



**NAMIBIA UNIVERSITY
OF SCIENCE AND TECHNOLOGY**

**FACULTY OF HEALTH, NATURAL RESOURCES AND APPLIED SCIENCES
SCHOOL OF NATURAL AND APPLIED SCIENCES
DEPARTMENT OF BIOLOGY, CHEMISTRY AND PHYSICS**

QUALIFICATION: BACHELOR OF SCIENCE	
QUALIFICATION CODE: 07BOSC	LEVEL: 7
COURSE CODE: MSC701S	COURSE NAME: MOLECULAR SPECTROSCOPY AND CHEMICAL SEPARATION METHODS
SESSION: JUNE 2023	PAPER: THEORY
DURATION: 3 HOURS	MARKS: 100

FIRST OPPORTUNITY EXAMINATION QUESTION PAPER	
EXAMINER(S)	DR JULIEN LUSILAO
MODERATOR:	A/PROF STEFAN LOUW

INSTRUCTIONS
<ol style="list-style-type: none">1. Answer ALL the questions in the answer book provided.2. Write and number your answers clearly.3. All written work MUST be done in blue or black ink.

PERMISSIBLE MATERIALS

Non-programmable calculators

ATTACHMENTS

List of Useful formulas and Constants

THIS QUESTION PAPER CONSISTS OF 8 PAGES (Including this front page and attachments)

Question 1

[25]

1.1 Define the following terms

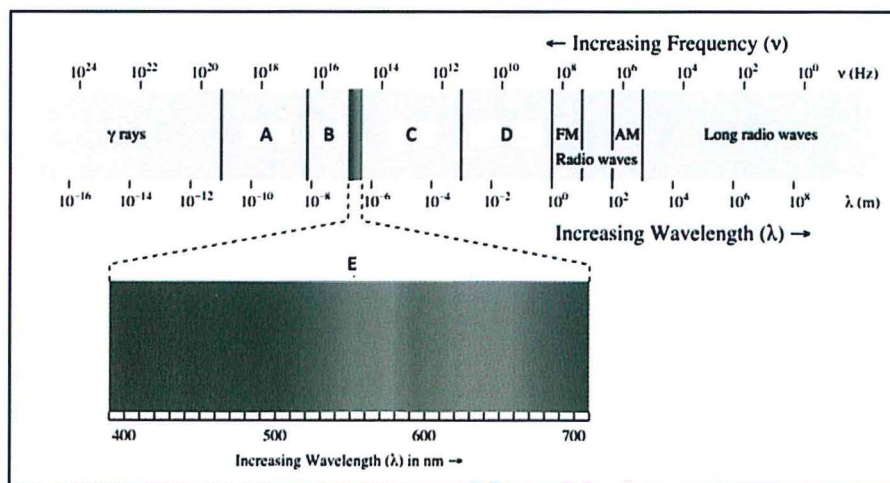
- (a) Detectors (2)
- (b) Transducers (2)
- (c) Radiant power (or intensity) (2)

1.2 What principal phenomena are known to cause inaccuracies in the measurement of transmittance (T) with spectrometric instruments? (3)

1.3 What is the experimental approach used by analytical chemists to circumvent the limitation mentioned in 1.2? (4)

1.4 Differentiate between the quantitative and qualitative information obtained with spectrometry techniques. (4)

1.5 The diagram below shows different regions of the electromagnetic spectrum.



(a) Name the regions labelled from A to E. (5)

(b) What type of quantum transitions are involved in the following regions of the above diagram?

- (i) A region (1)
- (ii) B region (1)
- (iii) C region (1)

Question 2

[25]

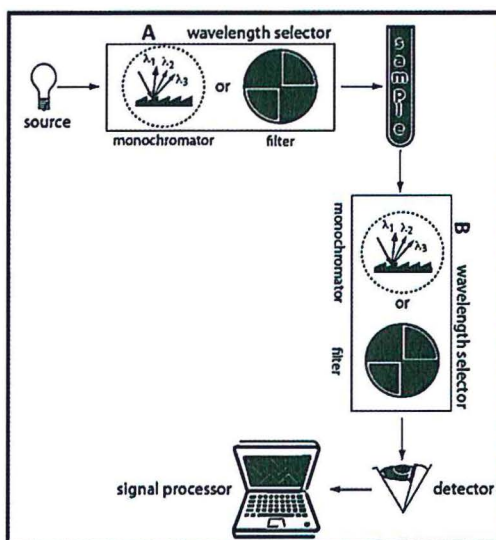
2.1 What are the considerations to be taken when developing a quantitative atomic absorption (AA) method? (5)

