namibia university
OF SCIENCE AND TECHNOLOGY

FACULTY OF HEALTH, APPLIED SCIENCES AND NATURAL RESOURCES

DEPARTMENT OF NATURAL AND APPLIED SCIENCES

QUALIFICATION: BACHELOR OF SCIENCE	
QUALIFICATION CODE: 07BOSC	**LEVEL:** 7
COURSE CODE: MSC701S	**COURSE NAME:** MOLECULAR SPECTROSCOPY AND CHEMICAL SEPARATION METHODS
SESSION: JUNE 2022	**PAPER:** THEORY
DURATION: 3 HOURS	**MARKS:** 100

FIRST OPPORTUNITY EXAMINATION QUESTION PAPER	
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INSTRUCTIONS
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 It is known that transmittance (T) and absorbance (A) cannot normally be measured accurately with spectrometric instruments. Provide reasons behind this limitation. (3)

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

1.3 What is the difference in the bandwidth obtained in atomic and molecular spectroscopy? Give the reason behind that difference. (3)

1.4 Associate the spectroscopic methods in 1 to 6 to their corresponding types of transition in A to F.

Type of spectroscopy	Type of quantum transition
1. Gamma-ray Emission	A. Bonding (valence) electrons
2. X-ray absorption, emission, fluorescence and diffraction	B. Spin of nuclei in a magnetic field
3. Ultraviolet-visible absorption, emission and fluorescence	C. Nuclear
4. Infrared absorption	D. Inner (core) electrons
5. Micowave absorption	E. Rotation/vibration of molecules
6. Nuclear Magnetic resonance	F. Rotation of molecules

(3)

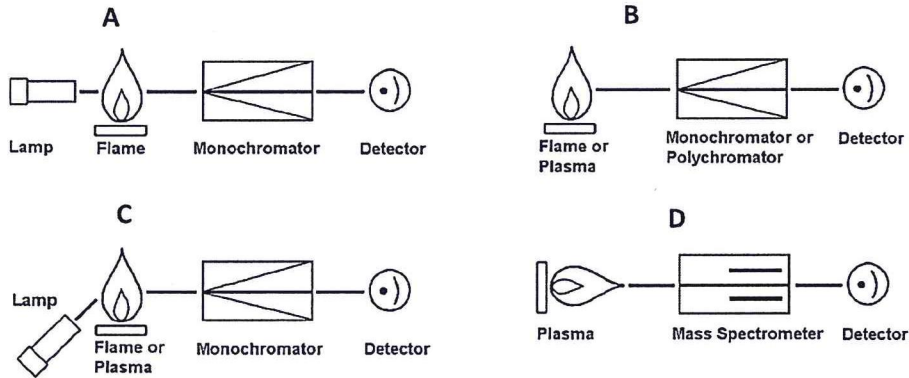1.5 Calculate and complete the missing data in the following table.

Wavelength (m)	Frequency (s^{-1})	Energy (J)
4.50×10^{-7}	_____	_____
_____	1.33×10^{15}	_____
_____	_____	7.20×10^{-19}

(6)

Question 2 [25]

2.1 The following diagram describe four different spectrometric techniques labelled A to D.

A

Lamp — Flame — Monochromator — Detector

B

Flame or Plasma — Monochromator or Polychromator — Detector

C

Lamp — Flame or Plasma — Monochromator — Detector

D

Plasma — Mass Spectrometer — Detector

(a) Provide the correct name for each of the techniques represented in the diagram and explain your choices. (8)

(b) Briefly describe the role of the monochromator shown in A, B and C. (2)

(c) Provide two other approaches that can be used in place of the flame in A. (2)

(d) Why is the lamp in C not positioned in line with the other components as in the case of A? (3)

2.2 The following diagram represents a spectroscopic instrument. Some of the labels in the diagram have been hidden and replaced by letters A to H.

