[Time: Three hours] **[Marks:80]**

Please check whether you have got the right question paper.

N.B.
1) All questions are compulsory
2) Figures to the right indicate full marks
3) Answer all sub questions together
4) Draw neat labelled diagram wherever necessary

Q.1 [A] Do as directed (Any eight) **(8)**

i. Define molecular ion peak in mass spectrum.
ii. Name a visualization technique used in TLC.
iii. Name a solute property detector used in HPLC chromatograph.
iv. Name a solvent suitable for use in ^{1}H-NMR spectroscopy.
v. Give an example of a cationic exchanger used in ion exchange chromatography.
vi. Give one important application of head space analysis.
vii. Define the term 'Accuracy' with respect to Analytical Method Validation.
viii Name a multicomponent analysis technique based on recording absorbances of sample in two different mediums/solvents.
ix Define retention time in chromatography.

Q.1 [B] Explain the following terms (Any three) **(6)**

i. Resolution in chromatography
ii. Precision
iii. Coupling constant
iv. Guard column in HPLC
v. Mass spectrum

Q.1 [C] Answer the following (Any two) **(6)**

i. Compounds X and Y were analysed on a 30 cm ODS column. Their retention times were 12.15 min and 20.5 min respectively. An unretained species passed through the column in 1.8 min. The peak width measured at the base were 0.45 min for X and 0.25 min for Y. Calculate the number of theoretical plates and HETP for compound X. indicate if this column is suitable for the analysis of X. Also calculate the resolution between X and Y.

ii. A fixed dose combination of three drugs A, B and C were analyzed by RP-HPLC, the log P of these were 3.5, 2.5 and 5.5 respectively. Predict their elution order and justify your answer. Indicate which of these is the most polar of the three drugs.

iii. A sample containing four compounds E, F, G and H was analysed on a RP-HPLC column of 25 cm. Their retention times were 2.05 min, 3.87 min, 12.52 min and 30 mins respectively. In this context answer the following questions.

- Suggest a means of increasing the retention time of 'H'without altering the mobile phase and the column.
- Predict what will happen if a shorter column is used.
- Indicate whether you will use isocratic/gradient mode of elution for the above separation, justify your answer.

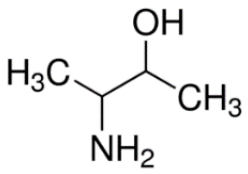
iv. A mixture of sample containing P, Q and R were separated on a normal phase TLC plate. The sample was applied at 1.0 cm from the bottom of plate. The distances measured from the point of sample application for P, Q and R were 2.5 cm, 5.5 cm and 7.0 cm respectively. The solvent front was recorded as 9 cm measured from the sample application point. Calculate the R_f values for P, Q and R and indicate the most polar compound of the three. Justify.

Q .2 Answer the following <u>(Any three)</u> (12)

[i] Enlist methods for multicomponent analysis by UV – Visible spectroscopy. Discuss any one in detail.

[ii] Predict the IR spectrum of the following compounds.

a) b)



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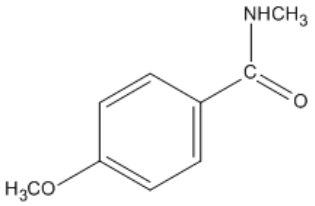
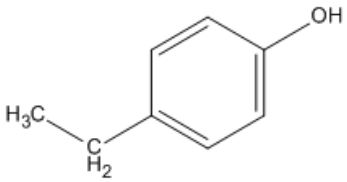


[iii] What do you understand by validation of analytical method? Illustrate how will you determine Limit of Detection (LOD) of a drug substance as per ICH guidelines.

[iv] Differentiate between the following using any suitable spectroscopy technique.



