UNIVERSITY OF SWAZILAND
Faculty of Health Sciences
Department of Environmental Health Science

B.Sc. Degree in Environmental Health Science
MAIN EXAMINATION PAPER DECEMBER 2015

TITLE OF PAPER : Instrumental methods for Environmental Analysis

COURSE CODE : EHM204

DURATION : 2 HOURS

MARKS : 100

INSTRUCTIONS : THERE ARE FIVE QUESTIONS IN THIS EXAM

: ANSWER ANY FOUR OUT OF THE FIVE QUESTIONS

: EACH QUESTION CARRIES A MAXIMUM MARK OF 25%

QUESTION 1

1.1 Standards addition is a commonly used method in many practical analyses. Discuss when an analyst would choose a standards addition over a method based on use of a calibration curve, and what key assumptions are necessary to apply standards addition. (5)

1.2 What is the difference between an instrument detection limit and a method detection limit? (2)

1.3.1 Discuss solvent extraction and include its disadvantages in the extraction of organics from water samples. (5)

1.3.2 Are multiple batch extractions a solution for the disadvantages you have given in your answer for question 1.3.1 ? (3)

1.4 Explain how solid-phase microextraction (SPME) and solid phase extraction work. (10)

[25]

QUESTION 2

2.1 In chromatography, what is meant by retention factor? (4)

2.2 Discuss the Plate theory in gas chromatography (use diagrams and equations in your discussion). (9)

2.3 Explain the principle of each of the following detectors used in GC, and to which kinds of analytes do the detectors respond:

(a) Flame ionization detector (FID)

(b) Electron capture detector (ECD)

(12)

[25]

QUESTION 3

3.1 Nitrite was measured by two methods in samples of rainwater and drinking Water. Nitrite analysis results are shown in table 1.

Table 1: Nitrite analysis data for the two methods

	Gas Chromatography	**Spectrophotometry**
Rainwater	0.069 ±0.005	0.063 ±0.008
	n=7	n=5
Drinking water	0.078 ±0.007	0.087 ±0.008
	n=5	n=5

3.1.1 What statistical test can be carried out to determine whether the two methods are in agreement? With the data provided, is the statistical test possible? If not, justify. (6)

3.1.2 For each method, does drinking water contain significantly more nitrite than rainwater at 95% confidence? (5)

3.2 The gravimetric analysis of a Nickel compound was developed and compared to a spectrophotometric method. The w/w percentage of Nickel in the compound was reported in table 2.

Table 2: Analysis results from two methods

Gravimetric analysis (w/w%)	**Spectrophotometric analysis (w/w%)**
20.10	18.89
20.50	19.20
18.65	19.00
19.25	19.70
19.40	19.40
19.90	

(a) Is there significant difference between the two methods? (4)

(b) In each data set, are there outliers? Use the appropriate statistical test to reject data points. (5)

(c) What are the confidence limits in both methods? (5)

[25]

Question 4

4.1 A TLC plate was developed using a 30 mL, 1:4:1 mixture of ethyl acetate, diethyl ether and hexane, respectively. Calculate the elution strength of this solution. (Required data is provided) (8)

4.2 Briefly explain why such a mixture would be used as opposed to using pure solvents. (2)

4.3 Define or give a mathematical equation for the following terms:

4.3.1 Precision

4.3.2 Gaussian distribution

4.3.3 Determinate error

4.3.4 Primary standard

(8)

4.4 What are the advantages of microwave acid digestion over wet digestion?

(3)

4.5 What sample preparation steps are involved in the analysis of metallic analytes in biological samples? (4)

[25]

Question 5

Calibration methods and curves necessary in many chemical measurements involving electrochemistry, spectroscopy and chromatography.

5.1 Many aspects of a calibration are part of the "figures of merit" for an analysis. Define 5 figures of merit which these could be evaluated in the process of establishing a calibration. (10)

5.2 A redox reaction of permanganate with hydrogen peroxide to produce oxygen gas and Mn(II) is:

$$MnO_4^- \longrightarrow Mn^{2+}$$

$$H_2O_2 \longrightarrow O_2$$

5.2.1 Complete and balance half reactions for both schemes by adding e-, H_2O and H^+, then write a balanced net ionic equation for the reaction. (7)

5.3 Describe the components that make up a gas chromatography instrument. You may use box diagram illustrations in your answer. (8)

[25]

