THE KENYA NATIONAL EXAMINATIONS COUNCIL

DIPLOMA IN ANALYTICAL CHEMISTRY

INSTRUMENTAL METHODS OF ANALYSIS

3 hours

INSTRUCTIONS TO CANDIDATES

You should have the following for this examination:
> *answer booklet;*
> *non-programmable scientific calculator.*

*This paper consists of **TWO** sections; A and B.*

*Answer **ALL** the questions in section A and any **THREE** questions from section B in the answer booklet provided.*

Each question in section A carries 4 marks while each question in section B carries 20 marks.

Maximum marks for each part of a question are as shown.

Candidates should answer the questions in English.

This paper consists of 6 printed pages.

Candidates should check the question paper to ascertain that
all the pages are printed as indicated and that no questions are missing.

## SECTION A (40 marks)

Answer ALL the questions in this section.

1. State **four** advantages of capillary columns over packed columns as used in GLC. (4 marks)

2. A 25.00 cm³ sample containing sodium produced a deflection signal of 32 units in a flame photometer. A second sample of an equal volume was spiked with 2.00 cm³ containing 5 mg of sodium and produced a deflection signal of 59 units. Calculate the concentration of sodium in the original sample in ppm. (4 marks)

3. The Golay infrared detector uses a phototube to generate the analytical signal, although infrared radiation has low energy which cannot excite electrons in a phototube. Explain this observation. (4 marks)

4. State **four** physical interferences encountered in AAS. (4 marks)

5. Two substances **A** and **B** have retention times of 12.8 and 7.4 minutes in an HPLC column. The dead time of the column is 1.3 minutes. Calculate the selectivity of the column. (4 marks)

6. Explain the effect of suspensions on absorbance in UV-Visible spectroscopy. (4 marks)

7. A 50.00 ppm solution of copper (II) sulphate has an absorbance of 0.8 in a colorimeter.

   (a) Calculate the instrumental sensitivity for copper (II) ions. (2 marks)

   (b) Describe how the sensitivity of a colorimeter for a given sample may be determined. (2 marks)

8. Explain why AAS does not suffer from spectral interferences. (4 marks)

9. (a) Calculate the theoretical number of IR absorption peaks for ethene molecule. (2 marks)

   (b) Explain the difference between the theoretical number of IR peaks in ethene molecule and the observed number of peaks in the IR spectrum of the compound. (2 marks)

10. (a) Explain how colorimetry may be used in analysis of colourless substances. (1 mark)

    (b) Explain the colorimetric advantage in (a) above. (1 mark)

    (c) State **one** condition for any colorimetric analysis. (1 mark)

    (d) State any other advantage of colorimetry other than the one explained in (b) above. (1 mark)

SECTION B (60 marks)

*Answer any **THREE** questions from this section.*

11. (a) One advantage of IR spectroscopy is structure elucidation of organic compounds. Describe how the structure of an organic compound may be obtained from its IR spectrum. (4 marks)

(b) Figure 1 shows the IR spectrum of an aliphatic organic compound with a molecular formula $C_6H_{12}O$. The compound gives a positive silver mirror test and has a boiling point of 129 ^{0}C. The compound is neutral to wet litmus paper. Use this information and the IR correlation table provided to propose a possible structure for the compound. (6 marks)

(c) Differentiate between Group and finger print regions of the IR spectrum of a compound. (6 marks)

(d) State **four** limitations of IR spectroscopy as a method of structure elucidation of organic compounds. (4 marks)