2.2 (a) Why are hollow cathode lamps preferred in AAS instruments instead of the lamps used in UV-Vis spectrometers? (2)

(b) Describe the principle of operation of a hollow cathode lamp. (5)

(c) What are chemical interferences in AAS technique and how do you correct them? (3)

2.3 The diagram below represents an instrument that measures fluorescence.



(a) What is the main advantage of replacing the filters in A and B by monochromators and what would the instrument be called in that case? (3)

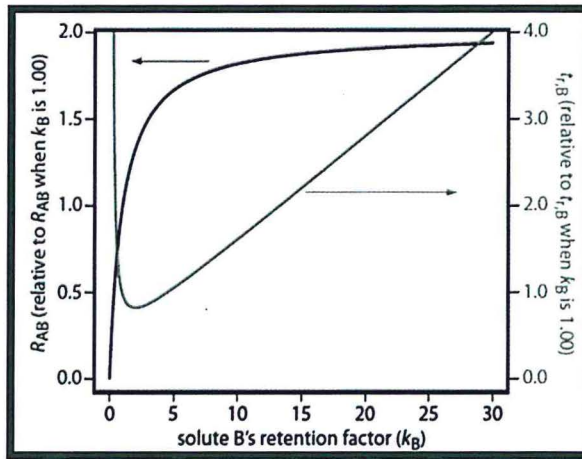
(b) Why is the detector perpendicular to the radiation source? (3)

(c) It has been reported that photoluminescence spectra are recorded by measuring the intensity of emitted radiation as a function of either the excitation wavelength or the emission wavelength. Using the above diagram as a reference, explain how both measurements (i.e., of excitation or emission spectra) can be made. (4)

Question 3

[25]

3.1 In the chromatographic separation of solutes A and B, one of the simplest ways to improve resolution between their peaks is to adjust solute B's retention factor as shown in the figure below.



(a) Use the figure to discuss the limitations of this simplistic approach in improving resolution between two peaks. (3)

(b) Describe how you can increase k_B without significantly changing the selectivity in gas chromatography (GC) and in liquid chromatography (LC). Explain your choices. (4)

3.2 In chromatography, the contributions of band broadening from multiple pathlengths (H_p) and mass transfer (H_s and H_m) are expressed as follow:

$$H_p = 2\lambda d_p$$

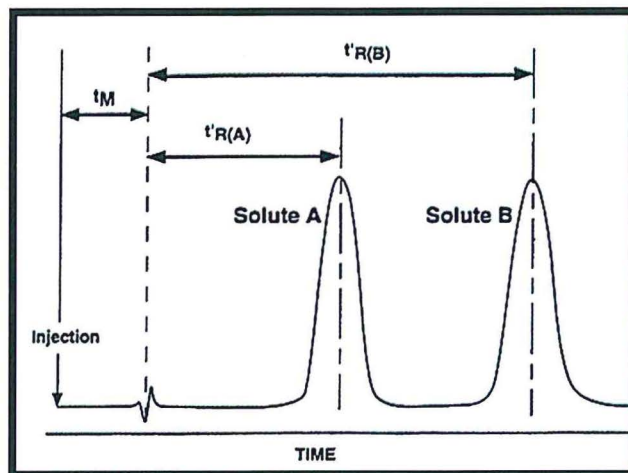
$$H_s = \frac{q k d_f^2}{(1+k)^2 D_s} u$$

$$H_m = \frac{f n (d_p^2, d_c^2)}{D_m}$$

(a) Define the terms d_c , d_f and d_p in the above expressions. (3)

(b) Briefly show how capillary columns (CCs) take advantage of the above expressions to produce sharp chromatographic peaks in GC analysis. (3)

3.3 Given the following chromatogram and a column length of 20 cm:



$t_M = 2 \text{ min}$; $t'_R(A) = 5 \text{ min}$; $t'_R(B) = 10 \text{ min}$

Calculate:

- (a) The retention factor for solutes A and B (2)
- (b) The number of theoretical plates for solutes A and B (for $w \sim 2 \text{ min}$) and the average number of theoretical plates. (5)
- (c) The selectivity (1)
- (d) The resolution between for the solutes A and B (2)
- (e) How would you classify the performance of the column based on the calculated retention factors? (2)

Question 4

[25]