Appendix 1

Tabulated values for the Q-test

N	68%	90%	95%	98%	99%
3	0.822	0.941	0.970	0.988	0.994
4	0.603	0.765	0.829	0.889	0.926
5	0.488	0.642	0.710	0.780	0.821
6	0.421	0.560	0.625	0.698	0.740
7	0.375	0.507	0.568	0.637	0.680
8	0.343	0.468	0.526	0.590	0.634
9	0.319	0.437	0.493	0.555	0.598
10	0.299	0.412	0.466	0.527	0.568
12	0.271	0.375	0.425	0.480	0.518
14	0.250	0.350	0.397	0.447	0.483
16	0.234	0.329	0.376	0.422	0.460
18	0.223	0.314	0.358	0.408	0.438
20	0.213	0.300	0.343	0.392	0.420

Table 3.2

Values of *F* at the 95% Confidence Level

	$\nu_1 = 2$	3	4	5	6	7	8	9	10	15	20	30
$\nu_2 = 2$	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.5
3	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.70	8.66	8.62
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.86	5.80	5.75
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.62	4.56	4.50
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	3.94	3.87	3.81
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.51	3.44	3.38
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.22	3.15	3.08
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.01	2.94	2.86
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.85	2.77	2.70
15	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.40	2.33	2.25
20	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.20	2.12	2.04
30	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.01	1.93	1.84

Table 3.1

Values of t for ν Degrees of Freedom for Various Confidence Levels[a]

ν	Confidence Level			
	90%	95%	99%	99.5%
1	6.314	12.706	63.657	127.32
2	2.920	4.303	9.925	14.089
3	2.353	3.182	5.841	7.453
4	2.132	2.776	4.604	5.598
5	2.015	2.571	4.032	4.773
6	1.943	2.447	3.707	4.317
7	1.895	2.365	3.500	4.029
8	1.860	2.306	3.355	3.832
9	1.833	2.262	3.250	3.690
0	1.812	2.228	3.169	3.581
5	1.753	2.131	2.947	3.252
0	1.725	2.086	2.845	3.153
5	1.708	2.060	2.787	3.078
›	1.645	1.960	2.576	2.807

$= N - 1 =$ degrees of freedom.

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	$F = N_A e$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\,66 \times 10^{-23}$ J K^{-1}
Gas constant	$R = N_A k$	$8.314\,51$ J K^{-1} mol^{-1}
		$8.205\,78 \times 10^{-2}$ dm^{3} atm K^{-1} mol^{-1}
		6.2364×10 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		
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 permittivity	$\varepsilon_o = 1/c^2\mu_o$	$8.854\,19 \times 10^{-12}$ J^{-1} C^{2} m^{-1}
	$4\pi\varepsilon_o$	$1.112\,65 \times 10^{-10}$ J^{-1} C^{2} m^{-1}
Vacuum permeability	μ_o	$4\pi \times 10^{-7}$ J s^{2} C^{-2} m^{-1}
		$4\pi \times 10^{-7}$ T^{2} J^{-1} m^{3}
Magneton		
Bohr	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24}$ J T^{-1}
nuclear	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27}$ J T^{-1}
g value	g_e	$2.002\,32$
Bohr radius	$a_o = 4\pi\varepsilon_o\hbar/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
Fine-structure constant	$\alpha = \mu_o e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_o^2$	$1.097\,37 \times 10^{7}$ m^{-1}
Standard acceleration of free fall	g	$9.806\,65$ m s^{-2}
Gravitational constant	G	$6.672\,59 \times 10^{-11}$ N m^{2} Kg^{-2}

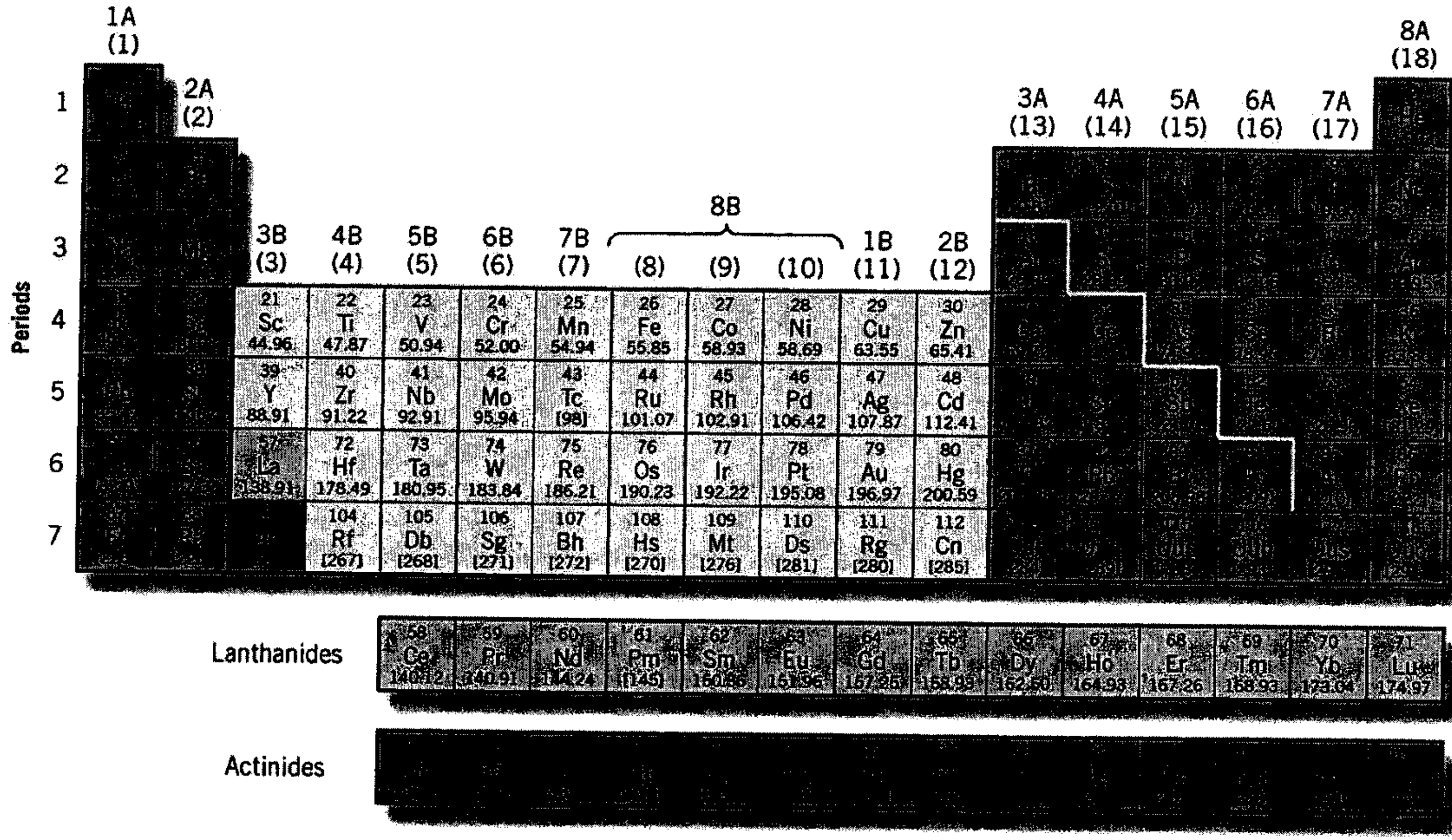
Conversion factors

1 cal	=	4.184 joules (J)	1 erg	=	1×10^{-7} J
1 eV	=	$1.602\,2 \times 10^{-19}$ J	1 eV/molecule	=	96 485 kJ mol^{-1}

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}

Solvent	MF MW	Bp (°C) Density (g/mL)	Hazards*	Dipole	Elution Stength (ε)
Hexane $CH_3(CH_2)_4CH_3$	C_6H_{14} 86.17	68.7 0.659	Flammable Toxic	0.08	0.01
Toluene $C_6H_5CH_3$	C_7H_8 92.13	110.6 0.867	Flammable Toxic	0.31	0.22
Diethyl ether $CH_3CH_2OCH_2CH_3$	$C_4H_{10}O$ 74.12	34.6 0.713	Flammable Toxic, CNS Depressant	1.15	0.29
Dichloromethane CH_2Cl_2	CH_2Cl_2 84.94	39.8 1.326	Toxic, Irritant Cancer suspect	1.14	0.32
Ethyl Acetate $CH_3CO_2CH_2CH_3$	$C_4H_8O_2$ 88.10	77.1 0.901	Flammable Irritant	1.88	0.45
Acetone CH_3COCH_3	C_3H_6O 58.08	56.3 0.790	Flammable Irritant	2.69	0.43
Butanone $CH_3CH_2COCH_3$	C_4H_8O 72.10	80.1 0.805	Flammable Irritant	2.76	0.39
1-Butanol $CH_3CH_2CH_2CH_2OH$	$C_4H_{10}O$ 74.12	117.7 0.810	Flammable Irritant	1.75	0.47
Propanol $CH_3CH_2CH_2OH$	C_3H_8O 60.09	82.3 0.785	Flammable Irritant	1.66	0.63
Ethanol CH_3CH_2OH	C_2H_6O 46.07	78.5 0.789	Flammable Irritant	1.70	0.68
Methanol CH_3OH	CH_4O 32.04	64.7 0.791	Flammable Toxic	1.7	0.73
Water HOH	H_2O 18.02	100.0 0.998		1.87	>1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