DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

NOVEMBER 2014 FINAL 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 **questions one (1)** and any other three **(3)** questions in this paper.

3. Marks for **<u>ALL</u>** 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] [COMPULSORY QUESTION]

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;

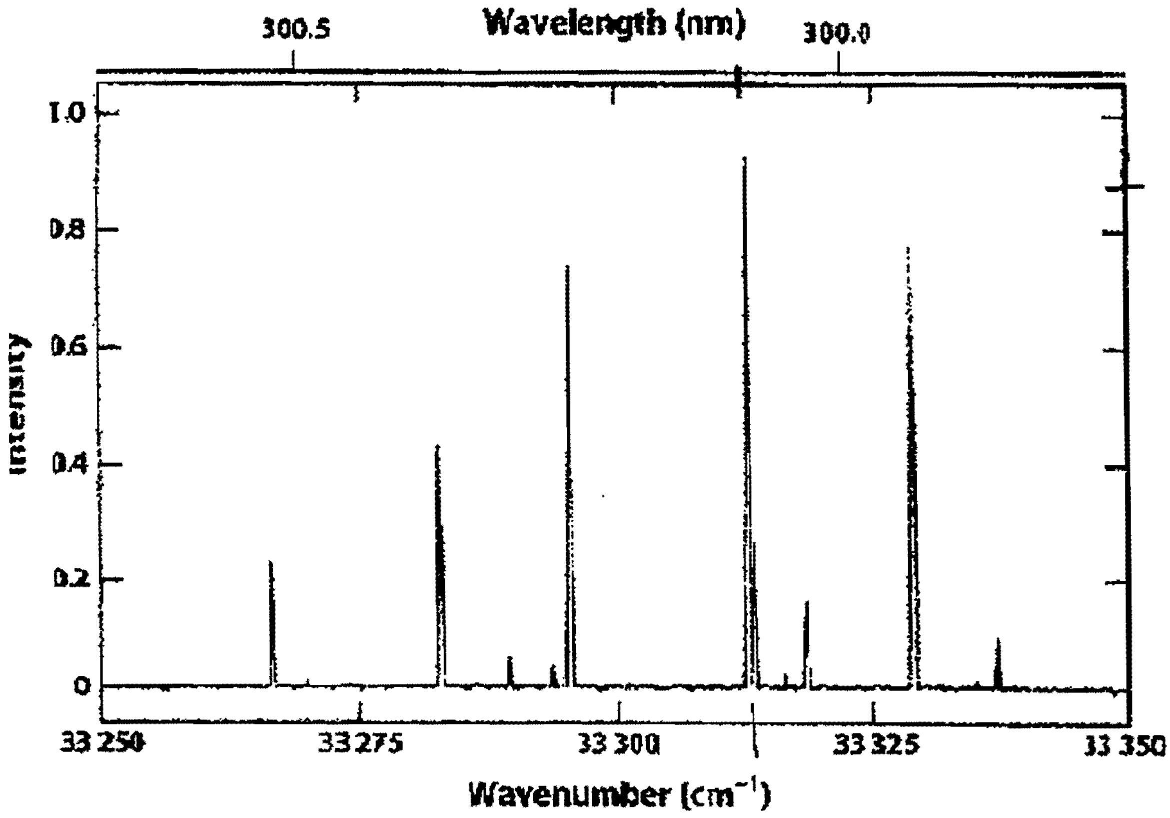
X-Rays	P	Visible	Q	Microwaves

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) Inductively Coupled Plasma (ICP) Emission Spectroscopy is the most widely used atomic spectroscopy today.

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

   ii) Use a diagram to explain why it is possible to measure up to 35 elements simultaneously using ICP. [4]

   iii) Which torch position would you choose in ICP-AES when analysing antimony in purified samples where the limit of detection (LOD) is an issue? Explain. [3]

b) Explain the following terms as used in UV-visible spectrometry and give examples

   i) Chromophore

   ii) Auxochrome

   iii) Bathochromic Shift

   iv) Hypochromic Effect [6]

c) What is the electron capture detector? Explain its basis for operation, why is N_2 necessary? What types of species are detected with the ECD? [5]

d) What do you understand by temperature programming in GC analysis? How does it help? [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) IR spectroscopy is a technique mostly used for qualitative analysis of organic compounds.

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

ii) Which of the molecules oxygen and hydrogen chloride is IR active and why? [2]

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

QUESTION 5 [25]

a) State Beer's Law as applied to spectroscopy, and explain all terms appearing in it. [3]

i) What is meant by "stray light" in spectroscopy? [1]

ii) Use equations to explain why stray light leads to negative deviations from Beer's Law [4]

b) One very useful detector in atomic spectrometry is the Photomultiplier Tube. Draw and label the "PMT', explain how it works. [5]

c) 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]

d) 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) Thermal Conductivity 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 78×10^{-2} m K

1atm	1 cal	1 eV	$1cm^{-1}$
$1.01325\times10^{5}\ Nm^{-2}$	4.184 J	$1.602\ 189\times10^{-19}$ J	0.124×10^{-3} eV
760torr		96.485 kJ/mol 8065.5 cm^{-1}	1.9864×10^{-23}J

SI-units:

