SEMESTER –I

ANALYTICAL TECH&SPECTROSCOPY - I

THEORY

Programme: M.Sc. **Max.Hours: 60**
Course Code: P20/CHE/DSC/104 **Hours per week: 4**
Type of course: DSC -4 **Max.Marks: 100**
No. of Credits : 4

Course Objectives:

- The objective is to learn principles and applications of various Chromatographic techniques.
- Nuclear Magnetic Resonance spectroscopy is a powerful and theoretically complex analytical tool, to develop the understanding of number, positions, intensities and splitting of signals.
- Infrared spectroscopy, an analytical technique that takes advantage of the vibrational transitions of a molecule for identifying functional groups of organic compounds.
- UV-Vis spectroscopy is used in analytical chemistry for quantitative determination of different analytes such as transition metal ions and conjugated organic compounds.

Course Outcome:

CO1: Discuss the techniques of chromatography and quantification of HPLC and GC Methods.

CO2: Explain the principle of 1H NMR spectroscopy, instrumentation, chemical shifts, Factors affecting them, signal integration, Spin-spin coupling, Coupling constants and factors affecting them and applications of 1H NMR spectroscopy.

CO3: Explain the principles of Rotational spectroscopy and calculate bond lengths andatomic mass from rotational spectra of diatomic molecules, Isotope effect on rotationalspectra

CO4: Explain the principles of Vibrational spectroscopy, an harmonic nature of vibrations , Stereo chemical effects on the absorption pattern and Isotope effect on vibrationalspectra

CO5: Discuss the Classical and Quantum theories of Raman effect.

CO6: Explain the principles of Ultraviolet/Visible Spectroscopy, Woodward-Fieserrulesand their applications

MODULE I - TECHNIQUES OF CHROMATOGRAPHY: (15 Hrs)

i. Introduction, Classification of chromatographic techniques, differential migration rates, partition ratio, retention time, relation between partition ratio and retention time, capacity factor, selectivity factor. Efficiency of separation- resolution, diffusion, plate theory and rate theory.

ii. **GC:** Principle, instrumentation, detectors- TCD, FID, ECD. Derivatisation techniques, PTGC.

iii. **HPLC:** Principle, instrumentation, detectors- UV detectors, Photodiode array detector, fluorescence detector.

iv. **Applications:** Methods of quantitation for GC and HPLC: GC analysis of hydrocarbons in a mixture, GC assay of methyl testosterone in tablets, atropine in eye drops. HPLC Assay of Paracetamol and Aspirin in tablets.

MODULE II - NMR SPECTROSCOPY-I (^{1}H NMR) (15 Hrs)

^{1}H NMR spectroscopy: Magnetic properties of nuclei, Principles of NMR Instrumentation, CW and pulsed FT instrumentation, equivalent and non equivalent protons, enantiotopic and diastereotopic protons, Chemical shifts, factors affecting the chemical shifts, electronegativity and anisotropy, shielding and deshielding effects, Signal integration, Spin-spin coupling: vicinal, germinal and long range, Coupling constants and factors affecting coupling constants.
Applications of 1H NMR spectroscopy: Reaction mechanisms (cyclic bromonium ion, electrophilic and nucleophilic substitutions, carbocations and carbanions), E, Z isomers, conformation of cyclohexane and decalins, keto-enoltautomerism, hydrogen bonding, proton exchange processes (alcohols, amines and carboxylic acids), C-N rotation. Magnetic resonance imaging (MRI). 1H NMR of organic molecules and metal complexes: ethyl acetate, 2- butanone, mesitylene, paracetamol, asprin, ethylbenzoate, benzyl acetate, 2-Chloropropionic acid, [HNi(OPEt3)4]+, [HRh(CN)5] (Rh I=1/2), [Pt(acac)2].

MODULEIII - ROTATIONAL,VIBRATIONAL AND RAMAN SPECTROSCOPY (15 Hrs)

a) **Microwave Spectroscopy:** Classification of molecules based on moment of inertia. Diatomic molecule as rigid rotator and its rotational energy levels. Selection rules (derivation not required). Calculation of bond lengths from rotational spectra of diatomic molecules.Isotope effect on rotational spectra.Calculation of atomic mass from rotational spectra.Brief description of microwave spectrometer.

b) **Vibrational Spectroscopy**. Vibrational energy levels of diatomic molecules, selection rules (derivation not required). Calculation force constant from vibrational frequency. Anharmonic

nature of vibrations.Fundamental bands, overtones and hot bands, Fermi Resonance.Vibrationrotation spectra diatomic molecules.Vibrations of poly atomic molecules.Normal modes of vibration, concept of group frequencies.Characteristics of vibrational frequencies of functional groups; Stereochemical effects on the absorption pattern in carbonyl group, cis-trans isomerism and hydrogen bonding.Isotopic effect on group frequency. IR spectra of metal coordinated $NO^{3-,}$ $SO4^{2-}$ and $CO3^{2-}$ ions.

c) Raman Spectroscopy- Classical and Quantum theories of Raman effect. Rotational Raman and Vibrational Raman spectra, Stokes and anti- Stokes lines.Complementary nature of IR and Raman spectra.

