UNIVERSITY OF ESWATINI

Department of Chemistry

NOVEMBER 2018 RE-SIT/SUPPLEMENTARY 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) Define the term spectroscopy (2)

b) Explain Max Plank's contribution in understanding Absorption and emission spectra of molecules in the UV-Vis spectrophotometry. (4)

c) (i) Draw a schematic energy level diagram that shows the following transitions (3)

$\sigma \longrightarrow \pi^*$
$\sigma \longrightarrow \sigma^*$
$\pi \longrightarrow \pi^*$
$n \longrightarrow \pi^*$
$n \longrightarrow \sigma^*$

(ii) Are all the above transitions allowed? (2)

(iii) Discuss how the nature of the solvent affects $n \rightarrow \pi^*$ and π-π^* transition. (4)

(iv) Discuss any other factor that affects transitions in UV-Visible spectroscopy (3)

d) Explain what you understand by Fluorescence and phosphorescence (2)

e) Explain the meaning of the following terms as applicable to fluorescence

i. Triplet and singlet states (2)

ii. Quenching (1)

iii. Intersystem crossing (1)

iv. Stokes shift (1)

QUESTION TWO (25 MARKS)

a) Using a sketch of partial Groatrian diagram of sodium (Na) explain the origin of atomic spectra (5)

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 (4)

c) State the light source for atomic absorption spectroscopy (AAS). Explain how it works, including why a different lamp must be used for each element. (7)

d) List the four common fuel oxidant combinations that are used in Flame atomic absorption spectrometer (FAAS). (4)

e) A major breakthrough in atomic absorption spectroscopy was the invention of graphite furnace atomic absorption spectrophotometer (GFAAS).

   i. Identify the physical stages involved in the GFAAS and describe the processes that occur during each stage. (3)

   ii. Outline two (2) advantages of GFAAS over FAAS (2)

QUESTION THREE [25 MARKS]

a) UV-Visible spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions and biological macromolecules. For a particular assay, your plot of absorbance versus concentration was not linear. Explain the possible reasons for this (6)

b) Draw the components of a double beam spectrophotometer and explain its advantages over the single beam spectrophotometer (5)

c) Draw and label a diagram of a monochromator (3)

d) Considering a typical spectrophotometer, what is the effect of decreasing exit slit width of a monochromator on the light incident to the sample? (3)

e) In 2014, the Eswatini Water Services acquired a new atomic spectrometer called Optima 8300 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-MS than they are in FAAS

iv. Other than Chemical interferences, list and describe two other causes of interference in flame atomic spectroscopy (3)

QUESTION FOUR [25 MARKS]

a) Draw and label the main components of a Gas chromatograph and explain how each component functions. (5)

b) Given the following chromatogram and a column length of 20 cm, calculate;

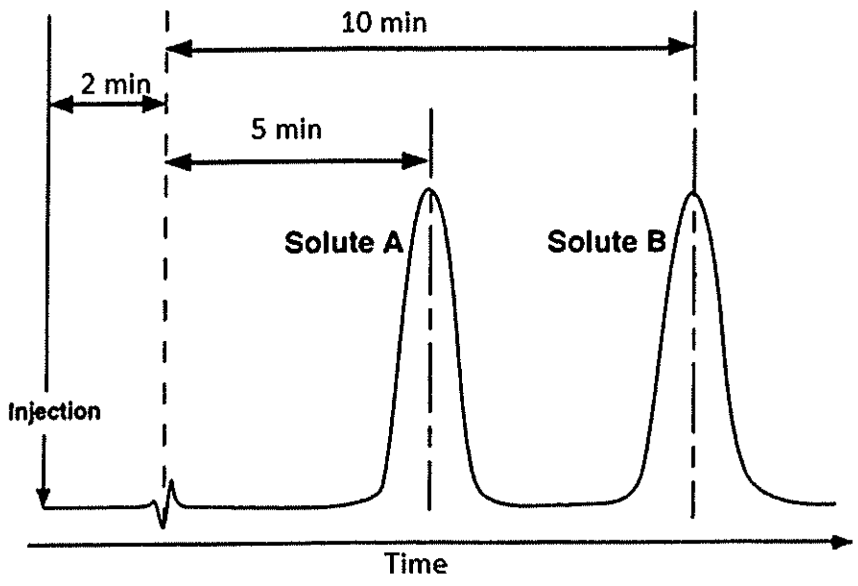
i. Capacity factor for solutes A and B (2)

ii. The number of theoretical plates (N) for solutes A and B given W_A and W_B are 1.5 and 2 minutes respectively. (2)

iii. Plate height for solutes A and B (2)

iv. Relative retention (1)

v. How would you classify the performance of the column based on the capacity factors? (1)



c) A number of factors contribute to experimental peak shapes. Describe the factors that contribute to broadening of atomic lines in atomic absorption spectroscopy (AAS) (6)

d) What are the characteristics of an ideal detector for gas chromatography (GC)? (6)

QUESTION FIVE [25 MARKS]

a) What are the characteristics of a good carrier gas and what gases are commonly used in GC? (3)

b) Why is the injection port of a GC kept at a higher temperature than the oven temperature? (2)

c) Why must sugars and fatty acids be derivatized before GC analysis while pesticides and aroma compounds need not be derivatized? (3)

d) What is solid phase extraction (SPE) and why is it advantageous over traditional Liquid-Liquid extraction (LLE). Give three (3) advantages. (5)

e) In High performance liquid chromatography (HPLC), what do you understand by normal and reverse phase chromatography (3)

f) You have been tasked with the analysis of chlorinated pesticides and polychlorinated biphenyls (PCBs) which are some of the organic micropollutants in the environment. Name the GC-detector which would be the most SELECTIVE in the analysis of these compounds? Explain your choice. Explain the operation of this detector (6)

g) List a universal detector that could be used in place of the detector listed above (part f). What are the advantages of this detector over other detectors? (4)

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 = 6.242×10^{18} eV