1 cal (thermochemical) = 4.184 J

dipole moment: 1 Debye = $3.335\ 64\times10^{-30}$ 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	$2.997\ 925\times10^{8}\ m^{-1}$
charge of proton	*e*	$1.602\ 19\times10^{-19}$ C
Faraday constant	F=L*e*	$9.648\ 46\times10^{4}\ C\ mol^{-1}$
Boltzmann constant	k	$1.380\ 66\times10^{-23}\ J\ K^{-1}$
Gas constant	R=Lk	$8.314\ 41\ J\ K^{-1}\ mol^{-1}$
		$8.205\ 75\times10^{-2}\ dm^{3}\ atm\ K^{-1}\ mol^{-1}$
Planck constant	h	$6.626\ 18\times10^{-34}$ Js
	$\hbar = \frac{h}{2\pi}$	$1.054\ 59\times10^{34}$ Js
Avogadro constant	L or N_{av}	$6.022\ 14\times10^{23}\ mol^{-1}$
Atomis mass unit	$u=10^{-3}$ kg/(Lmol)	$1.660\ 54\times10^{-27}$ kg
Electron mass	m_e	$9.109\ 39\times10^{-31}$ kg
Proton mass	m_p	$1.672\ 62\times10^{-27}$ kg
Neutron mass	m_n	$1.674\ 93\times10^{-27}$ kg
Vacuum permittivity	$\varepsilon_0 = \mu_0^{-1}c^{-2}$	$8.854\ 188\times10^{-12}\ J^{-1}\ C^{2}\ m^{-1}$
Vacuum permeability	μ_0	$4\pi\times10^{-7}\ Js^{2}C^{-2}\ m^{-1}$
Bohr magneton	$\mu_B = {}^{e\hbar}/_{2m_e}$	$9.274\ 02\times10^{-24}\ JT^{-1}$
Nuclear magneton	$\mu_N = {}^{eh}/_{2m_p}$	$5.05079\times10^{-27}\ JT^{-1}$
Gravitational constant	G or g	$6.67259\times10^{-11}\ Nm^{2}kg^{-2}$
Bohr radius	a_0	$5.291\ 77\times10^{-11}$ 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 47.88	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 ≡ 4.18 J	

Table 2: IR Correlation table for common functional groups

Functional group	**band (cm^{-1})**
$-CH_3$	2950–75 (s), 2870–90 (m), 1440–65 (m), 1370–90 (s)
$-CH_2$ (acyclic)	2910–40 (s), 2840–80 (m), 1440–80 (m), ~720 (w)
–CH	2880–90 (w), ~1340 (w)
$-C=CH_2$	2970–3070 (m), 1290-1420 (w), 860-900 (w)
–CH=CH– (*cis*)	675–730 (m)
–CH=CH– (*trans*)	960–70 (m)
–C=C–	1620–80 (m)
Aryl–H	3010–80 (m), 1000–1250 (w), 700–900 (m)
Aryl C=C	1590–1620 (v), 1575–90 (v), 1470–1525 (v), 1430–65 (v), 400–625 (m)
–C≡C–H	~3300–40 (s), 700–900 (m)
–C≡C–	2100–2250 (v)
water	~3700
water of crystallisation	3100–3700
O–H (free)	~3600 (v)
O–H (intermolecular H-bond)	3200–3500 (s)
O–H (intramolecular H-bond)	3400–3600 (s)
O–H	1260–1400 (s)
C–OH	1020–1200 (s)
Aryl-O–H	~3600 (m), 1180–1390 (s), 600–700 (s)
COO–H (dimer)	2500–3300 (s)
COO–H (chelated)	2500–2700 (s)
C–O–C (all kinds)	1050–1250 (v)
N–H	3200–3500 (m), 1500–1600 (s), 650–900 (s)
C–N	1020–1200 (m)
C(=O)N–H (amide)	3200–3400 (s), ~1450 (s), 1590–1650 (m)
C–F	1000–1400 (s)
C–Cl	600–800 (s)
C–Br	500–750 (s)
C–I	~500 (s)
NO_2	1660–1490 (s), 1390–1260 (s)
C≡N	~2250 (s)

Table 3: IR Correlation table for carbonyl groups

Functional group	**Type**	**band (cm^{-1}) (all strong absorptions)**
RC(=O)R′ ketones	saturated aliphatic	1715–45
	aryl	1650–1700
	α-β unsaturated	1660–1700
	cyclobutanone	~1780
	cyclopentanone	~1750
	α halo	1730–50
	β-diketone (enol form)	1580–1640
RC(=O)H aldehydes	sat aliphatic	1720–40
	α-β unsat	1685–1705
	aryl	1685–1715
	β-keto (enol form)	1645–70
	α-halo	1730–65
COOH carboxylic acids	sat. aliphatic (dimer)	1700–25
	sat. aliphatic (monomer)	1740–1800
	aryl (dimer)	1680–1710
	α-βunsat	1690–1715
	a halo (dimer)	1715–40
	H-bonded (intramolecular)	1650–80
	anion	1550–1610, 1300–1420
C(=O)-O-C=O acid anhydrides	sat aliphatic	1800–40, 1740–80
	α-β unsat, aryl	1780–1830, 1710–55
C(=O)X acid halides	X = Cl sat aliphatic	1790–1815
	X = Cl α-β unsat, aryl	1735–50, 1765–90
COOR Esters	sat aliphatic	1725–50
	α-β unsat, aryl	1705–40
	RCOOC=C	1750–1800
	α-keto	1740–60
	β -eto	1635–55
	α-halo	1740–70
	lactone (5 ring)	1760–80
C(=O)-N Amides	1º amide I	~1690
	amide II	~1600
	2º amide I	1670–1700
	amide II	1510–50
	3º amide	1630–70
	lactam	1700
amino acids	Free	1390–1425, 1560–1600
C=N	oxime	1640–90
	imine	1640–90