

UNIVERSITY OF SWAZILAND
SECOND SEMESTER EXAMINATION 2012/2013

TITLE OF PAPER : **Instrumental Methods For Environmental Analysis - 2**

COURSE CODE : **EHS574**

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.

REQUIRED: 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) Explain the following terms:

- i) A normal calibration curve [2]
- ii) Matrix matching [2]

b) Briefly discuss how the multiple point external standardization, (the Normal Calibration curve) can be used to obtain the concentration of a sample during a FAAS analysis.

[8]

c) After all the necessary pretreatments, the ashed residue of 4.02g of a plant sample was dissolved in 10mL of 1:9 HNO₃, filtered, and diluted to 50mL in a volumetric flask. The following data were obtained during a this analysis for the concentration of Na by the flame atomic emission spectroscopic(FAES), method

<u>Sample</u>	<u>ppm Na</u>	<u>Emission (arbitrary units)</u>
blank	0	0
standard 1	2.00	90.3
standard 2	4.00	181
standard 3	6.00	272
standard 4	8.00	363
standard 5	10.00	448
sample		238

Determine the parts per million Na in the plant sample.. [13]

Question 2 (25 marks)

(a) State 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, HB, 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, was being isolated from an aqueous sample by solvent extraction method, using carbon tetrachloride as the extracting solvent. 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 of carbon tetrachloride? Justify your answer with appropriate calculations. [6]

Question 3 (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 1.0×10^{-7} 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 a metal chelate using a 1.0×10^{-4} M dithizone at pH 1.0; Take $K_a = 3.0 \times 10^{-5}$ [6]

Question 4 (25 marks)

- (a) For the following sets of chromatographic terms, explain/define the terms in each set and give an expression that relates them.
- (i) Retention time, t_R , adjusted retention time t'_R and dead time, t_M .
- (ii) Capacity factor, k , retention time, t_R and dead time, t_M .

- (iii) Volume flow rate, F , retention volume, V_R and retention time, t_R
(Each term needs to be defined only once) [9]
- (b) Explain the terms resolution, R_s , between two adjacent peaks in a chromatogram. [2]
- (c) A solute was eluted completely from a chromatographic column over a period of 2min. 24s. Calculate its retention volume if its flow rate is 24.0 mL/min. [4]
- (d) During the chromatographic analysis of a sample, two adjacent peaks, A and B appear with the following features:

Component	t_R (min)	W (min)
A	8.36	0.96
B	9.54	0.64

- (i) Calculate the resolution between A and B. [3]
- (ii) If the retention time for an unretained solute is 1.20min, calculate the selectivity factor for A and B. [3]
- (iii) Calculate the capacity factors for A and B. [4]

Question 5 (25 marks)

- (a) In gas Chromatography (GC), what is column efficiency? How is its value influenced by N , the number of theoretical plates and H , the plate height? What other factors influence it? [5]
- (b) Explain the term 'temperature programming' with respect to GC analysis. With the aid of a graphical illustration, show how its use affects the resolution, R , the retention time and the number of solutes eluted during a GC analysis. Summarize its advantages over the isothermal method. [11]
- (c) Give five general applications of 'Gas Chromatographic Analysis'. Give four examples of industries and/or laboratories in Swaziland in which this method is being routinely employed for analysis. [9]

Question 6 (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' of a solute during TLC experiments:
- (i) Give its definition. [1]
- (ii) Using a diagrammatic illustration only, demonstrate how it can be measured. [4]
- (e) Give four factors that influence the Rf Value of a compound. [4]

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	GROUPS																																																			
	I	II	III	IV	V	VI	VII	VIII	VIII	VIII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII																															
1	IA H 1.008	IIA He 4.003																																																		
2	Li 6.941	Be 9.012																																																		
3	Na 22.990	Mg 24.305																																																		
4	K 39.098	Ca 40.078																																																		
5	Rb 85.468	Sr 87.62																																																		
6	Cs 132.91	Ba 137.33																																																		
7	Fr 223	Ra 226.03																																																		
			TRANSITION ELEMENTS																																																	
			Sc 44.956	Ti 47.88	V 50.942	Cr 51.996	Mn 54.938	Fe 55.847	Co 58.933	Ni 58.69	Cu 63.546	Zn 65.39	Ga 69.723	Ge 72.61	As 74.922	Se 78.96	Br 79.904	Kr 83.80	Rb 85.468	Sr 87.62	Y 88.906	Zr 91.224	Nb 92.906	Mo 95.94	Tc 98.907	Ru 101.07	Rh 102.91	Pd 106.42	Ag 107.87	Cd 112.41	In 114.82	Sn 118.71	Sb 121.75	Te 127.60	I 126.90	Xe 131.29	Ba 137.33	Hf 178.49	Ta 180.95	W 183.85	Re 186.21	Os 190.2	Ir 192.22	Pt 195.08	Au 196.97	Hg 200.59	Tl 204.38	Pb 207.2	Bi 208.98	Po (209)	At (210)	Rn (222)

Atomic mass —
Symbol —
Atomic No.

*Lanthanide Series
**Actinide Series

140.12	140.91	144.24	(145)	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.04	174.97
Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
232.04	231.04	238.03	237.05	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(260)
Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

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

General data and
fundamental
constants.

Quantity	Symbol	Value
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	$F = eN_A$	$9.5435 \times 10^4 \text{ C mol}^{-1}$
Boltzmann constant	k	$1.380\,66 \times 10^{-23} \text{ J K}^{-1}$
Gas constant	$R = kN_A$	$8.314\,51 \text{ J K}^{-1} \text{ mol}^{-1}$ $8.205\,78 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$
Planck constant	h	$6.626\,07 \times 10^{-34} \text{ J s}$
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34} \text{ J s}$
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†	μ_0	$4\pi \times 10^{-7} \text{ J s}^2 \text{ C}^{-2} \text{ m}^{-1}$
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	$R_\infty = m_e e^4/8h^3 c$	$1.097\,37 \times 10^5 \text{ cm}^{-1}$
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	μ	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	