DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

JUNE/JULY 2016 SUPPLEMENTARY EXAMINATION

TITLE OF PAPER : **Analytical Chemistry II: Fundamentals of Spectrophotometry**

COURSE NUMBER : **C304**

TIME : **3 HOURS**

Important Information :

1. Each question is worth 25 marks.
2. Answer **ANY four (4)** questions
3. Marks for **ALL** procedural calculations will be awarded.
4. Start each question on a fresh page of the answer sheet.
5. Diagrams must be large and clearly labelled accordingly.
6. This paper contains an appendix of chemical constants
7. Additional material: graph paper and data sheet

You are not supposed to open this paper until permission has been granted by the chief invigilator

QUESTION 1 [25]

a) Differentiate between **"Spectroscopy"** and **"Spectrometry"** [4]

b) Several analytical techniques are based on the absorption of energy from different parts of the electromagnetic spectrum.

The following diagram shows part of the electromagnetic spectrum;

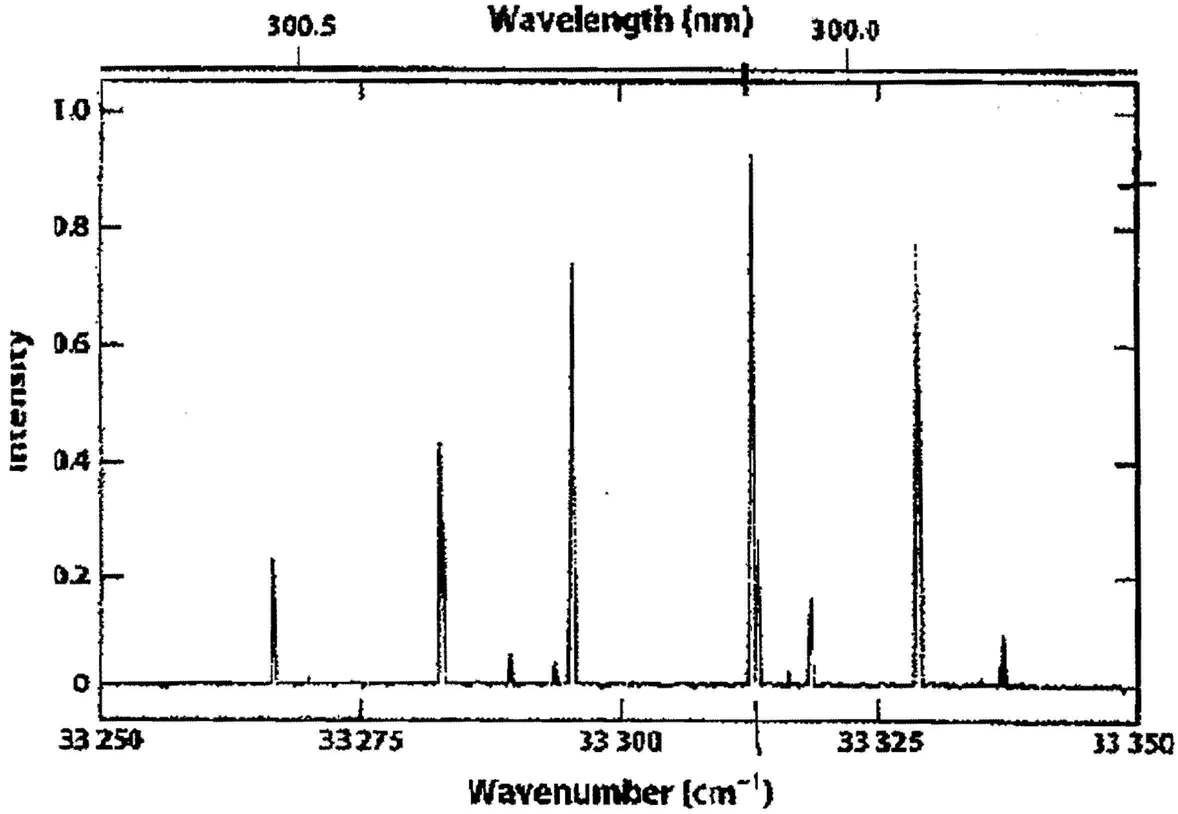
X-Rays	P	Visible	Q	Microwaves

i) Identify the types of radiation labelled P and Q [2]

