



Bachelor of Science General Degree Examination – October 2023

Academic Year 2021/2022– Semester I

CHEMISTRY

APCH 21642 – Principles of Analytical Chemistry

Number of Questions: Four (04)

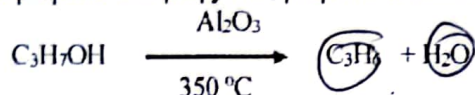
Time: Two (02) hours and 10 min. reading time

Number of pages: Six (06)

Answer all questions.

(1) Answer all parts.

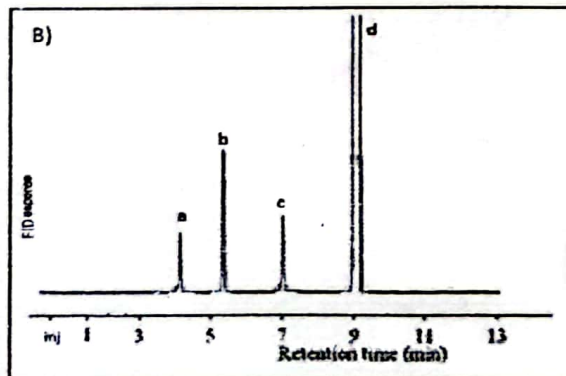
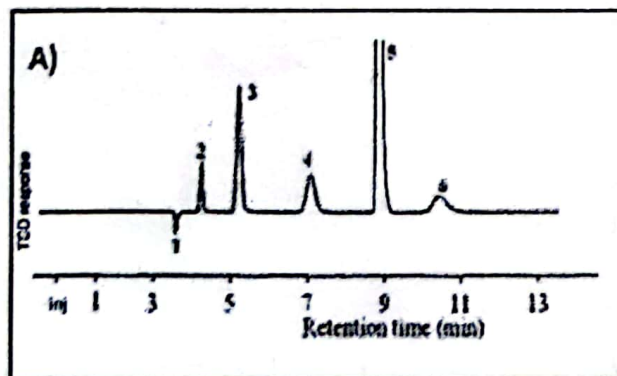
A. In a study of dehydration of propanol into propylene, propanol is heated with Al_2O_3 at 350°C (623 K),



The product obtained also contains unreacted reactants, the byproducts including propane and hydrogen. The resultant mixture is bubbled into methanol and injected into a GC which is fixed with a fused silica column (20.0 m x 0.53 mm ID). UMP

The carrier gas used was ultra-pure He at a flow rate of 28 mL/min and the injection temperature was 105 °C. The oven temperature was maintained from 40-250 °C. The two chromatograms given below have been obtained by using two different detectors for the above analysis.

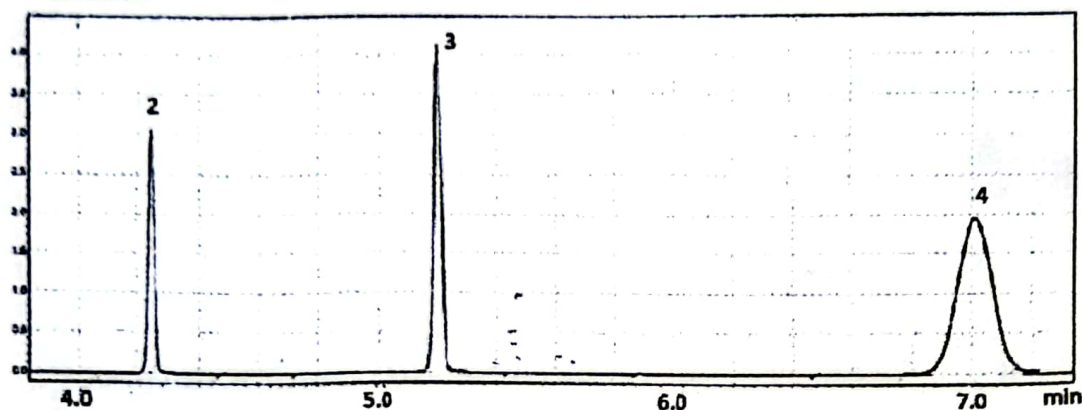
Chromatogram (A) is when a thermal conductivity detector (TCD) was used and (B) is when a flame ionization detector (FID) was used on the same eluents under similar conditions.



