Mdala

UNIVERSITY OF SWAZILAND
SECOND SEMESTER EXAMINATION 2008/2009

TITLE OF PAPER	**:**	**Instrumental Methods For Environmental Analysis - 2**
COURSE CODE	**:**	**EHS 574**
TIME ALLOWED	**:**	**Two (2) HOURS**
INSTRUCTIONS	**:**	**Answer any Four (4) Questions. Each Question Carries 25 Marks**

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) Sate the Nernst's distribution law. Give its mathematical expression and define all the parameters involved in it. [3]

(b) The distribution coefficient, K_D and distribution ratio, D, are terms used during the solvent extraction analysis:
  (i) Differentiate these two terms.
  (ii) Give an example to illustrate the difference. [4]

(c) For the extraction of a weak acid whose anion does not penetrate the organic phase, and is monomeric in both phases:
  (i) Supply the expression for its distribution ratio, D, and define all the parameters in it. [4]
  (ii) Discuss the factors that influence the value of D. [2]

(d) A solute, X, distributes between carbon tetrachloride and water while it was being analyzed by solvent extraction. If its distribution ratio is 85.0.
  (i) Calculate the % of X extracted from the aqueous phase when 50.0mL of a 1.0×10^{-3}M aqueous solution of X is extracted with 50.0ml of carbon tetrachloride. [6]
  (ii) Would you have preferred using two successive extractions, each with 25.0mL carbon tetrachloride? Justify your answer with appropriate calculations. [6]

Question 2 (25 marks)

(a) Describe the procedure for the solvent extraction of a solute from a 50mL aqueous sample, using 100mL carbon tetrachloride as the organic solvent. [6]

(b)
  (i) What is a chelating agent? [1]
  (ii) Write the equation for the formation of a metal chelate and identify the reactant and the products in the reaction. [3]
  (iii) Give two properties of a metal chelate formed during the solvent extraction of a metal as a metal chelate. [2]
  (iv) Give two examples of a chelating agent and one metal for which each of them is useful for extraction as a metal chelate. [3]

(c) Give the expression for the distribution ratio, D of a metal between two phases during its solvent extraction as a metal chelate. Hence briefly discuss the factors that influence the distribution ratio, D. [4]

(d) For a 0.1×10^{-6}M solution of a metal ion for which: $n = 2, K_{DL} = 1.1 \times 10^{4}$; $K_{DM} = 7.0 \times 10^{4}$; $K_f = 5.0 \times 10^{22}$. Estimate its distribution ratio during its extraction as metal a chelate using a 1.0×10^{-4}M dithizone at pH 1.0; $\mathbf{K_a = 3.0 \times 10^{-5}}$ **[6]**

Question 3 (25 marks)

(a) For the following chromatographic terms:

(i) Retention volume, V_r, retention time, t_r and volume flow rate of the mobile phase, F.

(ii) Capacity factor, k, retention time, t_r and dead time, tm

Define each of the terms and give an expression that relates the terms in each set. [5]

(b) 'Raising the column temperature' and 'Temperature programming' greatly affect the performance of a column during chromatographic analysis.

(i) What is meant by 'temperature programming' of a chromatographic column? [2]

(ii) Discuss the effects of the above two processes on the performance of a chromatographic column. [7]

(c) For the packed and the open tubular columns of a gas chromatograph:

(i) Give two differences in their structures. [2]

(ii) Give four advantages of open tubular columns over packed columns. [4]

(d) What are the function and ideal properties of the liquid (Stationary) phase of a G.C? [5]

Question 4 (25 marks)

(a) With respect to G.C, what is a chromatogram? Illustrate its use in this method for the qualitative and quantitative analysis of a sample. [6]

(b) In gas chromatography (G.C), what is column efficiency? How does it vary with N, the number of theoretical plates and H, the plate height? What other factors influence it? [5]

(c) The retention tine, t_r, of a solute is 25.0 s on a column with $N = 5.4 \times 10^3$

(i) Calculate $W_{1/2}$ (width at half the peak height). [4]

(ii) W, the expected base width of the solute's peak. [2]

(d) What are the function and the ideal properties of the solid support in a G.C packed column? [5]

(e) Give two examples of industries or establishments in Swaziland where G.C is employed for routine analysis, stating the specific type of each analysis carried out in each case. [3]

Question 5 (25 marks)

(a) Give three advantages of thin layer chromatography (T.L.C) over paper chromatography. [3]

(b) For the T.L.C.

(i) Give two examples each of the stationary phases and mobile phases commonly used for analysis. [4]

(ii) What stationary phases would you employ for the analysis of:

- a polar compound
- a weakly polar compound [2]

(c) Briefly describe the procedure for chromatogram development and detection of analyte spots. [7]

(d) For the 'Rf-Value' TLC experiments:

(i) Give its definition. [1]

(ii) Using a diagrammatic illustration only, demonstrate how it ca be measured. [4]

(e) Give four factors that influence the Rf Value of a compound. [4]

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	$R_\infty = m_e e^4/8h^3c$	$1.097\,37 \times 10^{5}$ 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

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
IA	IIA	IIIB	IVB	VB	VIB	VIIB		VIIIB		IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1.008 H 1																	4.003 He 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	18.998 F 9	20.180 Ne 10
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	35.453 Cl 17	39.948 Ar 18
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	79.904 Br 35	83.80 Kr 36
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	126.90 I 53	131.29 Xe 54
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	(222) Rn 86
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								

thanide 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
tinide 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.