ii) Identify which one of the five regions has radiation of lowest frequency [2]

c) Explain how and why molecular and atomic spectra are different. In other words, describe the differences in the spectra you record and then explain physically what happens within the atoms/molecules to give these differences. Use diagrams to illustrate [5]

d) This question relates to the following spectrum:



i) For the largest peak in the spectrum, calculate the energy in Joules per photon. Estimate any quantities you need from the scale on the spectrum [4]

ii) Calculate the frequency (in Hertz) for this same peak [2]

iii) In what region of the electromagnetic spectrum (e.g. x-ray, gamma ray, ultra violet and micro-wave) does this peak fall? [2]

e) Explain the different uses of atomic spectrometry in analytical chemistry? (Give 2) [4]

QUESTION 2 [25]

a) Sketch out the main components in FES and AAS and highlight the main difference [4]

b) Which group of elements can be determined by FES? Explain why the technique is limited to these elements [2]

c) What is the role of the monochromator in AAS? [2]

d) With an aid of a diagram describe how does a hollow cathode lamp works [5]

e) An **internal standard** in analytical chemistry is a chemical substance that is added in a constant amount to samples, the blank and calibration standards in a chemical analysis. The method of internal standards is used to improve the precision of quantitative analysis.

   i) Give two characteristics of a "good" internal standard. [2]

   ii) In ICP-MS analysis, choose one internal standards; Bi, Sc or In for each of the following analytes; Cd, Pb and Cr and explain why you chose as you did? [4]

   iii) Explain why an internal standard can be used for Inductively Coupled Plasma Emission ICP-AES but is not used for AAS [3]

f) Give an example of chemical interference in AAS. Describe the fundamental problem and how you would solve it [3]

QUESTION 3 [25]

a) The following two solvent systems were found to separate compounds X and Y by column chromatography (column more polar):

X: hexanes/ethyl acetate 10:1
Y: hexanes/ethyl acetate 10:4

Which is the more polar compound, X or Y? (2)

b) In order to separate a mixture of X and Y as in problem 3(a) by column chromatography:

i) Which solvent system must be used first? (2)

ii) Which compound will elute from the column first (assuming you chose the correct solvent)? (2)

iii) You only see one compound coming off the column when you suspect two. Where might the other compound be? How can you recover this compound? (2)

c) The design of different spectrophotometers depends on the type of measurement (e.g. atomic emission, atomic absorption, uv-visible absorption, fluorescence) they are intended to take.

i) Draw a block diagram of a single beam spectrophotometer that might be used for uv-visible molecular absorbance. (4)

ii) Write the specific components of each block of your block diagram. (3)

d) In 2001, the Swaziland Water Services Corporation acquired a new atomic spectrometer called Liberty 110 ICP.

(i) What does ICP stand for? [1]

(ii) Draw the ICP torch and label its components [4]

(iii) Concisely explain why chemical interferences are less common in ICP-AES than they are in flame AAS. (2)

(iv) List and describe each of the three (3) advantages that ICP has over flame atomic absorption spectroscopy. (3)

QUESTION 4 [25]

a) The Deuterium lamp is one of the radiation sources used in UV-visible spectroscopy. Using equations, explain how the lamp is able to produce a continuum radiation (160 – 380nm) [5]

b) Consider the reactions of two unknown compounds X and Y.

$$X + 2H_2 \rightarrow C_5H_{12}$$

$$Y + 2H_2 \rightarrow C_5H_{12}$$

i) Deduce the molecular formula of the two unknown compounds [2]

The UV spectra of the compounds are compared to pent-1-ene in the table below.

