UNIVERSITY OF SWAZILAND

FACULTY OF HEALTH SCIENCES

Department of Environmental Health sciences

Supplementary Examination 2013/14

Title : Instrumental methods for environmental analysis

Code : EHM 204

Time : 2 hours

Marks : 100

Instructions:

1. Answer any 4 questions,
2. Each question weighs 25 marks,
3. Start each question on a fresh page,
4. Diagrams and graphs should be large and clearly well labelled,
5. Non-programmable scientific calculators may be used.

Additional material;

- Graph papers (2),
- Periodic table,
- A table of scientific constants

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QUESTION 1

a) State the important factors to be considered when choosing a method for the analysis of an environmental sample. [5]

b) Explain the term 'sampling' as used in environmental analysis. What precautionary steps should be taken to ensure that a representative sample is taken for instrumental analysis? [5]

c) of the most common pre-treatment steps usually employed for environmental analysis. [5]

d) List three (3) figures of merit commonly used to express precision of an instrument. [3]

e) A solution containing 8.75 ppm $KMnO_4$ has a transmittance of 0.743 in a 1-cm cell at 540 nm. Calculate the molar absorptivity of $KMnO_4$. [5]

f) Give the most common material types that are used to make cuvettes employed as sample containers in a UV spectrometer. [2]

QUESTION 2

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

b) Explain the difference between 'real deviations' from Beer's law and those that are due from instrumental and chemical factors. [3]

c) Explain the observed differences in spectra between atomic and molecular absorptions. [4]

d) A sophisticated ultraviolet/visible/near-IR instrument has a wavelength range of 185 to 3000 nm.
   i. What are its wave number and frequency ranges? [4]
   ii. Hence, calculate the energy (J) of a photon emitted at this wavelength. [2]

e) Draw a large, clearly labeled schematic diagram of a double beam UV spectrometer. [6]

f) What are the advantages of a double beam over a single beam UV spectrometer? [2]

QUESTION 3

A pharmaceutical company is suspected of disposing effluent waste that contains the pollutant metal lead, into a river. Pharmaceutical wastes are considered difficult matrices to extract analytes from. To determine the concentration, a series of solutions are made by adding 0.1, 0.2, 0.3, 0.4 and 0.5 mL of a 10 mgL^{-1} lead standard solution to 100 mL aliquots of the unknown solution. The following results were obtained:

Volume std (mL)	0	0.1	0.2	0.3	0.4	0.5
Absorbance (au)	0.27	0.37	0.53	0.65	0.75	0.88

a) Define the following terms as applied above:
   i. Analyte,
   ii. Aliquot,
   iii. Matrix,

iv. Standard solution. [4]

b) Explain the phrase; 'extraction of analyte from matrix' with respect to atomic absorption spectrometry. [1]

c) Give one such example of an extraction technique that can be used to extract the lead. Justify your choice of technique. [4]

d) Calculate the concentration of lead at each standard addition in μgL^{-1}. [5]

e) Plot a calibration curve and determine the concentration of the unknown in μgL^{-1}. [6]

f) Express the concentration above (e) in mg/L. [2]

g) Describe what would happen if the concentration was below the detection limits of the instrument. What steps would you undertake to correct this problem? [3]

QUESTION 4

For the Electrothermal atomic absorption spectrometer (ETAAS) or graphite furnace,

a) State its advantages in elemental determinations, [4]

b) Discuss the stages involved in the atomization process of a sample, [8]

c) What is the role of the argon gas? [2]

d) Draw and fully label a schematic for a hollow cathode lamp. [5]

e) Explain the operation of a photomultiplier tube detector, using a schematic diagram to illustrate. [6]

QUESTION 5

For the inductively coupled plasma atomic emission spectroscopy (ICP-AES) and atomic absorption spectroscopy (AAS),

a) What are the advantages of an ICP flame over conventional flames? [2]

b) Give two (2) types of plasma commonly employed to generate a flame in ICP-AES. [2]

c) What are the advantages of ICP-AES over AAS technique? [5]

d) Explain the concept of nebulization using an appropriate schematic diagram. [5]

e) What is a monochromator? [2]

f) For a spectrometer, list the components of a monochromator and state the respective functions of each component given. [8]

g) What are chromophores? [1]

THE PERIODIC TABLE OF ELEMENTS

NON-METALS

METALLOIDS

METALS

Group	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
Period 1	1 **H** 1.008																	2 **He** 4.003
2	3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
3	11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.9	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
4	19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.90	23 **V** 50.94	24 **Cr** 52.01	25 **Mn** 54.9	26 **Fe** 55.85	27 **Co** 58.71	28 **Ni** 58.71	29 **Cu** 63.54	30 **Zn** 65.37	31 **Ga** 69.7	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.91	36 **Kr** 83.80
5	37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 91.22	42 **Mo** 95.94	43 **Tc** 98.9	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
6	55 **Cs** 132.9	56 **Ba** 137.3	71 **Lu** 174.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.8	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 196.9	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 208.9	84 **Po** 210	85 **At** 210	86 **Rn** 222
7	87 **Fr** 223	88 **Ra** 226.0	103 **Lr** 257	104 **Unq**	105 **Unp**	106 **Unh**	107 **Uns**	108 **Uno**	109 **Une**									

Lanthanides	57 **La** 138.9	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** 146.9	62 **Sm** 150.9	63 **Eu** 151.3	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0
Actinides	89 **Ac** 227.0	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** 237.1	94 **Pu** 239.1	95 **Am** 241.1	96 **Cm** 247.1	97 **Bk** 249.1	98 **Cf** 251.1	99 **Es** 254.1	100 **Fm** 257.1	101 **Md** 258.1	102 **No** 255

*Numbers below the symbol indicates the **atomic masses**; and the numbers above the symbol indicates the atomic numbers.*

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