UNIVERSITY OF SWAZILAND
FACULTY OF HEALTH SCIENCES
DEGREE IN ENVIRONMENTAL HEALTH SCIENCE
FINAL EXAMINATION PAPER, 2006

TITLE OF PAPER: INSTRUMENTAL METHODS FOR ENVIRONMENTAL ANALYSIS

COURSE CODE: EHS 537

DURATION: 3 HOURS

INSTRUCTIONS: ANSWER ANY FIVE QUESTIONS. EACH QUESTION CARRIES 20 MARKS.

NO PAPER SHOULD BE BROUGHT INTO OR OUT OF THE EXAMINATION ROOM.

START EACH QUESTION ON A SEPARATE SHEET OF PAPER.

A PERIODIC TABLE AND OTHER USEFUL DATA HAVE BEEN PROVIDED WITH THIS PAPER.

DO NOT OPEN THIS QUESTION PAPER UNTIL PERMISION TO DO SO IS GRANTED BY THE CHIEF INVIGILATOR.

Question I (20 marks)

(a) State the factors that would guide you in selecting an appropriate method for the analysis of an environmental sample. (4).

(b) Explain the term 'sampling' of an environmental sample for analysis. What steps should be taken to ensure that appropriate sampling has been carried out? (3).

©. Why is sample pretreatment usually a necessary step prior to the actual analysis of the sample? Give four of such pretreatment steps often employed for samples in environmental/analytical laboratories. (5)

(d) Using a labeled diagram, identify the basic components of a typical instrument for chemical analysis. State the functions of any one of the components and give an example in a named instrument. (8)

Question 2 (20 marks)

(a). explain the term 'deviation from Beer's law'. Using a graphical illustration distinguish between a positive and a negative deviation from Beer's law. (4)

(b) Briefly discuss the causes and possible corrections of real (true) deviation from Beer's law. (4)

(c). The combined absorbance, A_c, when a beam of radiation, made up of two wavelengths λ and λ^1 with molar absorptivities of ϵ and ϵ^1 respectively, pass through an absorbing solution is given by:

$$A_c = \log\{P_o + P_o^1\} - \log\{P_o 10^{-\epsilon bc} + P_o^1 10^{-\epsilon' bc}\}$$

(i). Assuming Beer's law applies, obtain this expression. (3)

(ii). What type of deviation from Beer's law (if any), occurs when: $\epsilon = \epsilon^1$, $\epsilon > \epsilon^1$, and $\epsilon < \epsilon^1$ (3)

(d). Stray radiations have been identified as one of the instrumental causes of deviation from Beer's law during spectroscopic analysis:

(i) What are their main features? (4)

(ii) Give the expression for the measured absorbance, A_m due to them, and define all the parameters involved in it. (2)

Question 3 (20 marks)

(a) Briefly describe how you would prepare a KBr pellet for the IR spectroscopic analysis of a sample. (3)

(b). Categorize the following spectroscopic methods as either 'absorption' or 'emission' and state the quantity measured in each case.

(i) FAES, (ii) FAAS, (iii) FAFS. (3)

(c). Identify at least one difference in the setup or design of the following pairs of instruments:
(i) FAES and FAAS, (ii) FAFS and FAES,
(iii) FAAS and FAFS. (3)

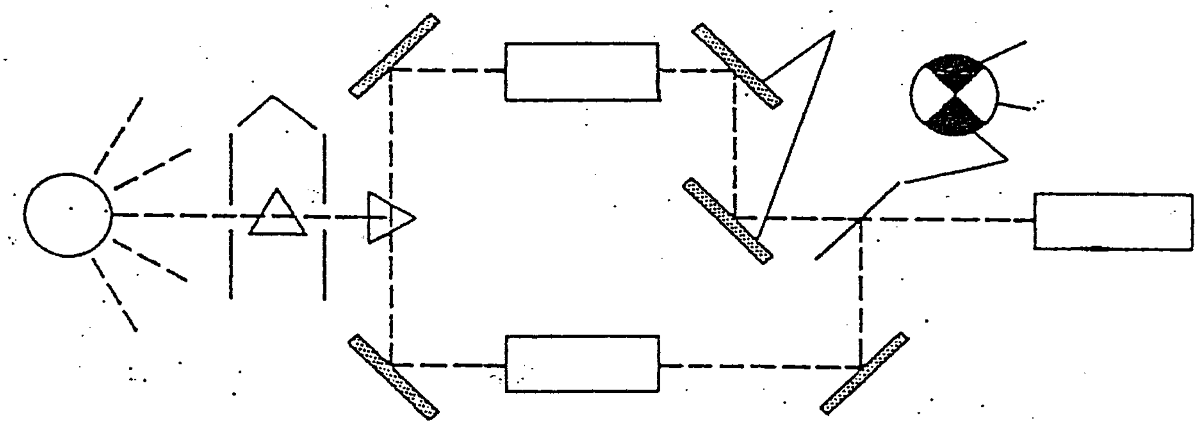
(d) Attached on the next page is the unlabelled diagram of a double beam in time configuration spectrophotometer:
(i) Label the diagram. (5)
(ii) Briefly discuss its working principles. (3)
(iii) Give its advantages over a single beam spectrophotometer. (2)
(iv) What is its advantage over a double beam in space configuration? (1)