- Assign the peaks in chromatogram (A) and briefly explain why the number of peaks is different in chromatogram (A) and (B).
 - Briefly explain why peak 1 in chromatogram (A) is a negative peak? $\rightarrow \text{H}_2$
 - Can we use H_2 as the carrier gas in obtaining the two chromatograms given above? Briefly explain your answer.
 - Sketch the expected chromatogram if an electron capture detector (ECD) was used for the above analysis under similar conditions.
- (55 marks)

B. Part of the zoomed chromatogram (A) is shown below.

Given that the peak widths at half-max for peaks 2, 3 and 4 respectively are 7.05, 8.81 and 17.63 seconds. Under these conditions, a gas not retained by the column elutes at 1.80 minutes.



calculate the following.

- Resolution of peak 2 and 3.
- Capacity factor of peak 3
- Estimate the asymmetric factor of peak 4.
- Number of theoretical plates and thereby the height equivalence of a theoretical plate with respect to peak 3. (45 marks)

$$N = 16 \left(\frac{t_R}{w} \right)^2 = 5.54 \left(\frac{t_R}{w_{1/2}} \right)^2$$

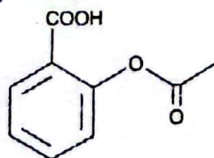
$$k' = K \frac{V_S}{V_m} = \frac{t'_R}{t_m}$$

$$\alpha = \frac{t'_{R2}}{t'_{R1}}$$

$$R_s = \frac{\Delta t_R}{w_{av}}$$

2. Answer all parts.

A. Aspirin shown below is 5 times more soluble in ethanol than in water. Its partition coefficient between diethyl ether and water is 3.5 at room temperature.

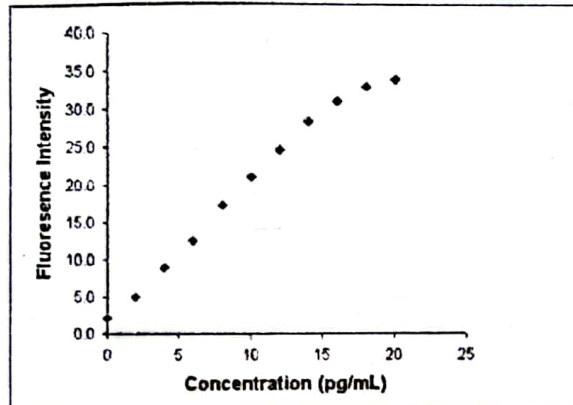


- 1.00 g of aspirin (MW 180.16 g mol⁻¹) is in 250.00 mL of water. If 50.00 mL of ethanol is used in two equal portions, find out the amount of aspirin that can be extracted into ethanol. *Handwritten: 25, 25*
- If 50.00 mL of ether is used, calculate the amount of aspirin that will be extracted to the organic phase. Show your calculations and state all assumptions made.
- Using appropriate equations, show that the above extraction is dependent on the pH of the medium.
- Based on your equation(s) will basic pH values enhance or reduce the efficiency of aspirin extraction into the ether. (40 marks)

B. A student uses a photometric calibration curve method to analyze the quantity of phosphate ions in a liquid fertilizer sample.

- i. Using the above analysis as an example, define the terms "selectivity" and "sensitivity" of an analytical technique. (10 marks)

- ii. In a fluorescence spectroscopic determination of tryptophan, the following plot was obtained.



