



**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> JULY 2019	<b>PAPER:</b> THEORY
<b>DURATION:</b> 3 HOURS	<b>MARKS:</b> 100

<b>SUPPLEMENTARY/SECOND OPPORTUNITY EXAMINATION QUESTION PAPER</b>	
<b>EXAMINER(S)</b>	DR JULIEN LUSILAO
<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 8 PAGES** (Including this front page and attachments)

## Question 1

[20]

- 1.1 Explain why many metals (M) are analysed in the form of metal-ligand complexes (ML) in UV-Vis absorption. (2)
- 1.2 It is critical in UV-Vis to measure the 100% transmittance (100%T). This measurement is always carried out with a sample blank. Provide a clear explanation of the relevance of 100%T in UV-Vis and the reason why a blank is used for that measurement. (4)
- 1.3 Give two reasons that explain why double-beam optics are preferred over single-beam optics in IR spectroscopy. (2)
- 1.4 Briefly explain the principle of atomic spectroscopy. (2)
- 1.5 The burner assemblies of atomic absorption spectrometers (AAS) are known to provide a long optical pathlength as well as a stable flame and they can also move horizontally and vertically. Explain the importance of the underlined properties in the statement above. (4)
- 1.6 The table below shows atomic emission lines for a Cr hollow cathode lamp.

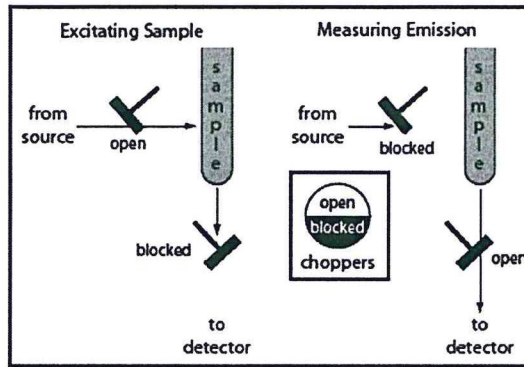
$\lambda$ (nm)	Slit width (nm)	mg Cr/L giving A = 0.20	P <sub>0</sub> (relative)
357.9	0.2	2.5	40
425.4	0.2	12	85
429.0	0.5	20	100
520.5	0.2	1500	15
520.8	0.2	500	20

- (a) Which analytical technique uses hollow cathode lamps and why? (2)
- (b) For the Cr hollow cathode lamp in the table above, which wavelength provides the best sensitivity? Explain your answer. (2)
- (c) When analysing samples containing  $\approx 10$  mg Cr/L, which wavelength(s) would you expect to provide a reasonable sensitivity with less uncertainty in the measured absorbance? Explain your choice. (2)

## Question 2

[20]

- 2.1 The following diagram represents a spectrophotometer used for measuring Phosphorescence:

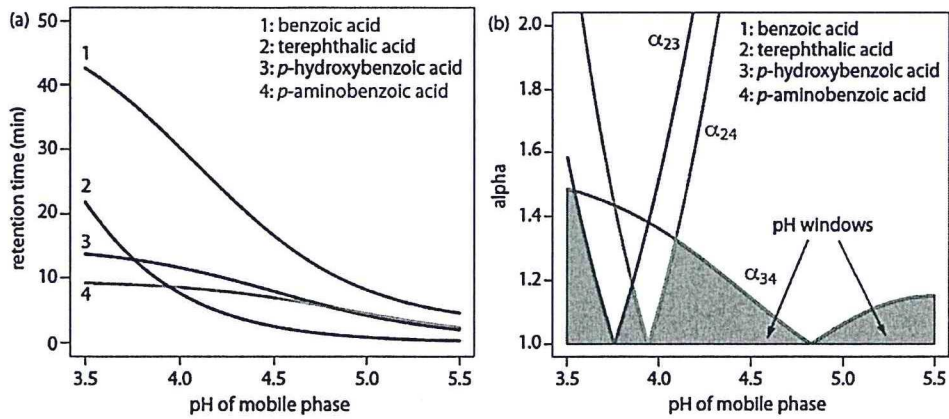


- Briefly explain how it operates. (5)
- 2.2 Briefly discuss the similarity and difference between a monochromator and a polychromator. (3)
- 2.3 Describe what the capabilities of a dual view ICP-OES instrument are. (2)
- 2.4 (a) Besides improving excitation and ionization efficiencies, what other advantage does the higher temperature of plasmas have over flames and furnaces? (2)
- (b) Name three types of plasma sources used in optical emission techniques. (3)
- 2.5 (a) What is a matrix modifier in atomic absorption spectroscopy (AAS) and which specific AAS technique requires the use of such modifiers? (3)
- (b) What is the general solution to overcome the problem of interferences encountered when using AAS techniques? (2)

