UNIVERSITY OF JOHANNESBURG

FACULTY OF SCIENCE

DEPARTMENT OF APPLIED CHEMISTRY

NATIONAL DIPLOMA : ANALYTICAL CHEMISTRY (3 YEARS)
NATIONAL DIPLOMA: ANALYTICAL CHEMISTRY (4 YEARS)

MODULE CET2BAA
ANALYTICAL CHEMISTRY 3 (INSTRUMENTAL TECHNIQUES)

CAMPUS **DFC**

NOVEMBER EXAMINATION

DATE: 6/11/2015 **SESSION: 14:00 – 16:00**

ASSESSOR: **MS H DU PLESSIS-FISCHER**

EXTERNAL MODERATOR: **MR A VAN ZYL**

DURATION: 2 HOURS **MARKS: 100**

NUMBER OF PAGES: 6 PAGES, INCLUDING A FORMULA SHEET.

INSTRUCTIONS: CALCULATORS ARE PERMITTED.

REQUIREMENTS: ANSWER BOOK.

QUESTION 1

1.1 What information does the capacity factor (retention factor) (k') give regarding a **solute in a column**? (2)

1.2 How can the resolution between two poorly resolved peaks most easily be increased in GLC? (2)

1.3 Match the following chromatographic symbols and statements by writing only the number and the corresponding letter in your answer book, e.g. **8 k**. (7)

Number	Symbol	Letter	Statement
1	A	**a**	Linear velocity of mobile phase
2	B/u	**b**	Mass transfer to & from stationary phase
3	C_Su	**c**	Solute concentration in stationary phase / solute concentration in mobile phase
4	C_Mu	**d**	Height equivalent to a theoretical plate
5	u	**e**	Multiple flow paths
6	H	**f**	Longitudinal diffusion
7	K_D	**g**	Mass transfer in mobile phase

[11]

QUESTION 2

The following data were obtained during an isothermal GC run. A liquid of 100.0% purity was injected (Run 1), followed by the unknown liquid under identical experimental conditions (Run 2). The run was terminated after 3.60 minutes.

Run	Sample	Volume injected (μL)	Retention time of peak (minutes)	Peak area
1	100% pure liquid	10.0	2.55	21315
2	Unknown liquid	15.0	2.26	1234
			2.55	8456
			3.50	7564

2.1 Name the evaluation method used for this determination. (1)

2.2 What is the meaning of the phrase "…isothermal GC run…"? (2)

2.3 Calculate the % (v/v) of the component in the unknown liquid that has a retention time of 2.55 minutes. (5)

[8]

QUESTION 3

3.1 Describe the operational principles of the flame ionisation detector (FID). (7)

3.2 Why is a packed column far shorter than an open tubular (OT) column? (2)

3.3 The following data were obtained from a 2.40 m long packed gas-liquid chromatography (GLC) column operated isothermally at 150°C:

Component	Retention time (minutes)	Peak baseline width (seconds)
Air	0.666	————
A	2.000	11.058
B	2.124	11.862

3.3.1 Calculate the peak resolution of components A and B. (2)

3.3.2 Calculate the required column efficiency that will give at least baseline resolution of the peaks on the original column. (8)

3.3.3 If you operated the column isothermally at 90°C, predict what would happen to the respective retention times and widths of peaks A and B. (2)

3.4 List the main disadvantage of the thermal conductivity detector (TCD) for GC. (2)

[23]

QUESTION 4

4.1 Name two detectors used for high performance liquid chromatography (HPLC). (2)

4.2 Describe a typical HPLC separation column used for LLC, and pay particular attention to the stationary phase. (5)

4.3 Given two closely eluting sample components eluting from a reversed-phase HPLC column.

4.3.1 Describe the term reversed-phase. (2)

4.3.2 Which of the two components will elute first? (1)

4.3.3 How must the mobile phase polarity be changed in order to increase the resolution between the two components? Explain. (2)

[12]

QUESTION 5

5.1 A calcium ion-selective electrode (ISE) and a saturated calomel electrode (SCE) combination were used to determine the calcium content of a milk sample.

