UNIVERSITY OF SWAZILAND

DEPARTMENT OF ENVIRONMENTAL HEALTH SCIENCE

SUPPLEMENTARY EXAMINATION 2012

TITLE OF PAPER: INSTRUMENTAL METHODS FOR ENVIRONMENTAL ANALYSIS – I

COURSE CODE: EHS573

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.

You are not supposed to open this paper until permission to do so has been granted by the Chief Invigilator.

Question 1(25 marks)

(a) Distinguish between classical and instrumental methods of analysis. [2]

(b) What are the unique advantages of instrumental methods of analysis over the classical methods? [4]

(c) List the principal classes of chemical instrumentation. Give two specific examples of instrumental techniques from each principal class given. [6]

(d) Using a labeled diagram, show the basic components of an instrument for chemical/environmental analysis, discuss the functions of any one of the components and give an example in named equipment. [8]

(e) List the salient performance characteristics of an instrument for environmental analysis. [5]

Question 2(25 marks)

(a) A given light radiation passes basic components from a medium x, to another medium y, having refractive indices n_x and n_y respectively. Given that $n_x > n_y$. In which of the two media does the radiation have a greater :

(i) Wavelength; (ii) Frequency; (iii) Energy ? [3]

(b)

(i) Define the terms 'Absorbance' and 'Transmittance' for an absorbing medium. [2]

(ii) Obtain an expression relating the two terms i.e A & T. [4]

(c) For a medium that obeys Beer's law;

(i) Discuss the variation of absorbance with the pathlength and concentration of the solution respectively at a given wavelength. [3]

(ii) For a poorly absorbing medium,, which cell would you prefer to use and why? – a 1.00-cm of a 4.00-cm cell. [3]

(d) A bismuth(III) complex solution has a molar absorptivity of $9.32 \times 10^3\ M^{-1}cm^{-1}$ at 470nm.

(i) Calculate the absorbance of a 6.24×10^{-5} M solution of the complex at 470nm in a 2.00-cm cell.

(ii) Estimate the %T of the solution in d(i).

(iii) What is the concentration (in M), of the complex in a solution having the same absorbance an the described in d9i0 when measured at 470nm in a 4.00-cm cell? [10]

Question 3(25 marks)

(a) Briefly discuss the causes of, and the corresponding corrections for true (real) deviations fro Beer's law. [6]

(b)

(i) What factors are responsible for instrumental deviation from Beer's law? [3]

(ii) How can instrumental deviation be generally minimized? [1]

(c) When a beam of polychromatic radiations, made up of two wavelengths, λ and λ^1 with molar absorptivities of ϵ and ϵ^1 respectively pass through an absorbing solution, the combined, A_c, is given by:

$A_c = \log(P_o - P_o^1) - \log(P_o 10^{-\epsilon bc} + P_o^1 10^{-\epsilon bc})$. What deductions can be made when:

(i) $\epsilon = \epsilon^1$ (iii) $\epsilon > \epsilon^1$ (iii) $\epsilon < \epsilon^1$ [6]

(d)

(i) Discuss the characteristics and effects of stray radiations during absorbance measurements.

(ii) Give the expression relating the measured absorbance, A_m in the presence of the stray radiation, P_s (Radiant power of stray radiation), P_o and P.

(iii) How is the value of the observed absorbance affected when the solution is highly concentrated and $P_s \approx P + P_s$?

(iv) Compare A_m(measured absorbance) with A (true absorbance) and hence deduce the type of deviation (positive or negative) from Beer's law caused by stray radiations. [9]

Question 4(25 marks)

(a) What is a monochromator? [1]

(b) For a spectrophotometer, list the components of a monochromator system and state the respective functions of each component given. [6]

(c) For each of the following spectral regions, suggest an appropriate monocromator prism material :
(i) Visible (ii) UV (iii) IR
Give an appropriate reason for your choice. [4]

(d) State the advantages and weaknesses of "diffraction gratings" when compared with a "glass prism" as monochromators for spectrophotometers. [4]

(e)

(i) Explain the term 'Disperson of a prism'. Hence, briefly describe the working principles of a prism as a monochromator. [6]

(ii) What are the factors that increase the resolution of a 'prism' and 'diffraction gratings' [4]

Question 5(25 marks)

(a) Distinguish between a selective detector and non-selective detector. Give an example of each type. [3]

(b) As briefly as possible, discuss the design, the region of use and the working principles of each of the following spectrophotometer detectors:
(i) The Photomultiplier tube, (ii) The thermocouple.
Give one major weakness of the Thermocouple as a detector. [15]

(c) What are the necessary precautions that should be taken in the handling of a cuvette/cell, during a UV spectrophotometeric analysis? [4]

(d) Describe how you would prepare a KBr pellet for an IR spectroscopic analysis of a sample. [3]

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	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e$	$5.291\,77 \times 10^{-11}$ m
Rydberg constant	$R_\infty = m_e e^4/8h^3 c$	$1.097\,37 \times 10^{5}$ 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 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										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
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	35.453 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								

*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.