- 4.1 What are the relevant criteria to consider when choosing a stationary phase in GC? (4)
- 4.2 What are the ideal features of a detector used in GC? (4)
- 4.3 Briefly discuss the main disadvantages of normal phase chromatography in HPLC. (4)
- 4.4 Provide the reason why conductivity detectors used in Ion-Exchange chromatography (IEC) have significant background signal and explain how this problem is minimized. (4)
- 4.5 Explain the general principle of electrophoresis (i.e., how it works). (4)
- 4.6 In the Van Deemter equation, $H = A + B/\mu + C\mu$

- (a) Which term(s) is (are) not applicable to capillary electrophoresis? Explain your answer. (3)
- (b) What is the direct implication of the observation made in (a) in terms of column efficiency? (2)

END

Physical Constants

Gas constant	R	= 8.315 J K ⁻¹ mol ⁻¹ = 8.315 kPa dm ³ K ⁻¹ mol ⁻¹ = 8.315 Pa m ³ K ⁻¹ mol ⁻¹ = 8.206 x 10 ⁻² L atm K ⁻¹ mol ⁻¹
Boltzmann constant	k	= 1.381 x 10 ⁻²³ J K ⁻¹
Planck constant	h	= 6.626 x 10 ⁻³⁴ J s ⁻¹
Faraday constant	F	= 9.649 x 10 ⁴ C mol ⁻¹
Avogadro constant	L or N_A	= 6.022 x 10 ²³ mol ⁻¹
Speed of light in vacuum	c	= 2.998 x 10 ⁸ m s ⁻¹
Mole volume of an ideal gas	V_m	= 22.41 L mol ⁻¹ (at 1 atm and 273.15 K) = 22.71 L mol ⁻¹ (at 1 bar and 273.15 K)
Elementary charge	e	= 1.602 x 10 ⁻¹⁹ C
Rest mass of electron	m_e	= 9.109 x 10 ⁻³¹ kg
Rest mass of proton	m_p	= 1.673 x 10 ⁻²⁷ kg
Rest mass of neutron	m_n	= 1.675 x 10 ⁻²⁷ kg
Permittivity of vacuum	ϵ_0	= 8.854 x 10 ⁻¹² C ² J ⁻¹ m ⁻¹ (or F m ⁻¹)
Gravitational acceleration	g	= 9.807 m s ⁻²

Conversion Factors

1 W	= 1 J s ⁻¹
1 J	= 0.2390 cal = 1 N m = 1 V C = 1 Pa m ³ = 1 kg m ² s ⁻²
1 cal	= 4.184 J
1 eV	= 1.602 x 10 ⁻¹⁹ J
1 L atm	= 101.3 J
1 atm	= 1.013 x 10 ⁵ N m ⁻² = 1.013 x 10 ⁵ Pa = 760 mmHg
1 bar	= 1 x 10 ⁵ Pa
1 L	= 10 ⁻³ m ³ = 1 dm ³
1 Angstrom	= 1 x 10 ⁻¹⁰ m = 0.1 nm = 100 pm
1 micron (μ)	= 10 ⁻⁶ m = 1 μ m
1 Poise	= 0.1 Pa s = 0.1 N sm ⁻²
1 ppm	= 1 μ g g ⁻¹ = 1 mg kg ⁻¹ = 1 mg L ⁻¹ (dilute aqueous solutions only)

Selected Formulae

$$R_{AB} = \frac{t_{r,B} - t_{r,A}}{0.5(w_B + w_A)} = \frac{2\Delta t_r}{w_B + w_A} \quad R_{AB} = \frac{\sqrt{N}}{4} \times \frac{\alpha - 1}{\alpha} \times \frac{k_B}{1 + k_B}$$

$$k = \frac{1 - \frac{t_m}{t_r}}{\frac{t_m}{t_r}} = \frac{t_r - t_m}{t_m} = \frac{t_r'}{t_m}$$

$$\alpha = \frac{k_B}{k_A} = \frac{t_{r,B} - t_m}{t_{r,A} - t_m}$$

$$N = 16 \left(\frac{t_r}{w} \right)^2$$

$$q = nF$$

$$\Delta G = -nFE$$

$$I = E/R$$

$$E = E^0 - RT/nF \ln ([B]^b/[A]^a)$$

$$E \text{ (for ISE): } E_{cell} = K + 0.05916/z \log[A]$$

$$E = h\nu \text{ (or } E = hc/\lambda)$$

$$A = -\log T = \log P_0/P \text{ and } A = \epsilon bc$$

$$\nu_{ep} = \mu_{ep} E$$

$$\mu_{ep} = \frac{q}{6\pi\eta r}$$