A 10.00 mL portion of the milk sample was digested and afterwards diluted to 50.00 mL in a volumetric flask. A cell potential of −0.0104 V was obtained for a volume of 25.00 mL of this diluted milk sample at 25ºC. The electrode was then calibrated by putting it in a standard calcium solution of concentration 3.38×10^{-2} M, for which a cell potential of 0.0100 V vs SCE was obtained under identical operating conditions. Report the calcium concentration in the milk sample as milligrams of Ca per 100 mL of milk.
[Molar mass: Ca = 40.08 g mol^{-1}] (9)

5.2 A saturated calomel electrode (SCE) was used as reference electrode in Question 5.1.

5.2.1 Make a labelled sketch of a commercial SCE and indicate the salt bridge on your sketch. (6)

5.2.2 Discuss two good practices to implement when using a reference electrode, and the reasons for implementing these. (3)

5.3 Describe the characteristics of the NIST buffer solutions. (5)

[23]

QUESTION 6

6.1 List <u>three</u> advantages of a coulometric titration. (3)

6.2 Calculate the molar concentration of $Ba(OH)_2$ in a 25.00 mL aliquot of a solution that required a constant current of 325.0 mA for 3 min and 45 sec to reach an end-point against electrogenerated H^+ in a coulometric titration using a cell for external generation of titrant. Show the balanced “titration” and “generation” reaction equations. (9)

[12]

QUESTION 7

7.1 Define the term *residual current* that is used in polarography, also mentioning its origin in your answer. (4)

7.2 From the following data obtained during the DC polarographic determination of an unknown Cd^{2+} solution, calculate the pCd of the unknown Cd^{2+} concentration (X): (5)

Solution composition	i_d Cd^{2+} (μA)	i_d Zn^{2+} (μA)
0.0800 M Cd^{2+} & 0.0500 M Zn^{2+}	30.00	24.00
X M Cd^{2+} & 0.0300 M Zn^{2+}	55.34	67.20

7.3 Zn^{2+} was added as an internal standard during the analysis in Question 7.2. List <u>three</u> criteria for a substance to be used as an internal standard in polarography. (3)

[12]

QUESTION 8

Briefly describe the principles of thermogravimetry (TG). (3)

[3]

FULL MARKS : 100

FORMULA SHEET

$$i = \frac{Q}{t}$$

1 F = 96485.0 C mol^{-1}

$$i_d = K \times n \times C \times D^{1/2} \times m^{2/3} \times t^{1/6} \qquad \text{where K = 706 or 607}$$

$$E = K + \left(\frac{0.05916}{z}\right) \times \log a_{ion} \qquad \text{at } 25^oC$$

$$E = E^\circ - \left(\frac{0.05916}{z}\right) \times \log\left(\frac{[\text{product 1}] \times [\text{product 2}]}{[\text{reactant 1}] \times [\text{reactant 2}]}\right) \qquad \text{at } 25^oC$$

$$i_d = i_{lim} - i_{resid}$$

$$H = 2\lambda d_P + \frac{2\gamma D_M}{u} + \left(\frac{f_S(k') \times d_f^2}{D_S}\right) \times u + \left(\frac{f_M\left(d_c^2, d_p^2, u\right)}{D_M}\right) \times u$$

$$k' = \frac{t'_R}{t_M} = \frac{(t_R - t_M)}{t_M} = K_D \times \left(\frac{V_S}{V_M}\right) = \frac{(C_S \times V_S)}{(C_M \times V_M)}$$

$$R_S = \left(\frac{\sqrt{N}}{4}\right) \times \left(\frac{(\alpha - 1)}{\alpha}\right) \times \left(\frac{k'_B}{(1 + k'_B)}\right)$$

$$R_S = 2 \times \frac{[(t_R)_B - (t_R)_A]}{(W_B + W_A)}$$

$$V_M = F \times t_M$$

$$V_R = F \times t_R$$

$$N = 16 \times \left(\frac{t_R}{W_b}\right)^2$$

$$N = 5.54 \times \left(\frac{t_R}{W_{1/2}}\right)^2$$

$$H = \frac{L}{N}$$

$$\alpha = \frac{(k')_B}{(k')_A} = \frac{(K_D)_B}{(K_D)_A}$$

$$u = \frac{L}{t_M}$$

$$\text{Efficiency} = \frac{N}{L} = \frac{1}{H}$$

$$(t_R)_B = \left(\frac{16R_S^2H}{u}\right) \times \left(\frac{(\alpha - 1)}{\alpha}\right)^2 \times \frac{(1 + k'_B)^3}{(k'_B)^2}$$