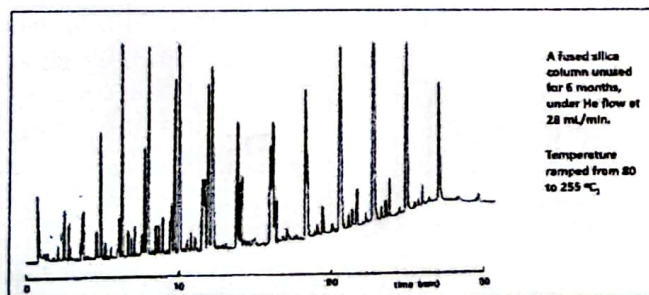
using the above analysis and marking on a sketch of the plot, define,

- Linear dynamic range
- working range.
- Limit of quantification
- If an analysis of a sample of tryptophan gives a fluorescence intensity of 46.0 can you analyze the sample and get the concentration of the analyte in the solution? Briefly explain.

(25 marks)

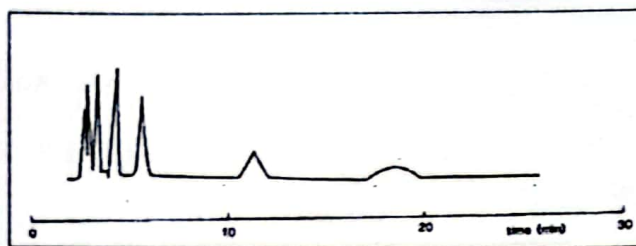
C. Examine the GC chromatograms given below and identify the shortcoming(s) and briefly state how you overcome/improve these analyses.

- i.

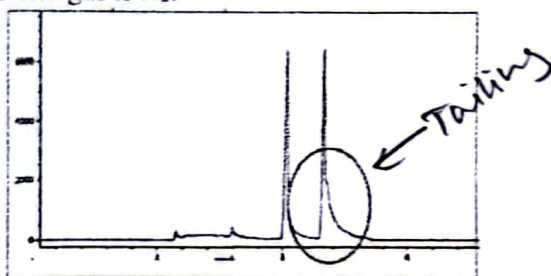


• Baseline shift
• Noise

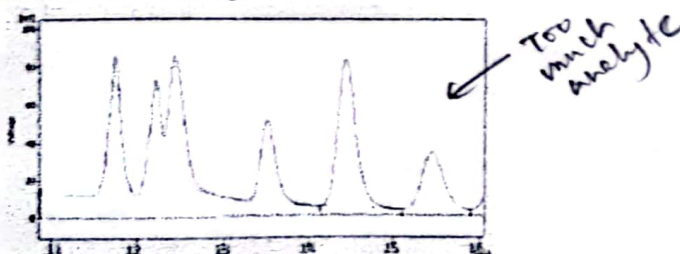
- ii. A GC siloxane capped silica column operated at a temperature of 100 °C isocritical temperature, with N₂ as the carrier gas and a flowrate of 30 mL/min with a FID detector.



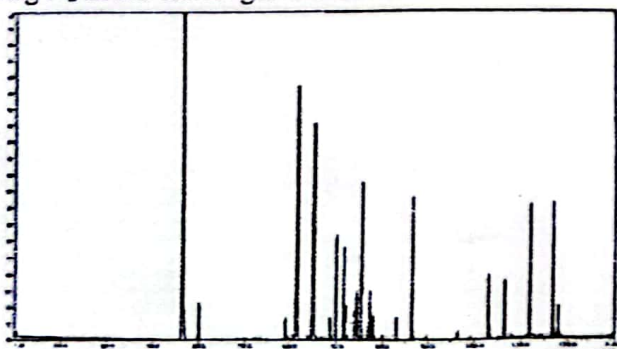
- iii. Methanol and ethanol injected to a packed alumina (Al_2O_3) column with a FID. Carrier gas is N_2 .



- iv. GC chromatogram of a mixture of alkyl chlorides using a C-18 non-polar column with He as the carrier gas and an ECD.



- v. Sample of hydrocarbon residues from a arson site send through a C-10 GC column using N_2 as the carrier gas and a FID.



