns in terms of the nature of its material and design. (6)

(c) For a HPLC:

(i) Identify three of the ideal properties required for HPLC detectors.

(ii) Differentiate between bulk property and solute property detectors. Give one example of each. (6)

(d) For the following HPLC detectors, discuss the main features/operating principles, including advantages, with the aid of a schematic diagram where possible:

(i) Refractive index detectors

(ii) Ultraviolet absorbance detectors with filters. (9)

General data and fundamental constants

Quantity	Symbol	Value
Speed of light†	c	$2.997\,924\,58 \times 10^{8}$ m s^{-1}
Elementary charge	e	$1.602\,177 \times 10^{-19}$ C
Faraday constant	$F = eN_A$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\,66 \times 10^{-23}$ J K^{-1}
Gas constant	$R = kN_A$	$8.314\,51$ J K^{-1} mol^{-1}
		$8.205\,78 \times 10^{-2}$ dm^{3} atm K^{-1} mol^{-1}
		62.364 L Torr K^{-1} mol^{-1}
Planck constant	h	$6.626\,08 \times 10^{-34}$ J s
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34}$ J s
Avogadro constant	N_A	$6.022\,14 \times 10^{23}$ mol^{-1}
Atomic mass unit	u	$1.660\,54 \times 10^{-27}$ kg
Mass of electron	m_e	$9.109\,39 \times 10^{-31}$ kg
proton	m_p	$1.672\,62 \times 10^{-27}$ kg
neutron	m_n	$1.674\,93 \times 10^{-27}$ kg
Vacuum permeability†	μ_0	$4\pi \times 10^{-7}$ J s^{2} C^{-2} m^{-1}
		$4\pi \times 10^{-7}$ T^{2} J^{-1} m^{3}
Vacuum permittivity	$\varepsilon_0 = 1/c^2\mu_0$	$8.854\,19 \times 10^{-12}$ J^{-1} C^{2} m^{-1}
	$4\pi\varepsilon_0$	$1.112\,65 \times 10^{-10}$ J^{-1} C^{2} m^{-1}
Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24}$ J T^{-1}
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27}$ J T^{-1}
Electron g value	g_e	$2.002\,32$
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
Rydberg constant	$R_\infty = m_e e^4/8h^3c\varepsilon_0^2$	$1.097\,37 \times 10^{5}$ cm^{-1}
Fine structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Gravitational constant	G	$6.672\,59 \times 10^{-11}$ N m^{2} kg^{-2}
Standard acceleration of free fall†	g	$9.806\,65$ m s^{-2}

† Exact (defined) values

Prefixes

f	p	n	μ	m	c	d	k	M	G
femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VII
1	1.008 H 1																
2	6.941 Li 3	9.012 Be 4										Atomic mass → Symbol → Atomic No. →	10.811 B 5	12.011 C 6	14.007 N 7	15.999 O 8	18.99 F 9
3	22.990 Na 11	24.305 Mg 12					TRANSITION ELEMENTS						26.982 Al 13	28.086 Si 14	30.974 P 15	32.06 S 16	35.45 Cl 17
4	39.098 K 19	40.078 Ca 20	44.956 Sc 21	47.88 Ti 22	50.942 V 23	51.996 Cr 24	54.938 Mn 25	55.847 Fe 26	58.933 Co 27	58.69 Ni 28	63.546 Cu 29	65.39 Zn 30	69.723 Ga 31	72.61 Ge 32	74.922 As 33	78.96 Se 34	79.90 Br 35
5	85.468 Rb 37	87.62 Sr 38	88.906 Y 39	91.224 Zr 40	92.906 Nb 41	95.94 Mo 42	98.907 Tc 43	101.07 Ru 44	102.91 Rh 45	106.42 Pd 46	107.87 Ag 47	112.41 Cd 48	114.82 In 49	118.71 Sn 50	121.75 Sb 51	127.60 Te 52	126.9 I 53
6	132.91 Cs 55	137.33 Ba 56	138.91 *La 57	178.49 Hf 72	180.95 Ta 73	183.85 W 74	186.21 Re 75	190.2 Os 76	192.22 Ir 77	195.08 Pt 78	196.97 Au 79	200.59 Hg 80	204.38 Tl 81	207.2 Pb 82	208.98 Bi 83	(209) Po 84	(210) At 85
7	223 Fr 87	226.03 Ra 88	(227) **Ac 89	(261) Rf 104	(262) Ha 105	(263) Unh 106	(262) Uns 107	(265) Uno 108	(266) Une 109	(267) Uun 110							

*Lanthanide Series	140.12 Ce 58	140.91 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.96 Eu 63	157.25 Gd 64	158.93 Tb 65	162.50 Dy 66	164.93 Ho 67	167.26 Er 68	168.93 Tm 69	173.04 Yb 70	174.9 Lu 71
**Actinide Series	232.04 Th 90	231.04 Pa 91	238.03 U 92	237.05 Np 93	(244) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(260) Lr 103

( ) indicates the mass number of the isotope with the longest half-life.