UNIVERSITY OF SWAZILAND

Faculty of Health Science

Department of Environmental Health Science

Supplementary Examination

July 2013

Title of paper: Instrumental Methods for Environmental Analysis-I

Course code: EHS 573/EHM 204

Time allowed: 2 HOURS

Marks allocation: 100 Marks

Instructions:

1) ANSWER **ANY FOUR 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

Question 1(25 marks)

(a) Identify the main factors that would guide you in selecting an appropriate method for the analysis of an environmental sample. [6]

(b) Explain the term 'sampling' of an environmental sample for analysis. What steps should be taken to ensure that an appropriate sampling has been carried out? [4]

(c) Why is sample pretreatment usually a necessary step prior to the analysis of the sample? Give four of the usual pre-treatment steps often employed during analysis of environmental samples. [5]

(d) Using a labeled diagram, identify the basic components of a typical instrument for chemical analysis. State the functions of any two of the components and give an example in a named instrument. [10]

Question 2 (25 marks)

(a) What is meant by the term 'deviation from Beer's law'? Using a graphical illustration, distinguish between positive and negative deviations from Beer's law. [4]

(b) Discuss the causes and possible corrections of true (real), deviation from Beer's law. [5]

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

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

(i) Assuming Beer's law holds, obtain this expression. [4]

(ii) What type of deviation from Beer's law (if any), occurs when:

$\epsilon = \epsilon^1$, $\epsilon > \epsilon^1$ and $\epsilon < \epsilon^1$? [6]

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

(i) What are the characteristics of these radiations? [4]

(ii) Give the expression for the measured absorbance, A_m, due to them and state the type of deviation they cause i.e. positive or negative. [2]

Question 3 (25 marks)

For the (Graphite furnace

a) Label drawn schematic diagram of it.. [3]

b) Give four of its advantages and three of its disadvantages over the flame AAS. [7]

c) Discuss the stages involved in the atomization process of a sample. [8]

d) Account for the uses of 'the flowing inert gas' and the Matrix modifier' during analysis involving the use of this method. [6]

Question 4 (25 marks)

a) For the following spectrophotometric methods:
FAAS, FAES, AFS, ICP, ICP-AFS
i) Classify them into two groups as 'emission' or 'absorption' methods.
ii) State the quantity measured in each case. [5]

b) Using the 'Spectronic 20' as a typical example of a single beam spectrophotometer
i) Label a well drawn schematic diagram of its optical train. [6]
ii) What materials are used for the source of radiation, the wavelength dispersing medium and the detector respectively? [3]
iii) Why is it referred to as 'a single beam instrument'? [1]

c) Briefly discuss the working principles of the FAES (flame atomic emission) spectrometry. [10]

Question 5(25 marks)

a) Identify 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) Give five advantages of ICP (Inductively Coupled Plasma) spectroscopic method of analysis over the other conventional speetroscopic methods. [5]

d) Briefly describe the working principles of ICP. [10]

Question 6(25 marks)

a) Explain the term interference with regards to flames and furnaces? [2]

b) Concerning the 'spectral', 'chemical'and 'ionization' interferences associated with flames and furnaces, discuss:

(i) Their causes

(ii) The steps normally taken to correct or eliminate each of them. [15]

c) (i) Give two examples each of a 'cool flame' and a hot flame'

(ii) Explain the following observation. "Although chemical interferences are more prevalent in 'cool' flames, these flame are often preferred for the analysis of alkali metals" [8]

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	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	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.

General data and fundamental constants

Quantity	Symbol	Value
Speed of light†	c	$2.997\,924\,58 \times 10^8\ \mathrm{m\,s^{-1}}$
Elementary charge	e	$1.602\,177 \times 10^{-19}\ \mathrm{C}$
Faraday constant	$F = eN_A$	$9.6485 \times 10^4\ \mathrm{C\,mol^{-1}}$
Boltzmann constant	k	$1.380\,66 \times 10^{-23}\ \mathrm{J\,K^{-1}}$
Gas constant	$R = kN_A$	$8.314\,51\ \mathrm{J\,K^{-1}\,mol^{-1}}$
		$8.205\,78 \times 10^{-2}\ \mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}$
		$62.364\ \mathrm{L\,Torr\,K^{-1}\,mol^{-1}}$
Planck constant	h	$6.626\,08 \times 10^{-34}\ \mathrm{J\,s}$
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34}\ \mathrm{J\,s}$
Avogadro constant	N_A	$6.022\,14 \times 10^{23}\ \mathrm{mol^{-1}}$
Atomic mass unit	u	$1.660\,54 \times 10^{-27}\ \mathrm{kg}$
Mass of		
electron	m_e	$9.109\,39 \times 10^{-31}\ \mathrm{kg}$
proton	m_p	$1.672\,62 \times 10^{-27}\ \mathrm{kg}$
neutron	m_n	$1.674\,93 \times 10^{-27}\ \mathrm{kg}$
Vacuum permeability†	μ_0	$4\pi \times 10^{-7}\ \mathrm{J\,s^2\,C^{-2}\,m^{-1}}$
		$4\pi \times 10^{-7}\ \mathrm{T^2\,J^{-1}\,m^3}$
Vacuum permittivity	$\varepsilon_0 = 1/c^2\mu_0$	$8.854\,19 \times 10^{-12}\ \mathrm{J^{-1}\,C^2\,m^{-1}}$
	$4\pi\varepsilon_0$	$1.112\,65 \times 10^{-10}\ \mathrm{J^{-1}\,C^2\,m^{-1}}$
Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24}\ \mathrm{J\,T^{-1}}$
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27}\ \mathrm{J\,T^{-1}}$
Electron g value	g_e	$2.002\,32$
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	$5.291\,77 \times 10^{-11}\ \mathrm{m}$
Rydberg constant	$R_\infty = m_e e^4/8h^3c$	$1.097\,37 \times 10^5\ \mathrm{cm^{-1}}$
Fine structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Gravitational constant	G	$6.672\,59 \times 10^{-11}\ \mathrm{N\,m^2\,kg^{-2}}$
Standard acceleration of free fall†	g	$9.806\,65\ \mathrm{m\,s^{-2}}$

† 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