SEMESTER –II

ANALYTICAL TECH & SPECTROSCOPY-II

THEORY

Programme: M.Sc. **Max.Hours 60**
Course Code: P20/CHE/DSC/204 **Hours per week:4**
Type of course: DSC – 8 **Max.marks:100**
No. of credits: 4

COURSE OBJECTIVES:

- The unit covers introduction of Basic and Advanced Electro-analytical techniques like Conductometry, Potentiometry and Introduction and Applications of Polarography, Cyclic Voltammetry etc.
- NMR II study is aimed at different spin systems in organic compounds, basics and applications of Heteronuclear NMR and introduction of Solid state NMR along with experimental methods of simplifying complex spectra.
- Application of Mass Spectroscopy to determine fragmentation, Molecular weight determination, and also introducing to advanced mass spectroscopic techniques like FAB, SIMS, MALDI etc.
- Electron Spin Resonance outlines the fundamental principles of systems containing unpaired electrons like Free radicals and Transition Metal complexes.
- Photoelectron Spectroscopy or ESCA gives the understanding of Principles and Applications for Metal ions and complexes using their Binding energies and Chemical shift values.

COURSE OUTCOMES:

CO1: Explain the instrumentation, types of currents and applications of DCpolarography in qualitative and quantitative analysis.

CO2: Give a brief account of (i) A.C.polarography (ii) Square-wave polarography (iii) Pulse polarography (iv) Differential pulse polarography and discuss their advantages over conventionald.c.polargraphy.

CO3: Discuss the principle, instrumentation, types and applications of amperometric titrations and Cyclic Voltammetry.

CO4: Give a brief account of the different types of thermo analytical methods.

CO5: Discuss the principles and applications of thermogravimetry, differential thermal Analysis and Differential scanning calorimetry.

CO6: Discuss the principles, chemical shifts, coupling constants, and application of 1H, 19F, 31P and solid state NMR spectroscopy.

CO7: Discuss the Principles and instrumentation of different types of mass spectrometer
CO8: Outline Salient features of fragmentation pattern of organic compounds
CO9: Discuss the Principle and Instrumentation of Photoelectron Spectroscopy, of Vibrational spectral data for ionized (M+) species.
CO10: Discuss principle, instrumentation of Electron Spin Resonance spectroscopy and its applications.

MODULE 1: ELECTRO AND THERMAL ANALYTICAL TECHNIQUES: (15Hrs)

I: Types and Classification of Electro analytical Methods:

a) D.C Polarography:. Instrumentation - Dropping mercury electrode- -polarogram. Types of Currents: Residual, Migration, Limiting. Two and Three electrode assemblies.Ilkovic equation (derivation not necessary) and its consequences.Applications of polarography in qualitative and quantitative analysis.Analysis of mixtures.Application to inorganic and organic compounds.Determination of stability constants of complexes.

b) Brief account of following techniques and their advantages over conventional d.c.polargraphy.

(i) A.C.polarography (ii) Square-wave polarography (iii) Pulse polarography (iv) Differential pulse polarography

c) Amperometric titrations: Principle, Instrumentation. Types and applications of amperometric titrations. Determination of SO42-, metal ions viz., Mg2+, Zn2+, Cu2+ and other substances.

d) Cyclic Voltammetry: Principle, instrumentation, Applications. Cyclic voltammetric study of insecticide parathion.

II: Thermal Analysis: Thermal techniques-Introduction, types of thermo analytical methods. Thermogravimetry principle and applications of thermogravimetry, differential thermal analysis- principle and applications of DTA.Differential scanning calorimetry. DSC: Principle, and application of DSC.

MODULE 2: NMR SPECTROSCOPY-II(^{1}H,^{19}FAND^{31}PNMR) (15 Hrs)

