

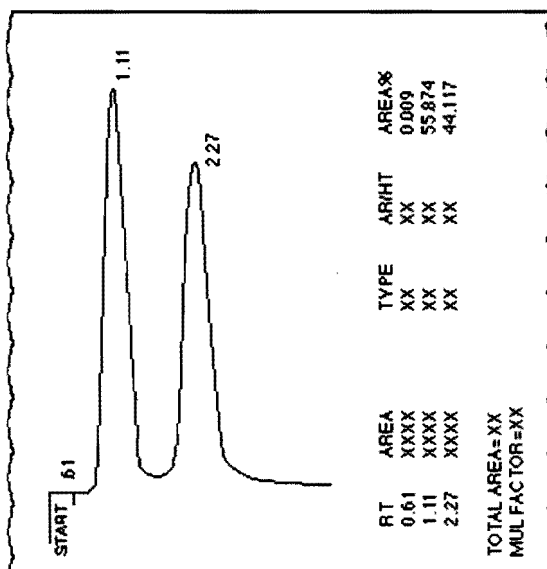
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SWAZILAND
NOVEMBER 2015 FINAL EXAMINATION

TITLE OF PAPER	:	Analytical Chemistry II: Fundamentals of Spectrophotometry
COURSE NUMBER	:	C304
TIME	:	3 HOURS
Important Information	:	<ol style="list-style-type: none">1. Each question is worth 25 marks.2. Answer questions one (1) and any other three (3) questions in this paper.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 constants7. Additional material: graph paper and data sheet

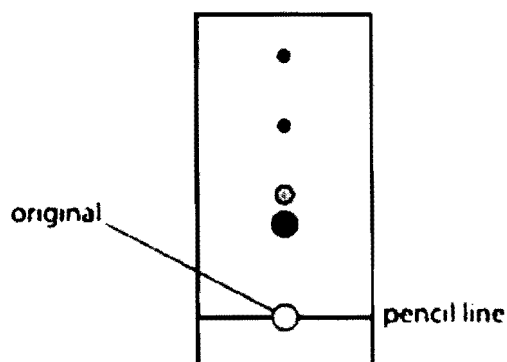
You are not supposed to open this paper until permission has been granted by the chief invigilator

QUESTION 1

- a) Study the chromatograph (below) of a mixture of Compounds A and B, run on the GC in the teaching lab at UNISWA.



- What is the retention time of compound A? Compound B? (1)
 - Which compound is present in a larger amount? Explain (2)
 - Which compound has the lower boiling point? Explain (2)
 - What would happen to the retention times of compounds A and B if the column temperature were raised? Explain (2)
 - You suspect that compound B is octane. What can you do to provide supporting evidence for this hypothesis? Explain 2 different ways how this can be achieved. (4)
- b) A student wanted to investigate the green colour in some leaves by paper chromatography using the organic solvent ethanol. The results are shown below:

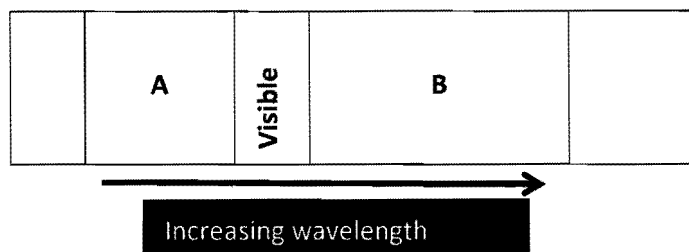


- i) Suggest why the student used ethanol and not water in her investigation. (1)
 - ii) State and explain the conclusion which the student can make about the colouring matter in the leaves. (2)
 - iii) Explain why some of the coloured material had not moved from the original spot. (2)
 - iv) Explain why a pencil and not a pen is used to draw the base line. (1)
 - v) Suggest why repeating the experiment with a different solvent may give more information. (2)
 - vi) Identify the mobile and stationary phase in the separation technique. (2)
- c) Outline how the technique of column chromatography could be used to separate a mixture of two compounds. (4)

QUESTION 2

- a) The structures of four organic compounds are shown below:
- W** $\text{CH}_2\text{ClCH}_2\text{Cl}$
- X** CH_2CH_2
- Y** CH_3CH_3
- Z** $\text{CH}_2\text{CHCHCH}_2$
- i) Identify the compounds that most strongly absorb ultraviolet radiation. Explain your choice (3)
 - ii) Identify the compound which absorbs ultra violet radiation of the longest wavelength, and explain your choice. (3)

