

**UNIVERSITY OF SWAZILAND**  
**Faculty of Science**  
**Department of Chemistry**  
**Final Examination 2011/2012**

**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.**

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

**Question 1 (25 marks)**

- (a) (i) Give the expression that relates retention volume and specific retention volume. What are the factors that determine the specific retention volume in a given solvent? (3)
- (ii) Assuming ideal behaviour, show how the retention time/volume is affected by increasing the 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) Discuss the effects of the capacity factor, selectivity factor and N on the resolution of two solutes by a given column. (3)
- (c) Two compounds A and B have retention times of 8.26 and 8.43min. respectively on a 20-m column. The peak widths (at base), 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  $\Delta t_r$ , with that obtained using the capacity factors.
- (v) What column length is required to achieve a resolution of 1.5? (12)

**Question 2 (25 marks)**

- (a) (i) Explain the term 'band broadening' in GC analysis. (1)
- (ii) With reference to 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 reference to 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:
- Decreasing the particle size.
  - Increasing the column temperature.
  - Increasing the thickness of the liquid coating material.
  - Increasing the linear gas flow rate. (2)

- (c) The analysis of n-hexane was carried out by injecting 2- $\mu$ L 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 rate, $t_r$ (s)	329.4	382.2	430.2	457.2	517.2	589.8	678.6	761.4
Peak Width (s)	21.0	23.4	25.8	28.2	32.4	40.8	48.6	57.0

- Prepare a van Deemter plot (i.e. plot HETP vs. flow rate). (8)
- Determine the optimum flow rate. (2)
- Calculate  $N$  and  $H$  (HETP), at the optimum flow rate. (4)

**Question 3 (25 marks)**

- Discuss three specific applications of GC method of analysis in everyday life, giving local examples in each case. (6)
- For the E.C.D. – GC detector,
  - Discuss its advantages, limitations and working principles.
  - Give two examples of its usual applications for real analysis. (8)
- Describe 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) In using a GC for the 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) Give three advantages and two disadvantages of HPLC when compared with GC as separation techniques. (5)
- (b) List five desirable characteristics of a liquid to be employed as a mobile phase for HPLC analysis. (5)
- (i) What is 'Polarity Index'? How is its principles employed during HPLC analysis? (3)
- (ii) In carrying out a reverse phase HPLC separation, a mobile phase mixture of 70%v/v water and 30%v/v methanol was used. Determine 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) The contents of a multivitamin tablet was being determined using an HPLC. A 5 $\mu$ L 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 5 $\mu$ L 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 100 mL 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) Give a brief account of the principles of capillary zone electrophoresis (CZE). What is its main limitation and how is it overcome by the micellar electrokinetic chromatography (MEKC)? (7)
- (c) Discuss the efficiency and solute resolution of capillary electrophoresis, indicating the parameters that influence them. (6)
- (d) CZE was employed for the analysis of  $\text{NO}_3^-$  in aquarium water using  $\text{IO}_4^-$  as an internal standard. Standard solutions of 30.00 ppm  $\text{NO}_3^-$  and 20.00 ppm of  $\text{IO}_4^-$  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 and 105.8  $\text{NO}_3^-$  and  $\text{IO}_4^-$  peak heights respectively. Estimate the concentration of the  $\text{NO}_3^-$  in the aquarium sample in ppm. (6)

**Question 6 (25marks)**

- (a) Draw and label a schematic diagram of a HPLC. (4)
- (b) Discuss the basic structural features of HPLC columns in terms of the nature of the material and the design. Account for these makeup. (6)
- (c) For an HPLC:
- (i) Give three of the ideal properties required for HPLC detectors.
  - (ii) Distinguish between bulk property and solute property detectors and 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)

Quantity	Symbol	Value	General data and fundamental constants
Speed of light†	$c$	$2.997\,924\,58 \times 10^8 \text{ m s}^{-1}$	
Elementary charge	$e$	$1.602\,177 \times 10^{-19} \text{ C}$	
Faraday constant	$F = eN_A$	$9.6485 \times 10^4 \text{ C mol}^{-1}$	
Boltzmann constant	$k$	$1.380\,66 \times 10^{-23} \text{ J K}^{-1}$	
Gas constant	$R = kN_A$	$8.314\,51 \text{ J K}^{-1} \text{ mol}^{-1}$ $8.205\,78 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ $62.364 \text{ L Torr K}^{-1} \text{ mol}^{-1}$	
Planck constant	$h$	$6.626\,08 \times 10^{-34} \text{ J s}$	
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34} \text{ J s}$	
Avogadro constant	$N_A$	$6.022\,14 \times 10^{23} \text{ mol}^{-1}$	
Atomic mass unit	$u$	$1.660\,54 \times 10^{-27} \text{ kg}$	
Mass of electron	$m_e$	$9.109\,39 \times 10^{-31} \text{ kg}$	
proton	$m_p$	$1.672\,62 \times 10^{-27} \text{ kg}$	
neutron	$m_n$	$1.674\,93 \times 10^{-27} \text{ kg}$	
Vacuum permeability†	$\mu_0$	$4\pi \times 10^{-7} \text{ J s}^2 \text{ C}^{-2} \text{ m}^{-1}$ $4\pi \times 10^{-7} \text{ T}^2 \text{ J}^{-1} \text{ m}^2$	
Vacuum permittivity	$\epsilon_0 = 1/c^2\mu_0$	$8.854\,19 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$	
	$4\pi\epsilon_0$	$1.112\,65 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$	
Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24} \text{ J T}^{-1}$	
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27} \text{ J T}^{-1}$	
Electron $g$ value	$g_e$	2.002 32	
Bohr radius	$a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2$	$5.291\,77 \times 10^{-11} \text{ m}$	
Rydberg constant	$R_\infty = m_e e^2/8h^3 c$	$1.097\,37 \times 10^5 \text{ cm}^{-1}$	
Fine structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$	
Gravitational constant	$G$	$6.672\,59 \times 10^{-11} \text{ N m}^2 \text{ kg}^{-2}$	
Standard acceleration of free fall†	$g$	9.806 65 $\text{m s}^{-2}$	

† Exact (defined) values

f	p	n	$\mu$	m	c	d	k	M	G	Prefixes
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	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
	IA 1.008 H	IIA	IIIB	IVB	VB	VIB	VII B	VIII			IB	II B	IIIA	IVA	VA	VIA	VII
1																	
2	6.941 Li 3	9.012 Be 4											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	174.97 Lu 71
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

\*\*Actinide Series

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