Wavenumber, cm⁻¹

Wavelength, μm
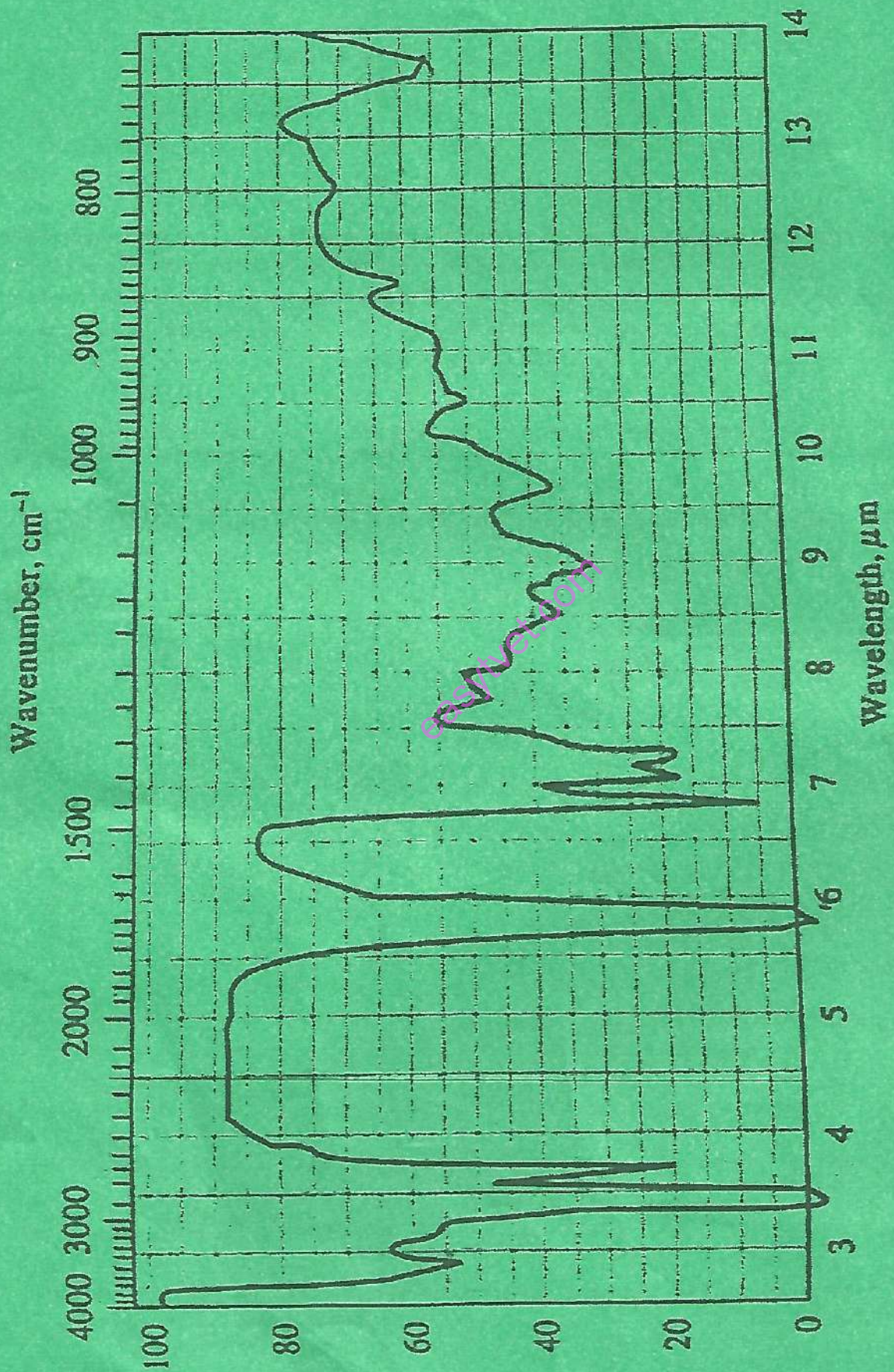
Fig. 1   Compound with molecular formula $C_6H_{12}O$

Table 1. Abbreviated Table of Group Frequencies for Organic Groups

Bond	Type of Compound	Frequency Range, cm⁻¹	Intensity
C—H	Alkanes	2850–2970	Strong
		1340–1470	Strong
C—H	Alkenes $\left(\!>\!C\!=\!C\!<^H\right)$	3010–3095	Medium
		675–995	Strong
C—H	Alkynes (—C≡C—H)	3300	Strong
C—H	Aromatic rings	3010–3100	Medium
		690–900	Strong
O—H	Monomeric alcohols, phenols	3590–3650	Variable
	Hydrogen-bonded alcohols, phenols	3200–3600	Variable, sometimes broad
	Monomeric carboxylic acids	3500–3650	Medium
	Hydrogen-bonded carboxylic acids	2500–2700	Broad
N—H	Amines, amides	3300–3500	Medium
C=C	Alkenes	1610–1680	Variable
C=C	Aromatic rings	1500–1600	Variable
C≡C	Alkynes	2100–2260	Variable
C—N	Amines, amides	1180–1360	Strong
C≡N	Nitriles	2210–2280	Strong
C—O	Alcohols, ethers, carboxylic acids, esters	1050–1300	Strong
C=O	Aldehydes, ketones, carboxylic acids, esters	1690–1760	Strong
NO₂	Nitro compounds	1500–1570	Strong

12. (a) The relative areas for five HPLC chromatographic peaks obtained in the separation of five steroids are given in table 2. The relative detector responses are also provided. Use this information to calculate the:

  (i) normalised peak area for each compound; (7 marks)

  (ii) percentage of each compound in the mixture. (10 marks)

 (b) Describe how the HPLC may be calibrated during the analyses in (a) above.

  (3 marks)

Table 2

Compound	Relative Peak Area (A)	Relative Detector Response (F)
Dehydro-epiandrosterone	27.6	0.70
Estradiol	32.4	0.72
Estrone	47.1	0.75
Testosterone	40.6	0.73
Estriol	27.3	0.78

13. (a) Draw a labelled diagram describing the gas chromatograph. (10 marks)

(b) (i) Name **three** detectors used in GLC. (3 marks)
(ii) Identify the most advantageous detector of the three named (i) above. (1 mark)
(iii) State **two** advantages of the detector identified in (ii) above. (2 marks)

(c) Explain the choice of the carrier gas in GLC. (3 marks)

(d) Name **two** gases used as carrier gases in GLC. (1 mark)

14. (a) Draw a labelled diagram describing a flame photometer. (11 marks)

(b) Outline the steps that lead to the production of analytical signal in FES. (9 marks)

15. (a) Explain the meaning of the statement 'absorbance is an additive property of matter' as used in UV-visible spectroscopy. (2 marks)

(b) A simultaneous determination for nickel and cobalt is based upon the absorption of their 8-hydroxyquinollinol complexes. Molar absorptivities corresponding to their absorption maxima are given in table 3.

Table 3

	Molar absorptivity ϵ	
	365 nm	700 nm
Co	3529	428.9
Ni	3228	10.2

(i) Explain the criteria used in selecting the wavelengths of analysis. (3 marks)

(ii) Calculate the molar concentrations of nickel and cobalt in a solution based on the absorption data in table 4. (15 marks)

Table 4

	Absorbance in 1.00 cm vial	
	365 nm	700 nm
Solution A	0.598	0.039

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