Question 4 (20 marks)

(a). For the 'Flame Atomic Absorption Spectroscopic technique:
(i) State the basic components of the instrumental set up. (3)
(ii) Give a brief account of its working principles. (4)
(iii) Give two examples of environmental analysis for which it can be employed. (2)

(b). The 'Hollow Cathode Lamp' is a vital part of a number of atomic spectroscopic instruments:
(i) Give two examples of such instruments. (1)
(ii) Using a schematic diagram as an additional illustrative discuss its configuration and working principles. (8)
(iii) What are the weaknesses of 'multi-element' types relative to the single element series? (2)

This page should be removed and attached to the answer script after labeling.



Question 5 (20 marks)

(a) (i) Explain the term 'source' with regard to Atomic Spectroscopic Methods. (1)

(ii) Give two commonly employed 'sources' in atomic spectroscopy and the instruments/methods in which they are used. (2)

(iii) State four of the idealized goals of any such sources. (4)

(b) What is an interference with regard to chemical analysis? How is an interference generally countered or corrected? (2)

© In the case of 'Vapourization' (or 'Chemical') interference commonly associated with flames and furnaces during spectroscopic analysis:

(i) Discuss its cause/origin. (1)

(ii) Using illustrative examples, discuss the methods usually employed for its correction/reduction. (10)

Question 6 (20 marks)

(a) State the Nernst distribution law. Give mathemathecal expression for it and define all the parameters involved in it. (3)

(b) Distinguish between distribution coefficient, K_D and distribution ratio, D, used during solvent extraction analysis. Illustrate this difference with an example. (4)

© For the extraction f a weak acid, HB, whose anion (B^-), does not penetrate the organic phase and is monomeric in both phases:

(i) **State** the expression for its distribution ratio and define all the parameters in it. (3)

(ii) Give two of the factors that influence the value of D. (2)

(d) A solute being extracted from water with carbon tetrachloride has a distribution ratio, D, of 85.0

(i) What percentage is extracted from the aqueous phase when 50.0mL of 1.0×10^{-3}M aqueous solution of the solute is extracted with 50.0mL of carbon tetrachloride? (5)

(ii) Would you have preferred employing two successive extractions, each with 25.0mL carbon tetrachloride? Explain.. (3)

Question 7 (20 marks)

(a) What is a chromatogram? Using an illustrative diagram, show how it is employed for both qualitative and quantitative analysis of a sample. (6)

(b) (i) What is 'Temperature programming' of a chromatographic column? (2)

(ii) Discuss the effects of 'Temperature programming' on the performance of a chromatographic column. (4)

© What is column efficiency with regards to gas chromatography? (1)

(d) A column produces an elution peak after 148s. Given that the width of the peak at half its height ($w_{1/2}$), is 3.30s:

(i) Calculate N, the number of theoretical plates in the column. (4)

(ii) If the column is 6ft 4in long, calculate the column efficiency, H(the H.E.T.P.) (3)

Question 8 (20 marks)

(a) Define R_f value, with regards to qualitative analysis in planar chromatography. (2)

(b) For the analysis of a polar compound using the TLC method, give a brief procedure for the:

(i) Preparation of the TLC plate (6)

(ii) Identification of the separated components/spots on the TLC plate. (6)

© Compare and contrast 'Thin Layer Chromatography' with the 'Paper Chromatography' with respect to:

(i) the nature of the stationary phases

(ii) the nature of the mobile phases

(iii) resolution and sensitivity. (6)

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1.008 H 1																	4.003 He 2
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	18.998 F 9	20.180 Ne 10
3	22.990 Na 11	24.305 Mg 12											26.982 Al 13	28.086 Si 14	30.974 P 15	32.06 S 16	35.453 Cl 17	39.948 Ar 18
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	79.904 Br 35	83.80 Kr 36
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	126.90 I 53	131.29 Xe 54
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	(222) Rn 86
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								

TRANSITION ELEMENTS

Key: Atomic mass → 10.811; Symbol → B; Atomic No. → 5

*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
**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.

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	$R_\infty = m_e e^4/8h^3 c \varepsilon_0^2$	$1.097\,37 \times 10^{5}$ 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}