UNIVERSITY OF ESWATINI

DEPARTMENT OF CHEMISTRY

NOVEMBER 2018 MAIN EXAMINATION

TITLE OF THE PAPER: SPECTRO-ANALYTICAL AND SEPARATION METHODS

COURSE CODE	:	C304/ CHE 312
TIME	:	3 HOURS
Important Information:		1. Each question is worth 25 marks.
		2. Answer any **Four (4)** questions in this paper.
		3. Marks for **ALL** the 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 for chemical constant.

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

QUESTION ONE [25 MARKS]

a) Draw a well labelled diagram of a sinusoidal wave (4)

b) What is the wavelength of a photon that has three times as much energy as that of a photon whose wavelength is 500 nm? (6)

c) What region of the electromagnetic spectrum would be associated with these photons? (2)

d) Absorbing groups or species are classified based on three types of transitions. List these types of electronic transitions. (3)

e) With the aid of the Jabloski diagram, discuss the various radioactive and non-radiative processes that take place during fluorescence and phosphorescence (6)

f) Explain in details why phosphorescence takes longer than fluorescence (4)

QUESTION TWO [25 MARKS]

(a) A solution containing only the thiourea complex of bismuth(III) has a molar absorptivity of 9.35×10^3 L.cm^{-1}mol^{-1} at 470 nm.

(i) What will be the absorbance of a 2.52×10^{-5} mol.L^{-1} solution of the complex when measured in a 12.5 mm cell? (3)

(ii) What will be the percentage transmittance of the solution described in (i) above? (3)

(b) State the Beer's law as applied in spectroscopy and explain all the terms appearing in it. (3)

(c) Deviations from Beer's law are classified into three categories. List these three categories, giving a detailed explanation and examples of each. (6)

(d) Discuss what bathochromic and hypsochromic shifts are in the UV-Visible spectrophotometry. What causes these shifts? (4)

(e) List two (2) differences between atomic and molecular absorption? (2)

(f) (i) What are the necessary conditions for a vibrating bond to be IR active? (2)

(ii) One of the major disadvantages of dispersive Infrared instruments is slow scanning of the spectrum. Describe how this challenge is overcome in Fourier Transform Infra-red (FT-IR) instruments. (2)

QUESTION THREE [25 MARKS]

(a) (i) Explain what you understand by a background in atomic spectroscopy measurements (1)

(ii) Explain the different background correction methods used in atomic spectroscopy. (6)

(iii) Explain three sources of interferences, giving examples of each and how this problem is solved in Flame atomic absorption spectroscopy (FAAS) (7)

(b) Explain the operation of a photomultiplier tube (PMT). What are the advantages of this detector over the phototube? (6)

(c) The hollow cathode lamp (HCL) is a line source in Atomic spectrophotometer. Explain what you understand by the term line source? Explain how a HCL works, including why a different lamp must be used for each element. (5)

QUESTION FOUR [25 MARKS]

(a) What are the differences between atomic and molecular spectroscopy? (3)

(b) Briefly describe the sequence of all events that will take place as soon as a sample solution is transported into the flame of an atomic absorption spectrophotometer (FAAS). (4)

(c) Identify the physical changes involved in the furnace program and describe the processes that takes place during each stage (3)

(d) Outline three (3) advantages of graphite furnace atomic absorption (GF-AAS) over FAAS (3)

(e) Explain what you understand by matrix modification in GFAAS and give examples of how this is achieved (4)

(f) In the analysis of ground water sample by AAS for Na the presence of high amount of Calcium (Ca) give rise to molecular interference due to the presence of a broad molecular band of CaOH and Co.

(i) Why would swapping to a nitrous oxide flame resolve this problem? (2)

(ii) When they swapped to N_2O/C_2H_2 flame, they added a large amount of potassium (K). Why did they do this? Explain this principle (3)

(iii) In another analysis of Na, Lanthanum was added to the samples and standards. Explain why it was necessary to Lanthanum to the standards and the samples. (1)

(iv) If we swapped to an inductively coupled plasma mass spectrometer (ICP-MS), would there be a problem due to the presence of Ca? Explain (2)

QUESTION 5 [25 MARKS]

a. Define the following terms as used in chromatography; (3)

   i. Resolution

   ii. Plate height

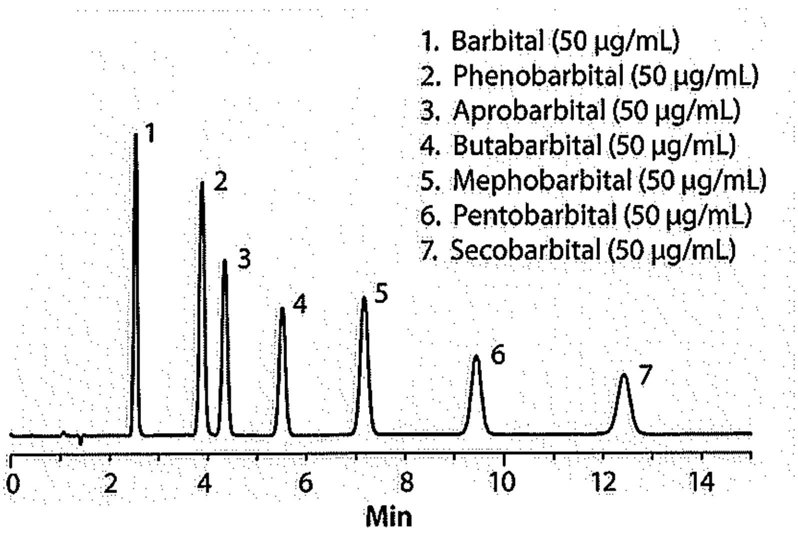
   iii. Elution

b. Explain the factors that lead to band broadening in gas chromatography (GC) (3)

c. List three (3) features of a good carrier gas for GC. List any three (3) commonly used carrier gases in GC. (5)

d. Differentiate between gradient elution and Isocratic elution as used in Liquid chromatography (LC) (2)

e. Given the HPLC chromatogram below for a mixture of barbiturates; assuming that barbital is more polar than phenobarbital which is more polar than Aprobarbital, etc. Was this experiment run under normal or reverse phase conditions? Explain (4)



f. Derivatization is the process of chemically modifying a compound to produce a new compound which has properties that are suitable for analysis using GC.

(i) Explain three (3) scenarios which would require the sample be derivatized before being analyzed using GC. (3)

(ii) Give three types of derivatization method and for each method, explain how derivatization is carried out. (5)

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	

ENERGY $1J = 6.242 \times 10^{18}$ eV