



**NAMIBIA UNIVERSITY  
OF SCIENCE AND TECHNOLOGY**

**FACULTY OF HEALTH AND APPLIED SCIENCES**

**DEPARTMENT OF NATURAL AND APPLIED SCIENCES**

<b>QUALIFICATION:</b> BACHELOR OF SCIENCE	
<b>QUALIFICATION CODE:</b> 07BOSC	<b>LEVEL:</b> 7
<b>COURSE CODE:</b> MSC701S	<b>COURSE NAME:</b> MOLECULAR SPECTROSCOPY AND CHEMICAL SEPARATION METHODS
<b>SESSION:</b> JUNE 2019	<b>PAPER:</b> THEORY
<b>DURATION:</b> 3 HOURS	<b>MARKS:</b> 100

<b>FIRST OPPORTUNITY EXAMINATION QUESTION PAPER</b>	
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<b>MODERATOR:</b>	DR STEFAN LOUW

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

**PERMISSIBLE MATERIALS**

Non-programmable calculators

**ATTACHMENTS**

List of Useful formulas and Constants

**THIS QUESTION PAPER CONSISTS OF 9 PAGES** (Including this front page and attachments)

**Question 1****[20]**

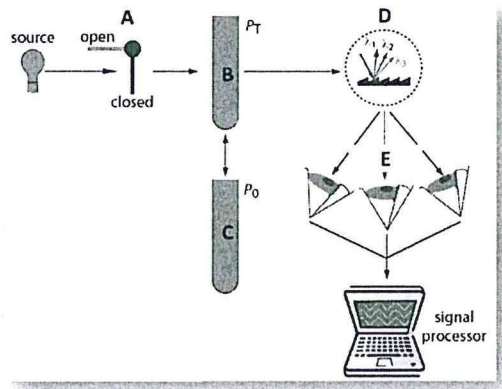
- 1.1 Explain the process of absorption in spectroscopy. (3)
- 1.2 Provide two general criteria that are required for an atom (or molecule) to absorb electromagnetic radiation. (2)
- 1.3 What is the difference in the bandwidth obtained in atomic and molecular spectroscopy? Give the reason behind that difference. (3)
- 1.4 List the three types of atomic spectroscopy. (3)
- 1.5 Briefly describe the similarity and difference between cold vapour and hydride generation techniques used in atomic spectroscopy. (4)
- 1.6 Given the table below

[Analyte] (M)	Absorbance	%T	Molar absorptivity ( $M^{-1} cm^{-1}$ )	Pathlength (cm)
$1.40 \times 10^{-4}$	0.157	69.7	1120	1.00
$7.51 \times 10^{-4}$	0.563	27.3	750	1.00
$2.56 \times 10^{-4}$	0.225	59.6	440	2.00
$1.20 \times 10^{-4}$	0.090	81.3	75	10.00
$8.46 \times 10^{-4}$	0.478	33.3	565	1.00

- (a) Explain the choice of the pathlength of 10.00 cm on the 4<sup>th</sup> row. (3)
- (b) What will %T be in the 5<sup>th</sup> row of the table if the analyte concentration is diluted by 50% and all other conditions are kept constant? (2)

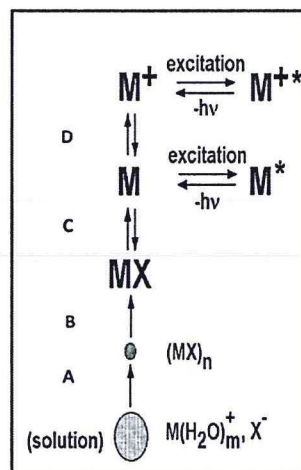
**Question 2****[20]**

- 2.1 The following diagram represents a spectrophotometer.



- (a) Name the components labelled B to E. (2)
- (b) What type of spectrophotometer is represented in the diagram? Explain. (2)
- (c) What type of light source is likely to be used in this technique (i.e. line or continuum)? Explain. (2)
- (d) What is component "A" and when do you use it in its "closed" position? (2)

2.2 The diagram below shows the processes taking place when a sample droplet is introduced into an ICP discharge.



Name the processes labelled as A to D in the diagram. (2)

2.3 Which parameters are used for the identification and quantification of analytes in atomic emission spectroscopy and why? (4)

2.4 (a) What does ICP-OES stand for? (1)

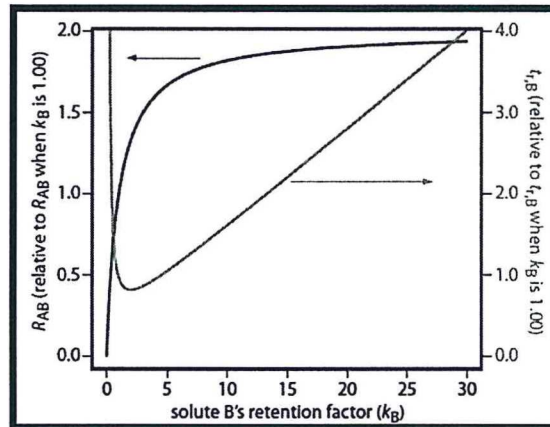
(b) Provide two advantages of using a peristaltic pump in an ICP-OES. (2)

2.5 List the main advantage and two disadvantages of ICP-OES. (3)

**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:

$$H_p = 2\lambda d_f$$

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

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

(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 (a) Researchers have reported the following retention factors for the reversed-phase separation of 2-aminobenzoic acid on a C18 column when using 10% v/v methanol as a mobile phase.

pH	<i>k</i>
2.0	10.5
3.0	16.7
4.0	15.8
5.0	8.0
6.0	2.2
7.0	1.8

Explain why pH affects the retention factor's value. (2)

- (b) A group of chromatography experts have reported the following retention factors for the reversed-phase separation of salicylamide (o-hydroxybenzamide) and caffeine (1,3,7 trimethylxantine).