### Question 3

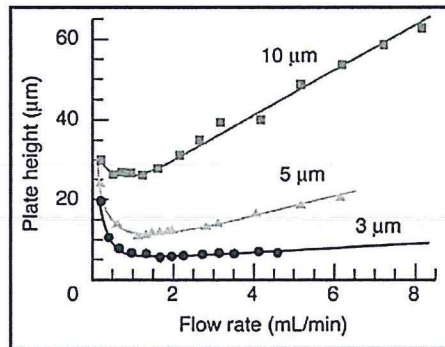
[25]

- 3.1 How do you adjust the selectivity,  $\alpha$ , in gas chromatography (GC) and in liquid chromatography (LC)? (2)
- 3.2 The figures below show how the mobile phase pH affect both (a) the retention time of the solutes,  $t_r$ , and (b) their selectivity,  $\alpha$ .



- (a) Why is the  $t_r$  of the 4 components in the diagrams decreasing with an increase in the mobile phase pH? (2)
- (b) What unwanted situation would occur if the analysis was carried using a mobile phase at pH between 4.8 -5.5? (1)
- (c) Figure (b) is also called a window diagram and is used to find the optimum separation by plotting  $\alpha$  for each pair of solutes. Explain, using this figure, what would the optimum mobile phase pH be to obtain the best chromatographic separation of these 4 components. (5)

3.3 The following figure shows the effect of flow rate on the column's plate height.



- (a) In the Van Deemter Equation:  $H = A + B/u + Cu$ , which parameter is affected by changing the flow rate of a chromatographic system and what is that parameter called? (2)
- (b) Explain the change (i.e. decreasing or increasing trend) observed in the size of the plate height when increasing the flow rate. (2)
- (c) Which optimum flow rate would you use to obtain the best efficiency with the three particle sizes in the figure above and why? (2)
- (d) Assuming you have two columns with particle sizes 3  $\mu\text{m}$  and 10  $\mu\text{m}$ . Which one

would you choose to carry out your analysis (assuming all other characteristics are similar for both columns) and why? (3)

3.4 The following data were obtained for four compounds separated on a 20-m capillary GC column.

Compound	$t_r$ (min)	w (min)
A	8.04	0.15
B	8.26	0.15
C	8.43	0.16

- (a) Calculate the number of theoretical plates for each compound and the average number of theoretical plates for the column. (2)
- (b) Calculate the average height (in  $\mu\text{m}$ ) of a theoretical plate. (2)
- (c) Explain why it is possible for each compound to have a different number of theoretical plates. (2)

**Question 4** [20]

4.1 Briefly explain the different injection systems used in GC. (6)

4.2 (a) What is reversed phase ion pairing chromatography (RPIPC)? (1)

(b) Discuss the role and characteristics of an ion-pairing agent. (4)

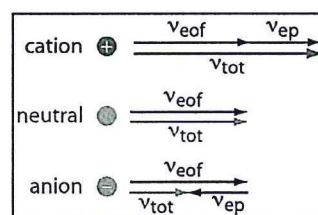
4.3 Briefly discuss the following myths in chromatography.

(a) You cannot reverse an HPLC column. (1)

(b) All  $C_{18}$  columns are the same. (1)

(c) Guard columns do not affect separation. (1)

4.4 Given the diagram below, explain the elution order of cations, neutral solutes and anions in electrophoresis.



(6)

**Question 5**

**[15]**

- 5.1 (a) An important concept in electrochemistry is that we cannot simultaneously control current and potential. What is the implication of this concept in the design of electroanalytical techniques? (3)
- (b) Provide the basic principle of a manual potentiostat. (2)
- (c) What is a "static" method in electrochemistry? Explain why the method is called static and name an equipment that relies on this concept. (4)
- (d) Define a junction potential. (2)
- 5.2 Show the line equation and determine the slope value (in mV) for the calibration of an ion selective electrode (ISE) used for the measurement of
- (a) pH. (2)
- (b) Calcium concentration. (2)

**END**

### Physical Constants

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

### Conversion Factors

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

### Selected Formulae

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

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

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

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

$$q = nF$$

$$\Delta G = -nFE$$

$$I = E/R$$

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

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

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

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