MODULE IV - ELECTRONIC SPECTROSCOPY (15 Hrs)

Electronic spectroscopy: Electronic spectra: Elementary energy levels of molecules-selection rules for electronic spectra; types of electronic transitions in molecules. Chromophores: Congugateddienes, trienes and polyenes, unsaturated carbonyl compounds, Benzene, mono substituted derivative (Ph-R), di substituted derivative ($R\text{-}C_6H_4\text{-}R'$) and substituted benzene derivatives ($R\text{-}C_6H_4\text{-}COR'$), Woodward-Fieser rules. Polynuclear aromatic compounds (Biphenyl, stilbene, naphthalene, anthracene, phenanthrene and pyrene). Heterocyclic systems. Absorption spectra of charge transfer complexes. Solvent and structural influences on absorption maxima, stereochemicalfactors.Cis-trans isomers, and cross conjugation.Beer's law application to mixture analysis and dissociation constant of a weak acid.

Reference Books:

1. Banwell and McCash.Fundamentals of Molecular Spectroscopy.
2. Barrow, G.M.Introduction to Molecular Spectroscopy.
3. Dyer,J.R. Absorption Spectroscopy of Organic Compounds.
4. Hames and Hooper. Biochemistry.
5. Pavia LampmanKriz. Introduction to Spectroscopy.
6. Watson. Pharmaceutical analysis.
7. William Kemp.NMR in Chemistry- A multinuclear introduction.
8. William Kemp. Organic Spectroscopy.
9. Kalsi, P.S. Spectroscopy of organic compounds.
10. Ebsworth, .E.A.V.Structural methods n Inorganic chemistry.
11. Yadav,L.D.S.Organic Spectroscopy.
12. Sharma,Y.R.Organic Spectroscopy.
13. Arhuldas. Molecular Spectroscopy.
14. Satyanarayana,D.N.Vibrational spectroscopy.

SEMESTER -I

ANALYTICAL TECHNIQUES & SPECTROSCOPY-I

THEORY MODEL PAPER

Course Code: P20/CHE/DSC/104 **Max Time: 2½ Hrs**
Credits:4 **Max Marks: 60**

SECTION-A

IAnswer the following Questions **4 x 10 = 40 M**

1. (a) Write the basic functioning of HPLC system? (CO1)

(b) Explain the principle of gas chromatographic technique? (CO1)

OR

2. (a) Briefly explain the classification of chromatographic techniques? (CO1)

(b) Explain the types of detectors in GC technique? (CO1)

3. (a) What is a chemical shift? Explain factors that influence chemical shift with suitable examples. (CO2)

(b) With the help of an example explain how NMR spectroscopy can be used to study C-N rotation. (CO2)

OR

4. (a) Write about the anisotropic effect of alkenes and alkynes. (CO2)

(b) What is spin-spin coupling? Explain germinal, vicinal and long range couplings with suitable examples. (CO2)

5. (a) Explain complementary nature of IR and Raman spectra. (CO5)

(b) Describe the isotopic effects on rotational spectra? (CO3)

OR

6. (a) Explain the following i) Fundamental bands ii) Overtones iii) Hot bands (CO4)

(b)How do you distinguish the inter and intra molecular hydrogen bonding by IR spectra (CO3)

7. (a) What are charge transfer complexes? Discuss their study by spectroscopic Techniques(CO6)
(b) Write the polar and non-polar solvent effect in electronic absorption spectra?(CO6)

OR

8 . (a) Write the applications of electronic spectra of metal complexes- "$3d^1$ and $3d^9$hexaaquo metal complexes. (CO6)
(b) Explain the Woodward Fieser rules? (CO6)

SECTION –B

II. Answer any <u>FIVE</u> **5 x 4 = 20 M**

9. Describe a photodiode detector used in HPLC? (CO1)

10. Write the different methods of gas chromatographic technique? (CO1)

11. How is PMR useful in the study of reaction mechanism involving carbocation. (CO2)

12. Draw the ^{1}HNMR spectrum of 2-butanone and explain. (CO2)

13. How many fundamental vibrational frequencies can be observed in the infrared absorption spectrum of H_2O and CO_2(CO4)

14. How do you distinguish Cis-trans isomers by IR spectroscopy? (CO3)

15. Write a note on the following:
(i) Hypochromic shift (ii) Beer's law of absorption to mixture analysis (CO6)

16. Write the selection rules of electronic spectra? (CO6)