Compound	λ_{max}
X	176
Y	211
Pent-1-ene	178

ii) Draw the structures of compounds X and Y and explain the choice of structure for each. [5]

c) A student wanted to determine a more accurate value for the solution of Mn^{2+}(aq) which was known to be between 0.10 and 0.010 M. She was provided with a solution of 1.00 M manganese (II) sulphate, $MnSO_4$. Describe how she could determine the unknown concentration using visible spectrometer and explain the importance of the Beer – Lambert law in the method used. [6]

d) Which type of GC detector is most commonly used? Explain its working principle and what are its limitations? [7]

QUESTION 5 [25]

a) IR spectroscopy is a technique mostly used for qualitative analysis of organic compounds.

   i) State what happens at molecular level when infrared radiation is absorbed. [2]

   ii) Explain the two criteria required for a molecule to absorb IR radiation. [4]

   iii) Which of the molecules iodine and hydrogen iodide is IR active and why? [3]

b) There are four isomeric alcohols with molecular formula $C_4H_{10}O$.

   i) Draw a structure for each of the four alcohols. [2]

   ii) Explain why the four compounds could not be easily distinguished by looking at their infrared spectra. [2]

a) Nebulization is a very wasteful approach to atomization.

   i) What does the term "nebulization" mean? [1]

   ii) Use diagrams to explain how nebulization is carried out in atomic spectroscopy. [4]

   iii) Use your answer in (c) ii above to explain why nebulization is considered inefficient. [2]

b) In chromatography, what do you understand by column efficiency and how is it expressed? Explain all terms appearing in the equation.
[5]

QUESTION 6 [25]

a) With the aid of a diagram, briefly but informatively explain how the following detectors work in chromatography:

i) Electron Capture Detector [4]

ii) Flame Ionization Detector [4]

b) Draw the main components of a GC. Explain the function of each function. [5]

c) What are the main differences between High Performance Liquid Chromatography and Gas Chromatography? [5]

d) The two most common types of columns used in high performance liquid chromatography (HPLC) are "C_8" and "C_{18}" columns

i)Explain the difference(s) between a "C_8" column and a "C_{18}" column [2]

ii) Explain why these two particular types of columns are used for "reverse phase" HPLC. [3]

e) Explain why it is necessary to use a "guard column" in an HPLC but not in a GC. [2]

Useful Relations					
$(RT)_{298.15K}$=2.4789 kJ/mol					
$(RT/F)_{298.15K}$=0.025 693 V					
T/K:	100.15	298.15	500.15	1000.15	
T/Cm^{-1}:	69.61	207.22	347.62	695.13	
1mmHg=133.222 N m^{-2}					
hc/k=1.438 78x10^{-2} m K					

1atm	1 cal	1 eV	$1cm^{-1}$
1.01325x10^{5} Nm^{-2}	4.184 J	1.602 189x10^{-19} J	0.124x10^{-3} eV
760torr		96.485 kJ/mol	1.9864x10^{-23}J
		8065.5 cm^{-1}	

SI-units:

1 cal (thermochemical) = 4.184 J

dipole moment: 1 Debye = 3.335 64x10^{-30} C m

force: 1N=1J m^{-1} = 1kgms^{-2}=10^{5} dyne   pressure: 1Pa=1Nm^{-2} =1Jm^{-3}

power: 1W = 1J s^{-1} potential: 1V =1 J C^{-1}

magnetic flux: 1T=1Vsm^{-2}=1JCsm^{-2} current: 1A=1Cs^{-1}

Prefixes:

p	n	m	m	c	d	k	M	G
pico	nano	micro	milli	centi	deci	kilo	mega	giga
10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