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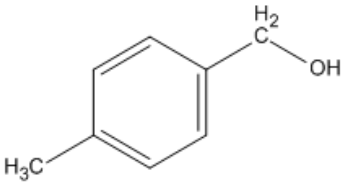


Q.3 [A] Answer the following <u>(Any three)</u> (12)

[i] Enlist the methods available for quantitative analysis in chromatography. Describe any one method in detail.

[ii] Enlist the different types of pumps used in HPLC. Explain with the help of a neat labelled diagram the construction and working of a reciprocating pump.

[iii] Give two points of difference between

a. HPLC and UPLC
b. HPTLC and HPLC

[iv] Illustrate the detectors used in GC. Describe the flame ionization detector, support your answer with a suitable diagram.

Q.4 **Answer the following (Any three)** **(12)**

[i] Discuss the development techniques used in paper chromatography. Give one specific application of paper chromatography.

[ii] Enlist the various components of a HPTLC instrument? Discuss sample application and detection in HPTLC.

[iii] Write a note on size exclusion chromatography highlighting the principle involved, stationary phases used and applications.

[iv] What do you understand by hyphenated techniques? Enlist interfaces in LC-MS. Describe any one in brief.

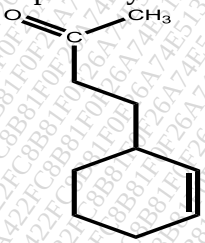
Q.5 **Answer the following (Any three)** **(12)**

[i] What is anisotropy in NMR? Depict the effect of anisotropy on chemical shift using two suitable examples.

[ii] How many peaks will be obtained in the ^1H NMR spectrum of ethyl methyl ketone. Give the approximate δ value and multiplicity of each peak.

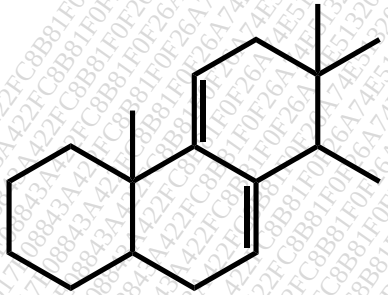
[iii] With the help of a block diagram, illustrate the basic components of a mass spectrometer. Explain the term tandem mass spectrometry.

[iv] Depict two mass fragmentation pathways for the compound given below.



Q.6 **Answer the following (Any three)** **(12)**

[i] Applying the principles of Woodward Feiser rules, predict the λ_{max} of the compound given below with appropriate justification.



[ii] A compound with molecular formula $C_6H_{12}O_2$ has the following spectral characteristics:

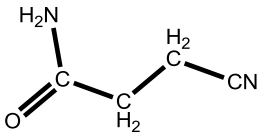
IR: 3500, 2990, 1715 cm^{-1}

^1H NMR:

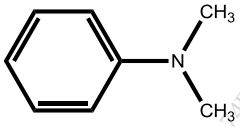
δ	Multiplicity	No. Of protons
1.25	s	6H
2.1	s	3H
2.6	s	2H
3.7	bs, D_2O exchangeable	1H

Deduce the structure and justify your answer

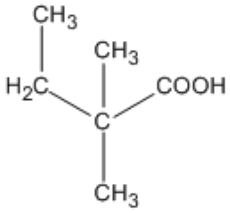
[iii] Predict the number of signals and the multiplicity of the signals in the ^1H NMR spectra of the following compounds.



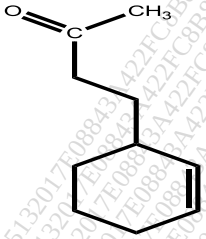
(a)



(b)



(c)



(d)

[iv] A compound with molecular formula $C_{10}H_{11}O_2Cl$ has the following spectral characteristics:
IR: 1745, 1600, 1500 cm^{-1}
^1H NMR

δ	Multiplicity	No. Of protons
2.0	s	3H
2.8	t	2H; J = 6Hz
4.1	t	2H, J = 6Hz
7.2	d	2H, J = 8Hz
7.3	d	2H, J = 8Hz

Deduce the structure and justify your answer

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