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57001

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Note:	Examiners can use their discretion for the correctness of answers besides the answers mentioned in the answer key	
Q.1.A.	Do as directed: (Any seven)	(7)
i.	Name any one mobile phase solvent which is used in RP-HPLC analysis Any polar solvent like methanol, water, CAN etc.	
ii.	Write the structure for molecular ion peak of ethanol, stating its m/z value $\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \overset{+}{\text{O}} - \text{H} \\ \text{(C}_2\text{H}_6\text{O)} \quad 24 + 6 + 16 = \boxed{46} \end{array}$	
iii.	Name a detector in HPLC that allows detection at different wavelength simultaneously Photo diode array detector	
iv.	Name any one mass analyser Any one mass analyse like Quadrupole ion filter, ion trap time of flight, time of flight etc.	
v.	Name the spectrometry technique that can distinguish different isotopes of an element- Mass spectrometry	
vi.	Name one reference standard used in $^1\text{H-NMR}$ spectroscopic analysis Tetra methyl silane	
vii.	Name any one spraying reagent used for visualisation of spots in TLC analysis Any suitable reagent like Dragendorff reagent, iodine in iodine chamber etc.	
viii.	Name any two types of columns used in gas chromatography Packed columns, capillary columns(Examples SCOT, WCOT,PLOT)	
Q.1.B.	Explain the following terms: (Any four)	(8)
i.	Chemical shift Formula, unit, factor affecting enlist 2M	
ii.	LOD in validation studies Limit of detection, formula to determine the same 2M	
iii.	Head space analysis Meaning, used in GC, residual solvent analysis 2M	
iv.	Fast atom bombardment technique Ionization technique in MS, soft ionization 2M	
v.	Internal standard – Used in Quantitative HPLC, Significance and concept of Area ratio 2M	

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Q.2.A.	Answer the following: (Any two)	(8)									
i.	With the help of suitable diagrams explain the working of reciprocating pump in HPLC Diagram 2 M, Explanation 2M										
ii.	Explain the principle of ion pair chromatography Principle 4M										
iii.	Enlist any four interfaces used in LC-MS. Explain any one interface in detail. Enlist 2M, Explanation 2M										
Q.2.B.	Two compounds 'A' and 'B' were analysed by RP-HPLC using a column of length 30 cm. The retention times of 'A' and 'B' were found to be 5.7 min and 6.9 min respectively. The peak widths measured at the base were 0.98 min and 1.0 min respectively. Calculate the number of theoretical plates for compound A. Justify whether the calculated number of theoretical plates can be accepted or not.	(3)									
	<table style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th></th> <th style="text-align: center;">R_t min</th> <th style="text-align: center;">W min</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">A</td> <td style="text-align: center;">5.7</td> <td style="text-align: center;">0.98</td> </tr> <tr> <td style="text-align: center;">B</td> <td style="text-align: center;">6.9</td> <td style="text-align: center;">1.0</td> </tr> </tbody> </table> $\begin{aligned} \text{No. of plates} &= 16 \left(\frac{R_t}{W} \right)^2 \\ &= 16 \left(\frac{5.7}{0.98} \right)^2 \\ &= 16 \left(\frac{32.49}{0.9604} \right) \\ &= 16 (33.8296) \\ &= \cancel{16}, 541.2736 \end{aligned}$ <p>Since number of plates are less this is not accepted.</p>		R_t min	W min	A	5.7	0.98	B	6.9	1.0	
	R_t min	W min									
A	5.7	0.98									
B	6.9	1.0									

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Q.3.A.	Answer the following: (Any two)	(8)
i.	With the help of an inverted tree diagram explain the formation of a quartet for CH ₂ protons of ethyl bromide. Quartet to be shown with the inverted tree diagram 4M Refer to the standard book	
ii.	<p> <chem>CH3-CH2-CH2-Cl</chem> and <chem>CH3-CH2-O-CH2-Cl</chem> </p> <p>1) NMR Spectroscopy</p> <div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> <p><chem>CH3-CH2-CH2-Cl</chem></p> <p>CH₃ CH₂ CH₂ Cl</p> <p>3 signal</p> <p>↓</p> <p>triplet 3H</p> <p>↓</p> <p>sextet 2H</p> <p>↓</p> <p>triplet 2H</p> </div> <div style="text-align: center;"> <p><chem>CH3-CH2-O-CH2-Cl</chem></p> <p>CH₃ CH₂ O CH₂ Cl</p> <p>triplet 3H</p> <p>quartet 2H</p> <p>singlet 2H</p> <p>3 signals</p> </div> </div> <p>2) Mass Spectrometry</p> <p><chem>CH3-CH2-CH2-Cl</chem> → <chem>CH3-CH2-CH2+</chem> C₃H₇ 43</p> <p><chem>CH3-CH2-O-CH2-Cl</chem> → <chem>CH3-CH2-O-CH2+</chem> C₃H₇O + Cl</p> <p style="margin-left: 100px;"> +36 +7 +16 <hr style="width: 50px; margin-left: 0;"/> 59 </p>	