General Data		
speed of light	c	2.997 925x10^{8} m^{-1}
charge of proton	e	1.602 19x10^{-19} C
Faraday constant	F=Le	9.648 46x10^{4} C mol^{-1}
Boltzmann constant	k	1.380 66x10^{-23} J K^{-1}
Gas constant	R=Lk	8.314 41 J K^{-1} mol^{-1}
		8.205 75x10^{-2} dm^{3} atm K^{-1} mol^{-1}
Planck constant	h	6.626 18x10^{-34} Js
	$\hbar = \frac{h}{2\pi}$	1.054 59x10^{34} Js
Avogadro constant	L or N_{av}	6.022 14x10^{23} mol^{-1}
Atomis mass unit	u=10^{-3} kg/(Lmol)	1.660 54x10^{-27} kg
Electron mass	m_e	9.109 39x10^{-31} kg
Proton mass	m_p	1.672 62x10^{-27} kg
Neutron mass	m_n	1.674 93x10^{-27} kg
Vacuum permittivity	$\varepsilon_o = \mu_o^{-1}c^{-2}$	8.854 188x10^{-12} J^{-1} C^{2} m^{-1}
Vacuum permeability	μ_o	4πx10^{-7} $Js^{2}C^{-2}$ m^{-1}
Bohr magneton	$\mu_B = e\hbar/2m_e$	9.274 02x10^{-24} JT^{-1}
Nuclear magneton	$\mu_N = e\hbar/2m_p$	5.05079x10^{-27} JT^{-1}
Gravitational constant	G or g	6.67259x10^{-11} $Nm^{2}kg^{-2}$
Bohr radius	a_o	5.291 77x10^{-11} m

Periodic Table of the Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** 1.0079																	2 **He** 4.0026
3 **Li** 6.941	4 **Be** 9.0122											5 **B** 10.811	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.180
11 **Na** 22.990	12 **Mg** 24.305											13 **Al** 26.982	14 **Si** 28.086	15 **P** 30.974	16 **S** 32.066	17 **Cl** 35.453	18 **Ar** 39.948
19 **K** 39.098	20 **Ca** 40.078	21 **Sc** 44.956	22 **Ti** 47.83	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.847	27 **Co** 58.933	28 **Ni** 58.69	29 **Cu** 63.546	30 **Zn** 65.39	31 **Ga** 69.723	32 **Ge** 72.61	33 **As** 74.922	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
37 **Rb** 85.468	38 **Sr** 87.62	39 **Y** 88.906	40 **Zr** 91.224	41 **Nb** 92.906	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 105.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57 **La** 138.91	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	75 **Re** 186.21	76 **Os** 190.2	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.03	89 **Ac** 227.03	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (263)	107 **Bh** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Ds** (?)	111 **Rg** (?)							

Lanthanides	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.97	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
Actinides	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** 237.05	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

PHYSICAL CONSTANTS AND UNITS

Table 1 : General Physical Constants

Constant	Symbol	SI Units	Non-SI Units
Velocity of Light	c	2.9979×10^{8} m s^{-1}	
Electronic charge	e	-1.6022×10^{-19} C	
Avogadro's constant	N_A	6.0220×10^{23} mol^{-1}	
Atomic mass unit	u	1.6606×10^{-27} kg	
Electron rest mass	m_e	9.1095×10^{-31} kg	
Proton rest mass	m_p	1.6726×10^{-27} kg	
Neutron rest mass	m_n	1.6750×10^{-27} kg	
Planck's constant	h	6.6262×10^{-34} J s	
Rydberg constant	R_H	1.0974×10^{7} m^{-1}	
Ideal gas constant	R	8.314 J mol^{-1} K^{-1}	0.08206 l atm mol^{-1} K^{-1}
Gas molar volume (STP)	V_o	2.21414×10^{-2} m^{3} mol^{-1}	22.4 l mol^{-1}
Boltzmann constant	k	1.3807×10^{-23} J K^{-1}	
Faraday constant	F	96485 C mol^{-1}	
Gravitational acceleration	g	9.80 m s^{-2}	
Permittivity of a vacuum	ε_o	8.8542×10^{-12} F m^{-1}	
Mechanical equivalent of heat		1 calorie $\equiv$ 4.18 J	

Table of Characteristic IR Absorptions

frequency, cm^{-1}	*bond*	*functional group*
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H–bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1°, 2° amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C≡C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (v)	C≡N stretch	nitriles
2260–2100 (w)	–C≡C– stretch	alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α, β–unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	α, β–unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	alkenes
1650–1580 (m)	N–H bend	1° amines
1600–1585 (m)	C–C stretch (in–ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in–ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH_2X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1°, 2° amines
900–675 (s)	C–H "oop"	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C≡C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides

m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp