DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

NOVEMBER 2017 MAIN EXAMINATION

TITLE OF PAPER	**:Analytical Chemistry II: Fundamentals of Spectrophotometry**
COURSE NUMBER	**:C304/CHE 312**
TIMEHOURS	**: 3 Hours**
Important Information	: Each question is worth 25 marks.
	: Answer **questions one (1)** and any other three **(3)** questions in this paper.
	: Marks for **ALL** procedural calculations will be awarded.
	: Start each question on a fresh page of the answer sheet.
	: Diagrams must be large and clearly labelled accordingly.
	: This paper contains an appendix of chemical constants.
	: Additional material: data sheet.

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

Question 1 [25 Marks]

a) Define the following terms:

(i) eluent,

(ii) isocratic elution,

(iii)Doppler broadening,

(iv)Sputtering [8]

b) Various analytical instruments used for the analysis of metals/elements have unique sample introduction methods. Outline the sample introduction in Flame Atomic Absorption Spectroscopy (FAAS) [5].

c) Draw a schematic of a radiation source most suitable for atomic absorption spectroscopy (AAS), labelling all its parts. [5]

d) Soxhlet extraction method is one of the methods used to analytes of interest from solid samples for GC analysis. Another method which can be used is the headspace. Compare the two methods by first giving a brief description of each and giving the advantages and disadvantages of each. [5]

e) Given the HPLC chromatogram (Figure 1) below for a mixture of nucleosides, calculate the resolution between the Guanosine and Adenosine peaks using your best estimate of the required parameters from the chromatogram. [3]

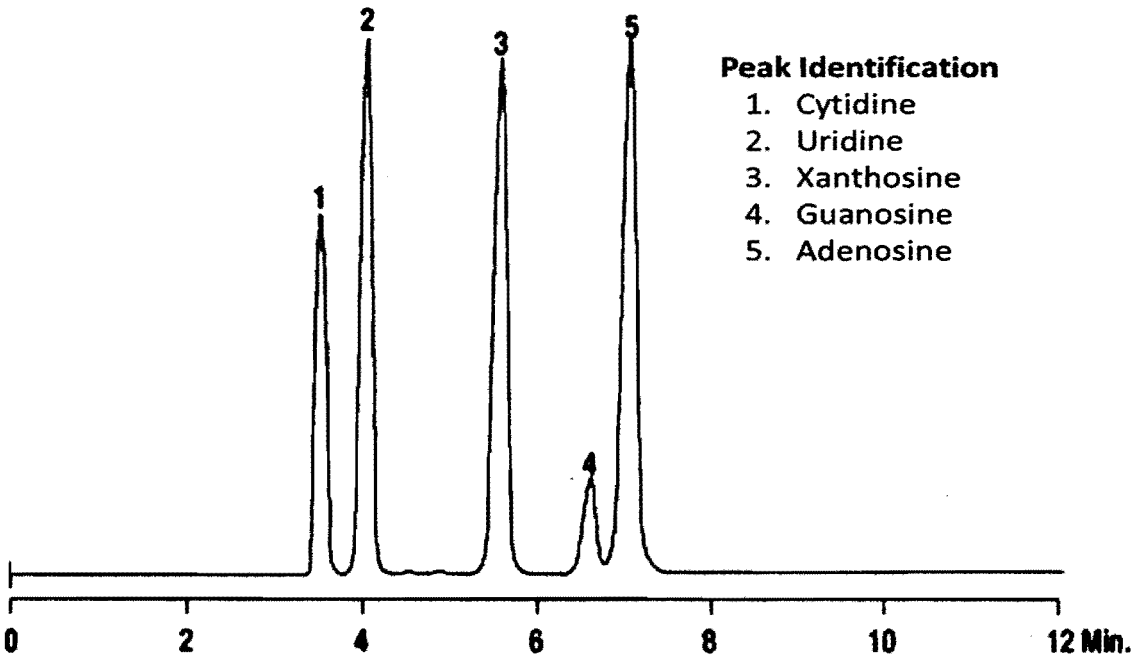

Figure 1: HPLC chromatogram for a mixture of nucleosides

Question 2 [25 Marks]

a) Why is the injection port of a GC at a higher temperature than the oven temperature? [2]

b) Why must sugars and fatty acids be derivatized before GC analysis while pesticides and aroma compounds need not be derivatized [3]

c) What is solid-phase extraction and why is it advantageous over traditional liquid-liquid extraction? Give three (3) advantages [6]

d) What are the criteria (two) for a molecule to absorb radiation, give full explanations [6]

e) Discuss substituent effects on a chromophore [8]

Question 3 [25 Marks]

a) Differentiate between ''Spectroscopy'' and ''Spectrometry'' [3]

b) The two most common columns in HPLC are C_8 and C_{18} columns. Explain (1) the difference(s) between these columns and (2) why these two particular types are used for "reverse phase" HPLC. [6]

c) With respect to Ca explain chemical interference in flame atomic absorption spectrometry and explain how it is eliminated [4]

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

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

(ii) Draw the ICP torch and label its components [6]

(iii) List and describe each of the three (3) advantages that ICP has over flame atomic absorption spectroscopy [3]

Question 4 [25 Marks]

a) How does the transmittance of a solution vary with (i) increasing concentration and (ii) increasing path length? [2]

b) Outline the process of sputtering in FAAS [5]

c) 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.

$$C_3H_8O \rightarrow C_3H_6O$$

A **B**

(i) Using H_2O as an example, describe what happens, at molecular level, during the absorption of infrared radiation. [3]

(ii) Explain the two criteria required for a molecule to absorb IR radiation. [2]

(iii) 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 1720 cm^{-1}. Explain what these results indicate about the structures of A and B. [3]

(iv) Draw the two possible structures of B. Label the functional group for each [4]

d) Two types of vibrations are possible after a molecule absorbs radiation. Choose one and discuss as elaborate as you can. [6]

Question 5 [25 Marks]

a) Soxhlet extraction is one of the methods used to isolate analytes of interest from solid samples for GC analysis. Another method which can be used is headspace. Compare the two methods by first giving a brief description of each and then give the advantages and disadvantages of each. [5]

b) What is the electron capture detector? (1), how does it operate? (2), why is N_2 gas necessary? (1), what types of species are detected with the ECD? (1). [5]

c) Draw the main components (give specific names for each component) of a GC. Explain how each component functions. [5]

d) What do you understand by temperature programming in GC analysis? Describe three scenarios when temperature programming would be used instead of isothermal elution. [4]

e) A 7.25 X 10-5 M solution of potassium permanganate has a transmittance of 47.1% when measure in a 210 mm cell at wavelength 525 nm. Calculate the absorbance, A, of this solution and the molar absorptivity of potassium permanganate. [6]

Question 6 [25 Marks]

a) Explain using diagrams, why atomic spectra appear as lines, whereas molecular spectra appear as bands [5]

b) With an aid of a diagram describe how does a hollow cathode lamp works [6]

c) List the various atomizers oftenly used in atomic spectroscopy. [6]

d) 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]

The End

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	$\varepsilon_0 = 1/c^2\mu_0$	$8.854\,19 \times 10^{-12}$ J^{-1} C^2 m^{-1}
	$4\pi\varepsilon_0$	$1.112\,65 \times 10^{-10}$ J^{-1} C^2 m^{-1}
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
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	$a_0 = 4\pi\varepsilon_0\hbar/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_0^2$	$1.097\,37 \times 10^{7}$ 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}

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1.008 H 1																	4.003 He 2
2	6.941 Li 3	9.012 Be 4											10.811 B 5	12.011 C 6	14.007 N 7	15.999 O 8	18.998 F 9	20.180 Ne 10
3	22.990 Na 11	24.305 Mg 12											26.982 Al 13	28.086 Si 14	30.974 P 15	32.06 S 16	35.453 Cl 17	39.948 Ar 18
4	39.098 K 19	40.078 Ca 20	44.956 Sc 21	47.88 Ti 22	50.942 V 23	51.996 Cr 24	54.938 Mn 25	55.847 Fe 26	58.933 Co 27	58.69 Ni 28	63.546 Cu 29	65.39 Zn 30	69.723 Ga 31	72.61 Ge 32	74.922 As 33	78.96 Se 34	79.904 Br 35	83.80 Kr 36
5	85.468 Rb 37	87.62 Sr 38	88.906 Y 39	91.224 Zr 40	92.906 Nb 41	95.94 Mo 42	98.907 Tc 43	101.07 Ru 44	102.91 Rh 45	106.42 Pd 46	107.87 Ag 47	112.41 Cd 48	114.82 In 49	118.71 Sn 50	121.75 Sb 51	127.60 Te 52	126.90 I 53	131.29 Xe 54
6	132.91 Cs 55	137.33 Ba 56	138.91 *La 57	178.49 Hf 72	180.95 Ta 73	183.85 W 74	186.21 Re 75	190.2 Os 76	192.22 Ir 77	195.08 Pt 78	196.97 Au 79	200.59 Hg 80	204.38 Tl 81	207.2 Pb 82	208.98 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86
7	223 Fr 87	226.03 Ra 88	(227) **Ac 89	(261) Rf 104	(262) Ha 105	(263) Unh 106	(262) Uns 107	(265) Uno 108	(266) Une 109	(267) Uun 110								

Atomic mass → 10.811
Symbol → B
Atomic No. → 5

TRANSITION ELEMENTS

140.12 Ce 58	140.91 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.96 Eu 63	157.25 Gd 64	158.93 Tb 65	162.50 Dy 66	164.93 Ho 67	167.26 Er 68	168.93 Tm 69	173.04 Yb 70	174.97 Lu 71
232.04 Th 90	231.04 Pa 91	238.03 U 92	237.05 Np 93	(244) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(260) Lr 103

*Lanthanide Series

**Actinide Series

( ) indicates the mass number of the isotope with the longest half-life.