



Seat No. _____

HN-003-028201

P. G. D. S. A. I. T. (Sem. II) Examination

April - 2023

**Advance Spectroscopic &
Thermal Methods of
Analysis for Pharma &
Chemical Products : Paper - 201**

Faculty Code : 003

Subject Code : 028201

Time : $2\frac{1}{2}$ Hours / Total Marks : 70

Instruction : All questions are compulsory and carry equal marks.

1 Answer the followings : (any **seven**) **14**

- (a) Define the terms: wavenumber and Frequency.
- (b) What is meant by (n+1) rule in spin-spin coupling in NMR?
- (c) Define the term: Base peak and Metastable ion.
- (d) How will you distinguish O-Nitrophenol and p-Nitrophenol using UV spectroscopy?
- (e) Write the application of DTA.
- (f) Write the strength and limitations of X-ray powder diffraction.
- (g) Explain TGA curve for Calcium oxalate.
- (h) How many peaks are obtained in CMR for o-xylene and p-chlorobenzoic acid.
- (i) write the full form of HMBC and COSY.
- (j) What is Hooks law in spectroscopy?

2 Answer the followings : (any **two**) **14**

- (a) Draw the block diagram of TGA and explain it in details.
- (b) Sketch the NMR spectrum of Ethyl benzene and explain splitting of each signal.
- (c) Discuss types of shift and bands in UV spectroscopy in details.

3 Answer the followings : **14**

- (a) Discuss Coupling constant in details in NAM spectroscopy.
- (b) Calculate the ^{13}C NMR value of each carbon of 2-butanol.

OR

3 Answer the followings : **14**

- (a) Draw the schematic diagram of IR Instrument and write its functioning.
- (b) Enlist the analyzer used in mass spectrometry, discuss any one of them in details.

4 Answer the followings : **14**

- (a) State the Principle of Mass spectrometry and also discuss the application of Mass spectroscopy.
- (b) How many types of electronic transition possible in Acetone and ethylene with respect to UV absorption.

5 Answer the followings : **14**

- (a) Discuss absorption due to carbonyl compound in UV spectroscopy in detail.
- (b) Write a brief account on Popal Notation with suitable example.
- (c) Explain Bragg's rule in p-XRD method.
- (d) Explain instrumentation of DSC.

Data Table of ¹³C NMR Exaples

TABLE 5.1

The ¹³ C Shift Parameters in Some Linear and Branched Hydrocarbons	
¹³ C Atoms	Shift (ppm) (A)
α	+9.1
β	+9.4
γ	-2.5
δ	+0.3
ε	+0.1
1° (3°)*	-1.1
1° (4°)*	-3.4
2° (3°)*	-2.5
2° (4°)	-7.2
3° (2°)	-3.7
3° (3°)	-9.5
4° (1°)	-1.5
4° (2°)	-8.4

*The notations 1° (3°) and 1° (4°) denote a CH₃ group bound to a R₂CH group and to a R₃C group, respectively. The notation 2° (3°) denotes a RCH₂ group bound to a R₂CH group, and so on.

TABLE 5.2

The ¹³ C Shifts for Some Linear and Branched Chain Alkanes (ppm from TMS)					
Compound	C-1	C-2	C-3	C-4	C-5
Methane	-2.3				
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2		
Pentane	13.9	22.8	34.7	22.8	13.9
Hexane	14.1	23.1	32.2	32.2	23.1
Heptane	14.1	23.2	32.6	29.7	32.6
Octane	14.2	23.2	32.6	29.9	29.9
Nonane	14.2	23.3	32.6	30.0	30.3
Decane	14.2	23.2	32.6	31.1	30.5
Isobutane	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Isohexane	22.7	28.0	42.0	20.9	14.3
Neopentane	31.7	28.1			
2,2-Dimethylbutane	29.1	30.6	36.9	8.9	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH ₃)	
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
2,3-Dimethylpentane	7.0	25.3	36.3	(14.6, 3-CH ₃)	