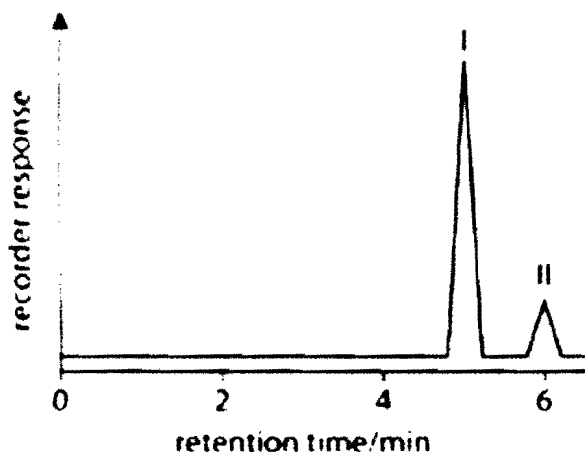
- b) β -carotene has a molar absorptivity (ϵ) of $100\,000\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ at a certain wavelength. Calculate the amount of carotene in a $1.0 \times 1.0 \times 1.0\text{ cm}$ cell needed to absorb 90% of the incident radiation. (4)
- c) The figure below depicts the visible region of the electromagnetic spectrum and the two regions nearest to it.



- i) Name the regions labelled A and B, identify the atomic and molecular processes associated with each region and compare the energies of the photons involved in these processes. (5)
- ii) State, giving a reason, which region (A or B) could be used to:
- Test for metal atoms (1)
 - Obtain information about the strengths of bonds (1)
- d) What is liquid - liquid extraction? What is the other name for liquid – liquid extraction? (4)
- e) Another method which can be used for extraction is the solid phase extraction. Give four advantages of using SPE over the liquid – liquid extraction. (4)

QUESTION 3

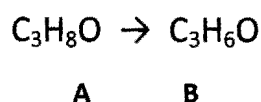
- a) The amount of caffeine ($\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$) added to paracetamol ($\text{C}_8\text{H}_9\text{NO}_2$) tablets must be carefully controlled. Small amounts of caffeine can increase the pain-relieving properties of the paracetamol, but large amounts of caffeine in combination with paracetamol can lead to liver damage. A paracetamol tablet was analyzed using HPLC and the following chromatogram produced.



- i) Explain why HPLC and not GC is used to analyse the tablet. (3)
 - ii) Identify which of the peaks corresponds to caffeine and explain your choice. (2)
 - iii) Explain the relative retention times of the two substances. (3)
- b) Derivatization is the process of chemically modifying a compound to produce a new compound which has properties that are suitable for analysis using a GC.
- i) Explain three (3) scenarios which would require that a sample be first derivatized before being analysed using GC. (3)
 - ii) Give the three main types of derivatization methods. For each of the methods;
 - Explain how the derivatisation is carried out.
 - Give one example of a reagent used to achieve the form of derivatisation. (9)
- c) Which detector is used for the analysis of halogenated hydrocarbons using the GC method? Give a brief description of how this detector operates. (5)

QUESTION 4

- a) Organic compounds are often identified by using more than one analytical technique. Some of these techniques were used to identify the compounds in the following reaction.



- i) Using H₂O as an example, describe what happens, at molecular level, during the absorption of infrared radiation. (3)

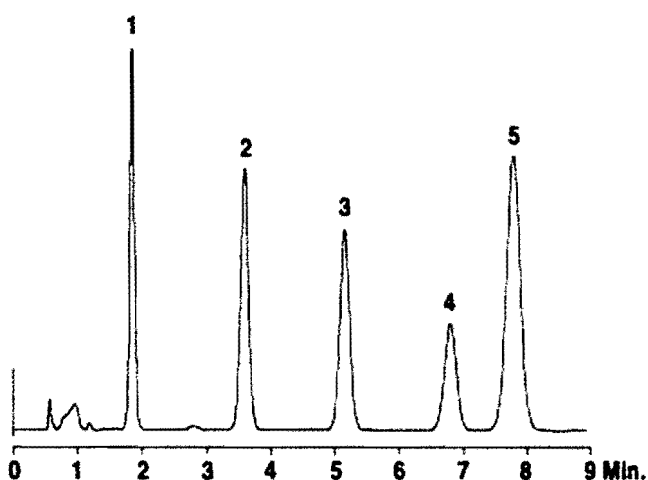
- ii) The infrared spectrum of A showed a broad absorption at 3350cm^{-1} . The infrared spectrum of B did not show this absorption, but instead showed absorption at 1720cm^{-1} . Explain what these results indicate about the structures of A and B. (3)
 - iii) Draw the two possible structures of B. Label the functional group for each (4)
- b) State the light source for AAS. Explain how it works, including why a different lamp must be used for each element (6)
 - c) A major breakthrough in atomic absorption spectrophotometry was the invention of graphite furnace AA.
 - i) What is the major difference between flame AA and graphite furnace AA? Use diagrams to support your answer. (3)
 - ii) Identify the physical stages involved in the furnace program and describe the processes that occur during each stage. (3)
 - iii) Outline three (3) advantages of graphite furnace AA over flame AA. (3)