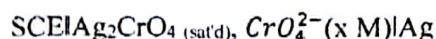
(25 marks)

3. Answer all parts

A. Briefly define following terms

- Indicator electrode
- Reference electrode

B. Consider the following cell,



- Generate an equation that relates $p\text{CrO}_4^{2-}$ to the cell potential (E_{cell}).
- Calculate $p\text{CrO}_4^{2-}$ when the cell potential is 0.34 V at 25 °C.

The potential of the saturated calomel electrode is 0.24 V at 25°C. $E^\circ (\text{Ag}_2\text{CrO}_4, \text{Ag}) = 0.44 \text{ V}$

(30 marks)

C.

- What is the major advantage of using a mercury electrode compared with platinum electrode as a working electrode in voltammetry.
- What are the two (02) major sources of residual current in linear scan polarography.

(20 marks)

D. The purity of a sample of $\text{K}_3\text{Fe}(\text{CN})_6$ was determined using linear-potential scan hydrodynamic voltammetry at a glassy carbon electrode. The sample was prepared for analysis by diluting a 0.046 g sample to volume in a 50.0 mL volumetric flask. The limiting current for the sample was found to be 1.78 μA . A standard addition of 0.400 mL of 0.279 M $\text{K}_3\text{Fe}(\text{CN})_6$ increased the current to 3.35 μA . Determine the purity of the sample of $\text{K}_3\text{Fe}(\text{CN})_6$. (Atomic weight: K = 39.10 amu, Fe = 55.847 amu, C = 12.01 amu, N = 14.01 amu)

(40 marks)

4. Answer all parts.

A. Unlike other cereal crops, rice tends to contain more arsenic (As) depending on the variety and area of cultivation. The As in rice could be a more toxic form leading to illnesses like cancer. In the following study 50 mg of a rice sample was digested with 1.0 mL of 10% v/v HNO_3 and 2.0 mL of 2% $\text{K}_2\text{S}_2\text{O}_8$ at 80 °C for three hours. Then the total volume was adjusted for 10 mL. After centrifuging the solution, the supernatant was analyzed for the total As content using atomic absorption spectroscopy. The blank solution was prepared in the same manner except the analyte.

- Explain briefly the method used to analyze As using atomic absorption spectroscopy.

(10 marks)

Hydride
Germination.
Volatile
hydride

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- ii. The following readings were obtained during analysis. Using a suitable calibration plot find the As content in the rice sample as $\mu\text{g/L}$.

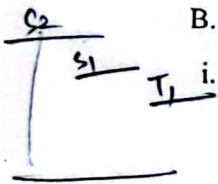
As ($\mu\text{g/L}$)	Absorbance
0	0.005
0.2	0.010
0.4	0.015
0.6	0.026
0.8	0.036
Brown rice sample	0.035
Brown rice – polished sample	0.030
White rice sample	0.025
White rice – polished sample	0.020

(30 marks)

- iii. If the minimum permissible levels of As in food is $100 \mu\text{g/kg}$. Identify which of the above rice varieties are safe to consumption. Suggest a reason for this observation. (10 marks)

- iv. Briefly explain why matrix effects are minimum with the As analysis with method described in (i). (10 marks)

B. Answer all parts

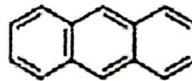


- i. Fluorescence and phosphorescence always come at lower energy than the excitation energy (excitation $\lambda <$ emission λ). Explain this statement using a suitable energy level diagram (Jablonski diagram). (10 marks)

- ii. The UV-Visible spectrum of benzene indicates a band at λ_{max} at 255nm while anthracene indicate λ_{max} at 477nm. Briefly explain this observation.



benzene



anthracene

(10 marks)

- iii. Using the schematic diagram of a Hollow cathode lamp (HCL) state why for each element analyzed you need the HCL for the metal.



(10 marks)

- iv. Explain the role of potassium chloride (excess) added to the sample during Ca analysis using atomic absorption spectroscopy. (10 marks)