TABLE 5.3

Incremental Substituent Effects (ppm) on Replacement of H by Y in Alkanes. Y is Terminal or Internal* (+ downfield, - upfield)					
Terminal	Internal				
	α	β	γ		
Y	Terminal	Internal	Terminal	Internal	
CH ₃	+ 9	+ 6	+10	+ 8	-2
CH=CH ₂	+20		+ 6		-0.5
C≡CH	+ 4.5		+ 5.5		-3.5
COOH	+21	+16	+ 3	+ 2	-2
COO ⁻	+25	+20	+ 5	+ 3	-2
COOR	+20	+17	+ 3	+ 2	-2
COCl	+33	+28		+ 2	
CONH ₂	+22		+ 2.5		-0.5
COR	+30	+24	+ 1	+ 1	-2
CHO	+31		0		-2
Phenyl	+23	+17	+ 9	+ 7	-2
OH	+48	+41	+10	+ 8	-5
OR	+58	+51	+ 8	+ 5	-4
OCOR	+51	+45	+ 6	+ 5	-3
NH ₂	+29	+24	+11	+10	-5
NH ₃ ⁺	+26	+24	+ 8	+ 6	-5
NHR	+37	+31	+ 8	+ 6	-4
NR ₂	+42		+ 6		-3
NR ₃ ⁺	+31		+ 5		-7
NO ₂	+63	+57	+ 4	+ 4	
CN	+ 4	+ 1	+ 3	+ 3	-3
SH	+11	+11	+12	+11	-4
SR	+20		+ 7		-3
F	+68	+63	+ 9	+ 6	-4
Cl	+31	+32	+11	+10	-4
Br	+20	+25	+11	+10	-3
I	- 6	+ 4	+11	+12	-1

*Add these increments to the shift values of the appropriate carbon atom in Table 5.2 or to the shift value calculated from Table 5.1.

Source: F.W. Wehrli, A.P. Marchand, and S. Wehrli, *Interpretation of Carbon-13 NMR Spectra*, 2nd ed., London: Heyden, 1983.

TABLE 5.9

Substituent	C-1 (Attachment)	C-2	C-3	C-4	C of Substituent (ppm from TMS)
H	0.0	0.0	0.0	0.0	
CH ₃	9.3	+0.7	-0.1	-2.9	21.3
CH ₂ CH ₃	+15.6	-0.5	0.0	-2.6	29.2 (CH ₂), 15.8 (CH ₃)
CH(CH ₃) ₂	+20.1	-2.0	0.0	-2.5	34.4 (CH), 24.1 (CH ₃)
C(CH ₃) ₃	+22.2	-3.4	-0.4	-3.1	34.5 (C), 31.4 (CH ₃)
CH=CH ₂	+9.1	-2.4	+0.2	-0.5	137.1 (CH), 113.3 (CH ₂)
C≡CH	-5.8	+6.9	+0.1	+0.4	84.0 (C), 77.8 (CH)
C ₂ H ₅	+12.1	-1.8	-0.1	-1.6	
CH ₂ OH	+13.3	-0.8	-0.6	-0.4	64.5
CH ₂ OCCH ₃	+7.7	-0.0	-0.0	-0.0	20.7 (CH ₂), 66.1 (CH ₂), 170.5 (C=O)
OH	+26.6	-12.7	+1.6	-7.3	
OCH ₃	+31.4	-14.4	+1.0	-7.7	54.1
OC ₂ H ₅	+29.0	-9.4	+1.6	-5.3	
OCCH ₃	+22.4	-7.1	-0.4	-3.2	23.9 (CH ₂), 169.7 (C=O)
CH	+8.2	+1.2	+0.6	+5.8	192.0
CCH ₃	+7.8	-0.4	-0.4	+2.8	24.6 (CH ₂), 195.7 (C=O)
CC ₂ H ₅	+9.1	+1.5	-0.2	+3.8	196.4 (C=O)
CCF ₃	-5.6	+1.8	+0.7	+6.7	
COH	+2.9	+1.3	+0.4	+4.3	168.0
COCH ₃	+2.0	+1.2	-0.1	+4.8	51.0 (CH ₂), 166.8 (C=O) 168.5
CCl	+4.6	+2.9	+0.6	+7.0	
C≡N	-16.0	+3.6	+0.6	+4.3	119.5
NH ₂	+19.2	-12.4	+1.3	-9.5	
N(CH ₃) ₂	+22.4	-15.7	+0.8	-11.8	40.3
NHCCH ₃	+11.1	-9.9	+0.2	-5.6	
NO ₂	+19.6	-5.2	+0.9	+6.0	
N=C=O	+5.7	-3.6	+1.2	-2.8	129.5
F	+35.1	-14.3	+0.9	-4.5	
Cl	+6.4	+0.2	+1.0	-2.0	
Br	-5.4	+3.4	+2.2	-1.0	
I	-32.2	+9.9	+2.6	-7.3	
CF ₃	+2.6	-3.1	+0.4	+3.4	
SH	+2.3	+0.6	+0.2	-3.3	
SCH ₃	+10.2	-1.8	+0.4	-3.6	15.9
SO ₂ NH ₂	+15.3	-2.9	+0.4	+3.3	
Si(CH ₃) ₃	+13.4	+4.4	-1.1	-1.1	

*See D. E. Ewing, *Org. Magn. Reson.*, 12, 499 (1979) for chemical shifts of 709 monosubstituted benzenes.

