



FACULTY OF SCIENCE

DEPARTMENT OF CHEMICAL SCIENCES
NATIONAL DIPLOMA: ANALYTICAL CHEMISTRY (4 YEARS)
DIPLOMA IN ANALYTICAL CHEMISTRY (4 YEARS)

MODULES CET2BAA / CETAIB3
ANALYTICAL CHEMISTRY 3 (INSTRUMENTAL TECHNIQUES)

CAMPUS DFC

NOVEMBER EXAMINATION

DATE: 19/11/2019

SESSION: 12:30 – 14:30

ASSESSOR:

MS H DU PLESSIS

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 Describe the main features of chromatography as an instrumental analytical technique. (6)
- 1.2 According to the fundamental resolution equation, the resolution between two poorly resolved chromatographic peaks can be increased by increasing the number of plates (N) and increasing the selectivity factor (α).
- 1.2.1 List two ways to increase the number of plates, N. (2)
- 1.2.2 List two ways to increase the selectivity factor, α . (2)
- 1.3 Identify three experimental variables from the Van Deemter equation that will decrease the value of the HETP for a packed GLC column. (3)

[13]

QUESTION 2

A well-known coffee brand of instant coffee was analysed for its caffeine content by reversed-phase HPLC using isocratic elution. A teaspoon (ca. 1.8 g) of instant coffee was dissolved in hot deionized water and after cooling to room temperature, it was diluted to a final volume of 500.00 mL in a volumetric flask. A 10.00 μ L portion of this diluted coffee sample was injected into the HPLC column and a peak area of 295 626 units was measured for the caffeine peak. A 10.00 μ L portion of a 100.00 mg/L caffeine standard was injected under identical conditions onto the column and a peak area of 226 724 units was measured for the resulting caffeine peak.

- 2.1 What type of calibration method was used in this analysis? (1)
- 2.2 Calculate the milligrams of caffeine in a 250.0 mL cup of this coffee. (5)
- 2.3 Explain what is meant by the term *reversed-phase*. (2)
- 2.4 Explain what is meant by the term *isocratic elution*. (1)

[9]

QUESTION 3

- 3.1 The following data were obtained during an isothermal gas chromatography (GC) run of a three-component mixture at 135°C on a 1.53 m long GLC column.

Component	Retention time (minutes)	Peak width (seconds)
A	1.250	6.720
B	1.469	7.860
C	1.592	8.520

- 3.1.1 Calculate the resolution between components A and B, as well as between components B and C. (4)
- 3.1.2 Calculate the length of column that will separate all of the components in the three-component mixture to the baseline, assuming all operating variables and conditions remain the same. (4)
- 3.1.3 What is meant by the phrase “...an isothermal run...”? (1)
- 3.2 State the sample application of gas-solid chromatography. (1)
- 3.3 Compare the flame ionisation detector (FID) and thermal conductivity detector (TCD) used in gas chromatography in terms of type of components detected, detection limit and linear range. (6)

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QUESTION 4

- 4.1 Name six components of a modern high performance liquid chromatograph (HPLC). [Half a mark will be allotted to each.] (3)
- 4.2 Describe the process of “sparging” in HPLC and comment on its purpose. (3)
- 4.3 Discuss extra-column band-broadening in HPLC, and its consequence for the design of the instrument. (3)

[9]

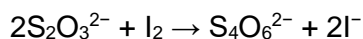
QUESTION 5

- 5.1 A glass pH ISE and SCE reference were used to determine the pH of an unknown soft drink. A volume of 25.00 mL of this soft drink was diluted to 100.00 mL in a volumetric flask. Then a volume of 20.00 mL of the diluted solution was pipetted into a beaker, the electrodes were inserted and a potential of +0.4660 V was obtained between the electrodes. When the electrodes were immersed in a standard buffer solution of pH = 4.349, the electrode system gave a cell potential of +0.5000 V. Calculate the pH of the unknown soft drink. (8)
- 5.2 A saturated calomel electrode (SCE) was used as reference electrode in Question 5.1. Make a labelled sketch of a commercial SCE and indicate the salt bridge on your sketch. (6)
- 5.3 Briefly discuss the properties and use of NIST buffers. (5)
- 5.4 Distinguish between a metal electrode of the first class and the second class. (3)

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QUESTION 6

- 6.1 The purity of sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) can be determined by titrating it coulometrically against electrolytically generated I_2 according to the following reaction equation:



A mass of 0.1342 g of an impure $\text{Na}_2\text{S}_2\text{O}_3$ sample was weighed and dissolved to 100.00 mL in a volumetric flask. A 10.00 mL portion was transferred to an electrochemical cell along with 25 mL of 1 M KI (an excess), 75 mL of a pH 7.0 phosphate buffer and several drops of starch indicator solution. A constant current of 36.45 mA applied for 221.8 seconds was necessary to complete the titration to the starch end point. Calculate the purity of the sodium thiosulphate sample. Remember to give the balanced “generation” reaction.

[Molar mass (g mol^{-1}): $\text{Na}_2\text{S}_2\text{O}_3 = 158.07$] (9)

- 6.2 List *three* errors that can occur in coulometric titrations. (3)
- 6.3 Name two types of working electrodes that are used for potentiostatic coulometry. (2)

[14]

QUESTION 7

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

7.2 The following data were obtained during the DC polarographic determination of a standard Pb^{2+} solution containing Cd^{2+} as internal standard:

Solution composition	$i_d \text{ Pb}^{2+} (\mu\text{A})$	$i_d \text{ Cd}^{2+} (\mu\text{A})$
0.00418 M Pb^{2+} & 0.00323 M Cd^{2+}	15.8	16.4

An unknown mixture was prepared by mixing 25.00 mL of the unknown (containing only Pb^{2+}) with 10.00 mL of a 0.0323 M Cd^{2+} standard and diluting it to a final volume of 50.00 mL. This unknown mixture was run under identical conditions on the DC polarograph and diffusion currents of 30.0 μA and 20.0 μA were measured for Pb^{2+} and Cd^{2+} , respectively. Calculate the concentration of Pb^{2+} in the original unknown solution. (6)

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

[13]**QUESTION 8**

Briefly describe the principles of differential scanning calorimetry (DSC). (4)

[4]**FULL MARKS: 100**

FORMULA SHEET

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

$$1 F = 96485.0 \text{ C mol}^{-1}$$

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

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

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

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

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

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

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

$$V_M = F \times t_M$$

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

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

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

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

$$V_R = F \times t_R$$

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

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

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

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