UNIVERSITY OF SWAZILAND

Faculty of Health Science
Department of Environmental Health Sciences
Final Examination 2011/12

Title of paper: Instrumental Methods for Environmental Analysis

Course code: EHS 573

Time allowed: 2 HOURS

Marks allocation: 100 Marks

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

Question1 (25 marks)

(a) Distinguish between the following terms:
(i) Precision and Accuracy, (ii) Precision and Bias. (4)

(b) What are the factors you would take into consideration before choosing an appropriate method for the analysis of a given sample? (4)

(c) Why is sample pretreatment necessary before carrying out the actual analysis on a given sample? Give four examples of such pretreatment steps often employed in analytical laboratories. (5)

(d) Why should the chemical environment of a sample be properly controlled during analysis? Give one such control measures that could be taken to assure accuracy of obtained data. (3)

(e) **State,** sequentially, the steps that should be followed in solving a given analytical problem (i.e. in the analysis of a given sample). (5)

(f) Define the' detection limit' of an analytical method.
Using a labeled figure, illustrate the useful concentration range of an analytical method.

(4)

Question 2 (25 marks)

(a) When a molecule absorbs a photon or radiation,
(i) Discuss the possible types of transitions it can undergo
(ii) Define the type of energy involved in each transition,
(iii) Arrange the energies involved in the transitions in decreasing order of their magnitudes. (8)

(b) (i) State Beer's law
(ii) State the mathematical expression for Beer's law, define all the terms in it and give their respective S.I. units. (5)

(c) The molar absorptivity, Є, of the solution of a compound is $9.32 \times 1O^{3} M^{-1} cm^{-1}$ at 508nm. Calculate:
(i) The absorbance of a $3.12 \times 1O^{-5}$M solution of the compound at 508nm in a 2.00 - cm cell.
(ii) The %T of the solution described in c(i), above,
(iii) The absorbance and the %T of the solution described in c(i) above when a 4.00 - cm cell is used, with the measurement also taken at 508nm. Based on Beer's law, account for the difference in the two absorbance values.

(12)

Question 3 (25 marks)

(a) Explain the expression "deviation from Beer's law". Use a graphical figure to differentiate between a positive and a negative deviation from Beer's law. (4)

(b) Discuss the causes and possible correction of real deviation from Beer's law. (4)

(c) A beam of polychromatic light consisting of two wavelengths λ, and $\lambda^{!}$, to which Beer's law is applicable is made to pass through an absorbing solution.

(i) Give an expression for the combined absorbance, A_c for the beam of light.

(ii) With appropriate explanation, what type of deviation from Beer's law occurs when: $\epsilon = \epsilon^{!}$, $\epsilon > \epsilon^{!}$ and $\epsilon < \epsilon^{!}$ respectively? (7)

(d) Occurrence of stray radiations within the instrument is a common feature during spectroscopic analysis.

(i) State the main characteristics of such radiations

(ii) Give the expression for the measured absorbance, A_m, in the presence of such radiations in terms of P_s (radiant power of stray radiation), P_o and P.

(iii) How is the value of A_m affected when the solution is highly concentrated and $P_s \approx P + P_s$? (7)

(e) Give three 'poor performance signals' of an instrument that can result in deviation from Beer's law. (3)

Question 4 (25 marks)

(a) Differentiate between a selective detector and nonselective detector. Give an example of each type. (3)

(b) Briefly discuss the design, the regions of application and operating principles of the following types of detectors:

(i) The photomultiplier tube.

(ii) The Thermocouple.

Give one major disadvantage of (ii). (15)

(c) (i) State the essential precautions that must be adhered to when using a cuvett/cell for UV Spectrophotometric measurements. Why are these steps important? (4)

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

Question 5 (25 marks)

(a) Give at least one difference in the instrumental design for the following atomic spectroscopic methods of analysis.
(i) AAS and FES; (ii) AAS and AFS; (iii) AFS and FES. (5)

(b) Which is more sensitive to flame temperature stability, AAS or FES and why? (5)

(c) (i) Give five advantages of ICP (Inductively Coupled Plasma) spectroscopic method of analysis over the other conventional spectroscopic methods. (5)
(ii) Briefly describe the working principles of ICP. (10)

Question 6 (25 marks)

(a) For the 'Hollow Cathode Lamp' of an Atomic Absorption Spectrophotometer:
(i) With the aid of a schematic diagram, give details of its configuration. (5)
(ii) Briefly describe its working principles. (6)
(iii) What are the disadvantages associated with the use of a multi-element 'Hollow Cathode Lamp'? (2)

(b) For the Electrothermal Atomic Absorption Spectrophotometer (EAAS):
(i) List three of its advantages over the Flame AAS. (3)
(ii) Discuss the stages involved in the atomization of a sample when using this method. (7)
(iii) Account for the use of a 'Matrix Modifier' during analysis involving the use of this method. (2)

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}

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

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.