Table 3.16 Influence of functional group X on the chemical shift positions (δ) of nearby carbons in alkene groups and benzene rings

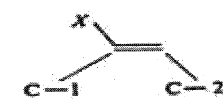
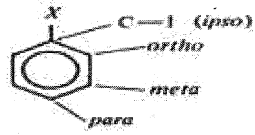

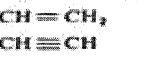
	Base values: ethylene (δ 123)		and benzene (δ 128)			
						
	Alkenes		Benzenes			
	C-1	C-2	C-1 (ipso)	ortho	meta	para
-CH ₃	10	-8	9	0	0	-2
R, 	16	-8	15	0	0	-2
R, 	23	-8	21	0	0	-2
-CH=CH ₂	15	-6	9	0	0	-2
-CH≡CH	-	-	-6	4	0	0
-C ₆ H ₅ , -Ar	13	-11	13	-1	1	-1
-F	25	-34	35	-14	1	-5
-Cl	3	-6	6	0	1	-2
-Br	-8	-1	-5	3	2	-2
-I	-38	7	-32	10	3	-1
-NH ₂	-	-	18	-13	1	-10
-NHR	-	-	20	-14	1	-10
-NR ₂	-	-	22	-16	1	-10
-NO ₂	22	-1	20	-5	1	6
-NHCOR, -NRCOR	-	-	10	-7	1	-4
-CN	-15	15	-16	4	1	6
-SH	-	-	4	1	1	-3
-OH	-	-	27	-13	1	-7
-OR	29	-39	30	-15	1	-8
-OCOR	18	-27	23	-6	1	-2
-COOH, -COOR, -CON<	4	9	2	2	0	5
-COR, -CHO	14	13	9	1	1	6
-SO ₃ H, -SO ₂ N<	-	-	16	0	0	4
-PMe ₂	-	-	14	1.6	0	-1
-PAr ₂	-	-	9	5	0	0

Table 3.15 Influence of functional group X on the chemical shift position (δ) of nearby carbons in alkane chains

$$X-C-C-C-C$$

$$\alpha \quad \beta \quad \gamma$$

X	α-shift			β-shift	γ-shift
	X-CH ₂ -	X-CH-	X-C-		
	1°	or 2°	3°		
-CH ₃	9	6	3	9	-3
-R: see table 3.11					
axial -CH ₃	1	-	-	5	-6
equatorial -CH ₃	6	-	-	9	0
(in cyclohexanes)					
-CH=CH ₂	22	16	12	7	-2
-C≡CH	4	-	-	3	-3
-C ₆ H ₅ , -Ar	23	17	11	10	-3
-F	70	-	-	8	-7
-Cl	31	35	42	10	-5
-Br	19	28	37	11	-4
-I	-7 to 20	-	-	11	-2
-NH ₂ , -NHR, -NR ₂	29	24	18	11	-4
-NO ₂	62	-	-	3	-5
-NHCOR, -NRCOR	10	-	-	0	0
-NH ₃ ⁺	25	-	-	7	-3
-CN	3	4	-	2	-3
-SH	2	-	-	2	-2
-OH	50	45	40	9	-3
-OR	50	24	17	10	-6
-OCOR	52	50	45	7	-6
-COOH, -COOR, -CON<	20	16	13	2	-3
-COR, -CHO	30	24	17	2	-3
-SO ₃ H, -SO ₂ N<	50	-	-	3	0

where A_n = characteristic value of the chemical shift of the observed C,
 which depends upon the number of H atoms (n) attached to it
 n = number of groups
 α = carbon atoms in the α -position
 γ = in γ and
 δ = in δ positions

The characteristic values of α , γ and δ C-atoms (i.e., A_n) to be used for the calculation depend upon the number of H atoms on the observed -C and are given in Table 3.23.