QUESTION 5

- a) State Beer's Law as applied to spectroscopy, and explain all terms appearing in it. (3)
- b) Deviations from Beer Lambert law classified into three categories. List these three categories, giving detailed explanation, causes and examples of each. (9)
- c) Use equations to explain why stray light leads to negative deviations from Beer's Law (4)
- d) An absorption in an electronic spectrum is recorded at $17\,000\text{cm}^{-1}$. What does this correspond to in nm? (2)
- e) Explain the process of atomization and why it is needed for analysis using the AAS. (3)
- f) Gratings are used in monochromators instead of prisms. Gratings have a very good resolving power in spectroscopy
 - i) Physically how does a grating look like[1]
 - ii) Use equations to explain how a grating works [3]

QUESTION 6

- a) Differentiate between "Spectroscopy" and "Spectrometry" (2)
- b) 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. (5)
- c) One very useful detector in atomic spectrometry is the Photomultiplier Tube. Draw and label the "PMT", explain how it works. (5)
- d) Considering a typical spectrophotometer what is the effect of decreasing the exit slit width of the monochromator on the light incident of the sample. (2)
- e) Given the HPLC chromatogram below for a mixture of barbiturates;



Peak Identification

1. Barbital (0.25 mg/ml)
2. Phenobarbital (0.1 mg/ml)
3. Talbutal (0.3 mg/ml)
4. Amobarbital (0.25 mg/ml)
5. Mephobarbital (0.1 mg/ml)

- i) Calculate the number of theoretical plates based on the Amobarbital peak using your best estimate of the required parameters from the chromatogram. (3)
- ii) Referring to the chromatogram at the top, assuming that barbital is more polar than phenobarbital which is more polar than talbutal, etc, was this experiment run under normal or reverse phase conditions? Explain (4)
- f) For the HPLC technique what is meant by gradient elution and give 2 scenarios why you would need to use it? (4)

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
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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)
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PHYSICAL CONSTANTS AND UNITS

Table 1 : General Physical Constants			
Constant	Symbol	SI Units	Non-SI Units
Velocity of Light	c	$2.9979 \times 10^8 \text{ m s}^{-1}$	
Electronic charge	e	$-1.6022 \times 10^{-19} \text{ C}$	
Avogadro's constant	N_A	$6.0220 \times 10^{23} \text{ mol}^{-1}$	
Atomic mass unit	u	$1.6606 \times 10^{-27} \text{ kg}$	
Electron rest mass	m_e	$9.1095 \times 10^{-31} \text{ kg}$	
Proton rest mass	m_p	$1.6726 \times 10^{-27} \text{ kg}$	
Neutron rest mass	m_n	$1.6750 \times 10^{-27} \text{ kg}$	
Planck's constant	h	$6.6262 \times 10^{-34} \text{ J s}$	
Rydberg constant	R_H	$1.0974 \times 10^7 \text{ m}^{-1}$	
Ideal gas constant	R	$8.314 \text{ J mol}^{-1} \text{ K}^{-1}$	$0.08206 \text{ l atm mol}^{-1} \text{ K}^{-1}$
Gas molar volume (STP)	V_0	$2.21414 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}$	22.4 l mol^{-1}
Boltzmann constant	k	$1.3807 \times 10^{-23} \text{ J K}^{-1}$	
Faraday constant	F	96485 C mol^{-1}	
Gravitational acceleration	g	9.80 m s^{-2}	
Permittivity of a vacuum	ϵ_0	$8.8542 \times 10^{-12} \text{ F m}^{-1}$	
Mechanical equivalent of heat		$1 \text{ calorie} \equiv 4.18 \text{ J}$	

Prefixes:

p	n	μ	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

Table of Characteristic IR Absorptions

<i>frequency, cm⁻¹</i>	<i>bond</i>	<i>functional group</i>
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 ₂ X)	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