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iii.	<p>Depict any two different types of fragmentation pathways for the following compound:</p> $\text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$ <p style="text-align: center;">+ O⁻ ↓ Fast moving electron.</p> $\text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$ <p style="text-align: center;">114</p> <p>1) α fission.</p> $\text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$ <p style="text-align: center;">+ O⁻ ↓</p> $\text{CH}_3 - \text{CH}_2 \cdot + \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$ <p style="text-align: center;">85</p> <p>2) McLafferty rearrangement.</p> $\text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$ <p style="text-align: center;">+ O⁻ ↓</p> $\text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \rightarrow \text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_2 + \text{CH}_2 = \text{CH} - \text{CH}_3$ <p style="text-align: center;">72</p>	<p style="text-align: right;">C₇H₁₄O C₇H₁₂O 72 + 84 72 + 14 16 + 16 <hr/>114</p> <p style="text-align: right;">C₅H₈O</p>
Q.3.B.	<p>With the help of diagram explain radial chromatographic technique in paper chromatography.</p> <p>Diagram 1M, Explanation 2M</p>	(3)
Q.4.A.	<p>Answer the following: (Any Two)</p>	(8)
i.	<p>Discuss electron impact method of ionization in mass spectrometry</p> <p>Diagram 1M, Explanation 3M</p>	
ii.	<p>Explain the effect of anisotropy on the chemical shift of alkene protons.</p> <p>Diagram 2M, Explanation 2 M</p>	

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iii.	Explain how precision studies for analytical method validation are carried out as described in ICH guidelines. Explanation 4M	
Q.4.B.	With the help of a diagram, explain the term asymmetry factor. Diagram 1M, Explain 2M	(3)
Q.5.A.	Answer the following: (Any Two)	(8)
i.	Discuss flame ionization detector used in gas chromatographic analysis. Complete explanation with the diagram 4M	
ii.	<p>Predict the structure of the following compound whose spectral characteristics are as follows:</p> <p>Molecular formula: C_7H_9N</p> <p>I.R. (cm^{-1}): 3433, 3350, 3034, 2900, 1300</p> <p>1H-NMR (δ-ppm) = 7.0-7.3 (m) (4H) 3.5 (s) (2H) 2.3 (s) (3H)</p> <p>Give appropriate justification for your answer.</p> <p>IHD = 4 1H NMR δ value at 7-7.3 ppm indicate presence of benzene ring.</p> <p>3433, 3350 primary amine 3034, aromatic C-H stretch 2900 C-H alkane stretch 1300 C-N stretch of amine</p> <p>assigned 4 benzene H CH CH₃</p> <p>neighbouring carbon with no H carbon with no H</p>	

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iii. Predict the structure of the following compound whose spectral characteristics are as follows: (Allylic coupling is ignored)

Molecular formula: $C_3H_6O_2$

I.R. (cm^{-1}): 3200-2800, 1670

1 H-NMR (δ -ppm) = 1.1 (t) (3H) - 6.5 Hz

2.3 (q) (2H) - 6.5 Hz

11.2 (broad s) (1H)

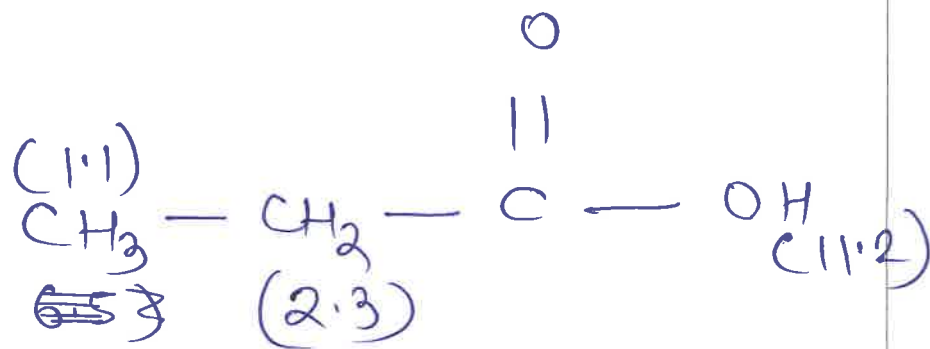
Give appropriate justification for your answer.

Assigned Neighbouring
 CH_3 $-CH_2$ same
 CH_2 $-CH_3$ J value
 $-OH$ carbm with no 'H' neighbour

$$IHD = \frac{2n+2 - no \text{ of } H}{2} = \frac{2(3)+2-6}{2} = \frac{2}{2} = 1$$

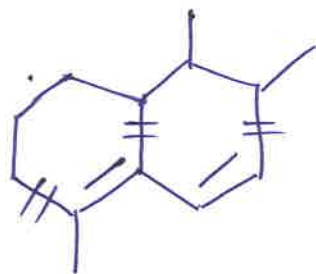
→ IR value of 1670 cm^{-1} indicate presence of $C=O$, and presence of oxygen in molecular formula confirm that.

→ 11.2 ppm NMR value indicates carboxylic acid $-OH$



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Q.5.B	Predict the λ_{\max} for the following compound showing UV absorbance:	(3)
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Parent diene 217 nm
 3 ring residues + 15 nm
 1 alkyl residue + 5 nm
 exocyclic double bond + 5 nm

 242 nm

Q.6.A.	Answer the following: (Any two)	(8)
i.	Explain the working of evaporative light scattering detector used in HPLC Explanation with diagram 4M	
ii.	Discuss any four factors affecting resolution in thin layer chromatography. Each factor 1 M x 4	
iii.	Explain multicomponent analysis by UV spectroscopy using Simultaneous equations method. Diagram, equation, explanation 4M	
Q.6.B.	Predict the positions of absorption bands in the IR spectra of the following compound:	(3)
	$\text{CH}_3 - \overset{\text{O}}{\underset{\text{ }}{\text{C}}} - \text{CH}_2 - \text{C} \equiv \text{C} - \text{CH}_3$ <p style="text-align: center;"> 1720 cm^{-1} 2200 cm^{-1} 2960 cm^{-1} </p> <p style="text-align: center;">nearby values can be considered.</p>	