Example

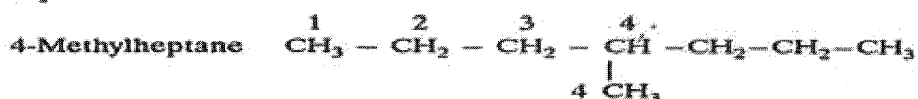


TABLE 3.23

Observed C	A_n	α	γ	δ
-CH ₃	6.80	CH ₃ 0 CH ₂ 9.56 CH 17.83 C 25.48	-2.99	0.49
-CH ₂ -	15.34	CH ₃ 0.0 CH ₂ 9.75 CH 16.70 C 21.43	-2.69	0.25
$\begin{array}{c} \\ -\text{CH} \\ \end{array}$	23.46	CH ₃ 0.0 CH ₂ 6.60 CH 11.14 C 14.70	-2.07	0.0
$\begin{array}{c} \\ -\text{C}- \\ \end{array}$	27.77	CH ₃ 0.0 CH ₂ 2.26 CH 3.96 C 7.35	0.86	0.0

Note: Methyl groups in α and all groups in β have no effect. Groups in γ position have negative or only slightly positive effect.

There are 5 groups of equivalent C-atoms.

$$\delta_C = A_n + n \alpha_{32} + n\gamma + n\delta \quad (\text{observed } \delta)$$

$$\delta_{(\text{CH}_3) \text{ C}_1} = 6.8 + 9.56 + (-2.99) + (2 \times 0.49) = 14.35 \text{ (qr)} \quad 14.35 \text{ (qr)}$$

$$\delta_{(\text{CH}_2) \text{ C}_2} = 15.34 + 9.75 + (2 \times (-2.69)) + 0.25 = 19.96 \text{ (tr)} \quad 19.96 \text{ (tr)}$$

$$\delta_{(\text{CH}_2) \text{ C}_3} = 15.34 + 9.75 + 16.70 + (-2.69) + 0.25 = 39.35 \text{ (tr)} \quad 39.35 \text{ (tr)}$$

$$\delta_{(\text{CH}) \text{ C}_4} = 23.46 + (2 \times 6.60) + (-2.07) = 34.59 \text{ (d)} \quad 34.59 \text{ (d)}$$

Table 3.13 δ values for the carbons in alkynes (sp)

REPRESENTATIVE ALKYNES		
acetylene (ethyne) $\text{CH}\equiv\text{CH}$ δ 72		
$\text{R}-\text{C}\equiv\text{CH}$	$\text{R}-\text{C}\equiv\text{C}-\text{R}'$	$\text{C}_6\text{H}_5-\text{C}\equiv\text{CH}$
83 66	82	83 78
$\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{R}$		$\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5$
86		90
EMPIRICAL PREDICTIONS FOR OTHER ALKYNE CARBONS		
Chemical shift (δ) = 72 + Σ (increments for carbon atoms)		
	$\text{C}-\text{C}-\text{C}-\text{C}-\text{C}\equiv\text{C}-\text{C}-\text{C}-\text{C}-\text{C}$ $\delta \quad \gamma \quad \beta \quad \alpha \quad \quad \alpha' \quad \beta' \quad \gamma' \quad \delta'$	
increments	+0.5 0 +5 +7	-6 +2 -1 +0.5
	base value 72	

Table 3.14 δ values for the carbons in aromatic and heterocyclic molecules (sp^2 and sp^3 carbons listed)

 benzene 128	 naphthalene 136 128 126	 anthracene 127 128 125	 phenanthrene 122 127 129 133 127																					
 tetralin 126 137 30 24 129	 indane 144 33 25 124 or 126	 acenaphthene 30 146 139 132 122 119 128	 acenaphthylene 129 138 124 128 127																					
 furan 111 144	 thiophene 127 125	 pyrrole 108 118	 pyridine 126 150																					
 tetrahydrofuran, THF 26 68	 tetrahydrothiophene 31 32	 pyrrolidine 26 47	 piperidine 26 27 48																					
 imidazole 122 136	 pyrazole 106 135	 GLUCOSE α -OH axial β -OH equatorial																						
		<table border="1"> <thead> <tr> <th></th> <th>C₁</th> <th>C₂</th> <th>C₃</th> <th>C₄</th> <th>C₅</th> <th>C₆</th> </tr> </thead> <tbody> <tr> <td>α-</td> <td>97</td> <td>75</td> <td>77</td> <td>70</td> <td>77</td> <td>62 38</td> </tr> <tr> <td>β-</td> <td>93</td> <td>72</td> <td>74</td> <td>70</td> <td>72</td> <td>62</td> </tr> </tbody> </table>			C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	α -	97	75	77	70	77	62 38	β -	93	72	74	70	72	62
	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆																		
α -	97	75	77	70	77	62 38																		
β -	93	72	74	70	72	62																		