H2

H1   H3

A   B   C P_T F   mirror   D P_0 G   mirror   semitransparent mirror   E
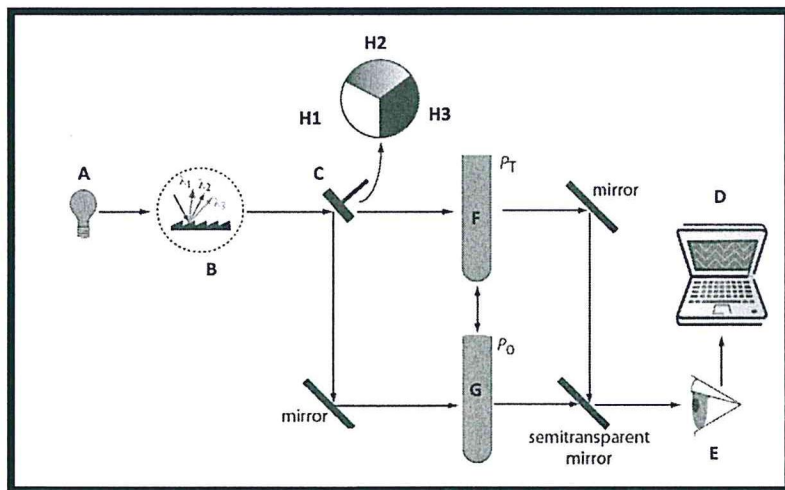
(a) The device labelled "C" can be switched to the three positions shown in H1 to H3. Provide the name of that device and clearly explain its role and the purpose of

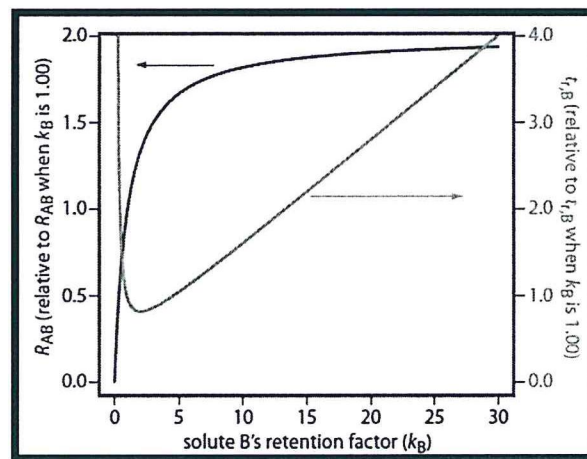these positions.   (6)

(b) What analytical instrument is represented by this diagram? Briefly justify your
    answer.   (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:
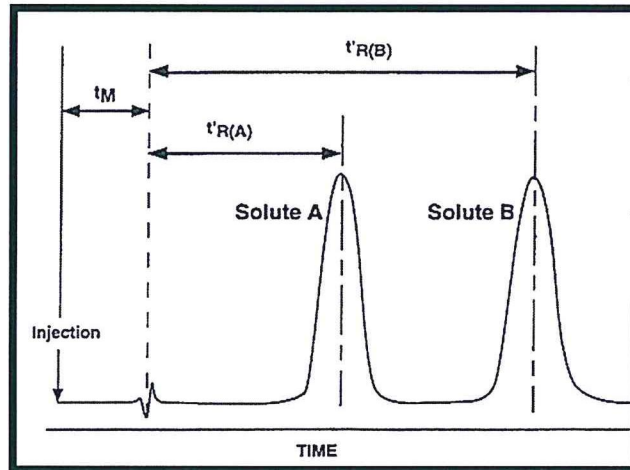
$$H_p = 2\lambda d_f$$

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

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

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

(b) Briefly show how do open tubular columns (OTCs) take advantage of these 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 min; t_R'(A) = 5 min; t_R'(B) = 10 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 ~ 2 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 Briefly discuss the advantages and limitations of thermal conductivity detectors used in GC. (4)

4.3 Differentiate between normal phase and reverse phase chromatography in terms of stationary phase and mobile phase polarity, solute elution order and the effect of increasing mobile phase polarity on the elution time. (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 principle of electrophoresis (CE). (4)

4.6 In the expression of the van Deemter equation: $H = A + B/u + Cu$

(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
Permitivity of vacuum	ε_o	= 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 μm
1 Poise	= 0.1 Pa s = 0.1 N sm^{-2}
1 ppm	= 1 μg g^{-1} = 1 mg kg^{-1}
	= 1 mg L^{-1} (dilute aqueous solutions only)

Selected Formulae

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

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

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

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

$q = nF$

$\Delta G = -nFE$

$I = E/R$

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

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

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

$A = -\log T = \log P_0/P$ and $A = \varepsilon bc$

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