UNIVERSITY OF SWAZILAND

Faculty of Health Science

Department of Environmental Health Sciences

Supplementary Examination July 2011

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

Question 1 (25 marks)

(a) *State* the factors that would help you in selecting the appropriate method for carrying out an analysis on a given environmental sample. [5]

(b) Define the term '*sampling*' of a sample for analysis.
Discuss very briefly the steps that should be taken to ensure that appropriate sampling has been carried out. [3]

(c) Why is sample pre - treatment necessary before carrying out the actual analysis on a given sample? Give four examples of pre-treatment steps commonly employed for samples in analytical laboratories. [5]

(d) With the help of a labeled diagram, identify *the basic components of an instrument* for chemical analysis. Discuss the functions of any two of the components and give an example in a named instrument. [12]

Question 2 (25 marks)

(a) Sensitivity and detection limit are two of the numerical criteria for selecting analytical methods:

(i) Explain these two terms. [2]

(ii) Identify and distinguish between the two types of sensitivities associated with instrumental techniques. [4]

(iii) State four other numerical criteria that can be employed for selecting an analytical method. [4]

(b) The aqueous solution of a sample, A, was analyzed using an instrumental method.

The calibration data obtained are shown in the following table:

Concentration (ppm)	0.00	2.00	6.00	10.00	14.00	18.00
No. of Replications, N	25.0	5.00	5.00	5.00	5.00	5.00
Mean Analytical Signal, S	0.031	0.173	0.442	0.702	0.956	1.248
Standard Deviation, s	0.00779	0.0094	0.0084	0.0084	0.0085	0.0110

For this method, calculate:

(i) The minimum analytical signal, $\mathbf{S_m}$.

(ii) The calibration sensitivity, **m** and

(iii) The detection limit, $\mathbf{C_m}$. [15]

[Question 3 (25 marks)

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

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

(c) The combined absorbance, A_c, when a beam of radiation made up of two wavelengths λ and λ^1, with molar absorbances of ϵ and ϵ^1 respectively, passes 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 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 4 (25 marks)

(a) What is a monochromator? [2]

(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 [5]
Give an appropriate reason for your choice.

(d) What are the advantages and disadvantages 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.

(ii) List are the factors that increase the resolution of a 'prism' and 'diffraction gratings' [8]

Question 5 (25 marks)

(a) Using the 'Spectronic 20' as a typical example of a single beam spectrophotometer;

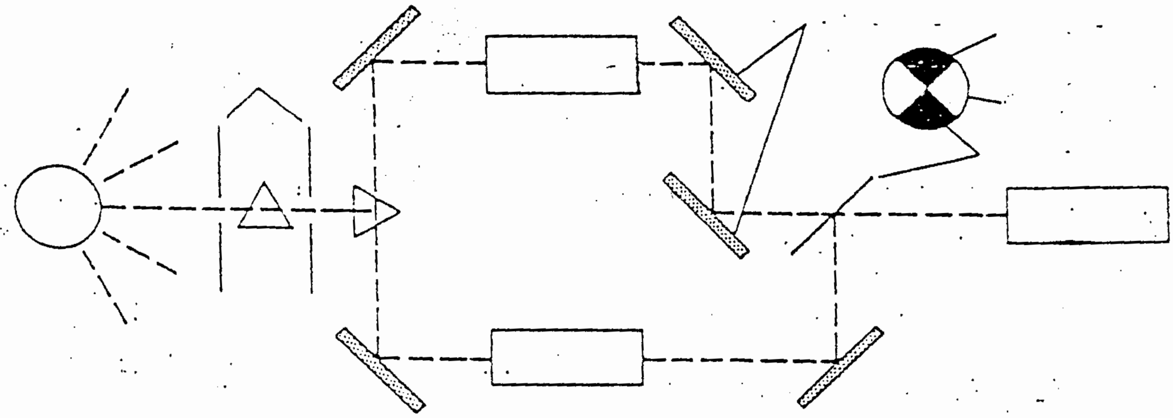
(i) Draw and label the sketchy diagram of its optical train.
(ii) State the material used for its source of radiation, the wavelength dispersing medium, and the detector. [9]

(b) Attached is the unlabelled diagram of a double beam in time configuration spectrophotometer:

(i) Label the diagram
(ii) Give a brief description of its working principles.
(iii) What advantages does it have over a single beam spectrophotometer
(iv) State one advantage it has over a double beam in space type off the Spectrophotometer. [11]

(c) With an accompanying and appropriate figure, briefly describe how to make a Beer's law calibration curve. Show how the concentration of an analyte can be obtained from the curve. [5]

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



Question 6 (25 marks)

For the elecrothermal atomic absorption spectrophotometry (EAAS), Discuss/Describe:

(a) Its main structural (configurational) features, using a schematic diagram as support. [7]

(b) The stages involved in the atomization process. [9]

(c) Absorbance measurement and use of matrix modifiers. [3]

(d) Its advantages and weakness when compared with the flame atomic absorption spectrometry. [6]

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	$F = eN_A$	$9.6485 \times 10^{4}\ C\ mol^{-1}$
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	$R_\infty = m_e e^4/8h^3c\varepsilon_0^2$	$1.097\,37 \times 10^{5}\ cm^{-1}$
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

Atomic mass →
Symbol →
Atomic No. →

TRANSITION ELEMENTS

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											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								

*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.