%v/v methanol	30%	35%	40%	45%	50%	55%
<i>k<sub>sal</sub></i>	2.4	1.6	1.6	1.0	0.7	0.7
<i>k<sub>caff</sub></i>	4.3	2.8	2.3	1.4	1.1	0.9

(i) Explain the trends in the retention factors for these two compounds. (2)

(ii) What is the advantage of using a mobile phase with a lower %v/v of methanol? Are there any disadvantages? (2)

- (c) Suppose you need to separate a mixture of benzoic acid, aspartame, and caffeine in a diet soda. The following information is available.

Compound	<i>t<sub>r</sub></i> in aqueous mobile phase of pH			
	3.0	3.5	4.0	4.5
Benzoic acid	7.4	7.0	6.9	4.4
Aspartame	5.9	6.0	7.1	8.1
Caffeine	3.6	3.7	4.1	4.4

Identify a pH level that will yield an acceptable separation. Explain your choice. (2)

- (d) Complete the following table. (4)

<i>N<sub>B</sub></i>	$\alpha$	<i>k<sub>B</sub></i>	<i>R</i>
100,000	1.05	0.50	
10,000	1.10		1.50
10,000		4.0	1.00
	1.05	3.0	1.75

**Question 4**

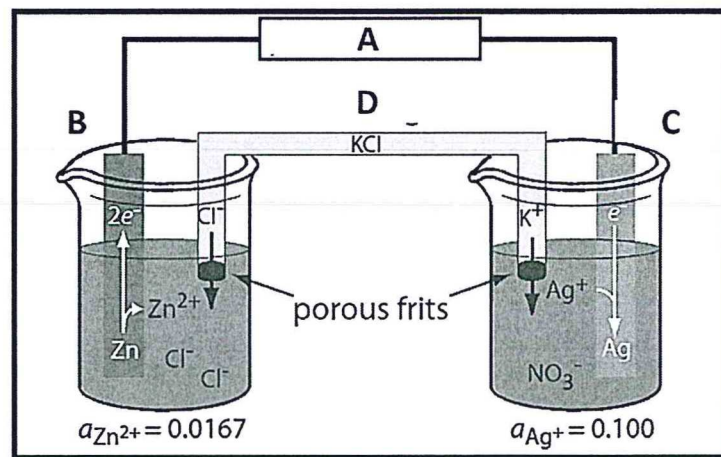
**[20]**

- 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 What technique is used in electrophoresis to separate neutral solutes? Briefly explain the principle of this technique. (4)

**Question 5**

**[15]**

5.1 Given the following electrochemical cell



- (a) Name the components A to D. (2)
- (b) Write the shorthand notation of the electrochemical cell. (3)
- (c) Write the reaction involved in each half-cell as well as the balanced overall reaction of the electrochemical cell. (3)

(d) Based on your answer in (c), which redox couple will have the higher standard potential ( $E^0$ ) and why? (2)

5.2 Briefly explain why the following conditions are to be avoided when working with glass a membrane electrode for pH measurement.

(a) Working with HF solutions at  $\text{pH} < 4$ . (1)

(b) Working with strongly alkaline solutions. (1)

(c) Exposing the membrane to abrasive substances (e.g.  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , soil samples). (1)

5.3 Why do dynamic electroanalytical methods employ three electrode cells whereas only two electrodes are enough for static methods? (2)

**END**

### Physical Constants

Gas constant	$R$	= 8.315 J K <sup>-1</sup> mol <sup>-1</sup> = 8.315 kPa dm <sup>3</sup> K <sup>-1</sup> mol <sup>-1</sup> = 8.315 Pa m <sup>3</sup> K <sup>-1</sup> mol <sup>-1</sup> = 8.206 x 10 <sup>-2</sup> L atm K <sup>-1</sup> mol <sup>-1</sup>
Boltzmann constant	$k$	= 1.381 x 10 <sup>-23</sup> J K <sup>-1</sup>
Planck constant	$h$	= 6.626 x 10 <sup>-34</sup> J s <sup>-1</sup>
Faraday constant	$F$	= 9.649 x 10 <sup>4</sup> C mol <sup>-1</sup>
Avogadro constant	$L$ or $N_A$	= 6.022 x 10 <sup>23</sup> mol <sup>-1</sup>
Speed of light in vacuum	$c$	= 2.998 x 10 <sup>8</sup> m s <sup>-1</sup>
Mole volume of an ideal gas	$V_m$	= 22.41 L mol <sup>-1</sup> (at 1 atm and 273.15 K) = 22.71 L mol <sup>-1</sup> (at 1 bar and 273.15 K)
Elementary charge	$e$	= 1.602 x 10 <sup>-19</sup> C
Rest mass of electron	$m_e$	= 9.109 x 10 <sup>-31</sup> kg
Rest mass of proton	$m_p$	= 1.673 x 10 <sup>-27</sup> kg
Rest mass of neutron	$m_n$	= 1.675 x 10 <sup>-27</sup> kg
Permittivity of vacuum	$\epsilon_0$	= 8.854 x 10 <sup>-12</sup> C <sup>2</sup> J <sup>-1</sup> m <sup>-1</sup> (or F m <sup>-1</sup> )
Gravitational acceleration	$g$	= 9.807 m s <sup>-2</sup>

### Conversion Factors

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

### Selected Formulae

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



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

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

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

$$q = nF$$

$$\Delta G = -nFE$$

$$I = E/R$$

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

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

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

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

$$v_{\text{ep}} = \mu_{\text{ep}} E$$

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