1H,19F,31PandsolidstateNMRspectroscopy:Firstorderandnonfirstorderspectrae.g., AX,AX2,AX3,A2X3,AMXandAB,ABC.Simplificationofcomplexspectra:increasedfield strength,deuteriumexchange,Lanthanideshiftreagentsanddoubleresonancetechniques. DiscriminationofenantiomersbyuseofchiralNMRsolvents(CSAs),chirallanthanideshift reagentsandMosher'sacid.NuclearOverhauserenhancement(NOE).Fluxional moleculesbullvalene, [η5-C5H5M],[η5-(C5H5)2Tiη1-(C5H5)2]and [η4C8H8Ru(CO)3]. 19FNMR spectroscopy:19Fchemical shifts, couplingconstants. Applications of19FNMR involvingcouplingwith19F,1Hand31P:1,2dichloro-1,1difluoroethane,BrF5,SF4,PF5, ClF3,IF5, CF3CH2OH31P NMR spectroscopy:31P chemical shifts, couplingconstants. Applications of31PNMR involvingcouplingwith31P,19F,1Hand13C:ATP,Ph3PSe,P4S3,H3PO4,H3PO3,H3PO2, HPF2, PF6-, PH3, [Rh (PPh3)Cl3] (Rh I=1/2)
IntroductiontosolidstateNMR:Magicanglespinning(MAS).ApplicationsofsolidstateNMR

MODULE 3: MASS SPECTROMETRY: (15 Hrs)

Origin of mass spectrum, principles of EI mass spectrometer. Types of fragments: odd electron and even electron containing neutral and charged species (even electron rule), Nitrogen rule, isotopic peaks, determination of molecular formula, metastable ion peaks. High resolution mass spectrometry. Salient features of fragmentation pattern of organic compounds including β-cleavage, Mclafferty rearrangement, retro Diels – Alder fragmentation and ortho effect. Principle of EI, CI, Fast Atom Bombardment (FAB),

Secondary Ion Mass Spectrometry (SIMS), Electrospray (ESI) ionization and Matrix Assisted Laser Desorption Ionization (MALDI) methods. Introduction to principle and applications of Gas Chromatography-Mass Spectrometry (GC-MS) and Liquid chromatography-Mass Spectrometry (LC-MS) techniques.

MODULE4: PHOTOELECTRON&ESRSPRECTROSCOPY: (15Hrs)

Photoelectron Spectroscopy

Principle and Instrumentation, Types of Photoelectron Spectroscopy – UPS & XPS. Binding Energies, Koopman's Theorem, Chemical Shifts. Photoelectron Spectra of Simple Molecules: N_2, O_2, F_2, - Vibrational Structure of PES Bands, Potential energy curves, Interpretation of Vibrational spectral data for ionized (M+) species, Prediction of Nature of Molecular Orbitals. ESCA in qualitative analysis, Principles of Auger electron spectroscopy.

Electron Spin Resonance

Introduction, principle, instrumentation, selection rules, interpretation of Lande's factor 'g'. Hyperfine and super hyperfine Coupling. Anisotropy in 'g' values and hyperfine coupling constants. Zero field splitting, Kramer's degeneracy and quadrupolar interactions.
Study of free radicals and transition metal complexes. Evidence for covalency in complexes, Ex.:-Cu(II) Bis -salcylaldimine, Bis-acetylacetanatovanadyl(II) and hexachloroiridium(IV) complexes.

References Books:

1. Spectroscopic identification of organic compounds by R.M. Silverstein and F.X. Webster.
2. Organic spectroscopy by William Kemp
3. Mass Spectrometry for Chemists and biochemists by M. Rose and R.A. W. Johnstone
4. Spectroscopic methods in organic chemistry by D.H. Williams and I. Fleming
5. Practical Pharmaceutical Chemistry by A. H. Beckett and J.B. Stenlake
6. Biological Mass Spectrometry by A.L. Burlingame
7. Principles and Practice of Biological Mass Spectrometry by Chhabil Das
8. Spectrscopic identification of organic compounds by R.M.Silverstein. G.C.Bassler and T.E.Morrill
9. NMR-A multinuclear introduction by William Kemp
10. Stereochemistry of Carbon compounds by Ernest L Eliel / Samuel H. Wilen
11. Principles of Polarography, Heyrovsky.
12. Principles of Polarography, Kapoor.
13. Modern Electroanalytical methods, edited by C.Charlot, Elsevier Company.
14. Principles of Instyrumental analysis, Skoog, Holler and Nieman, Harcourt Asia PTE Ltd.
15. Analytical Chemistry-An Introduction, Skoog, West, Holler and Crouch, Saunders College Publishing.
16. Prinicples of Instrumental Analysis, Skoog and Leary, Saunders College Publishing.
17. International series of Monographs, Vol. **53**: Photoelectron Spectroscopy, Edited by D. Beckerand D. Betteridge 1972.
18. Structural methods in inorganic chemistry, E.A.V. Ebsworth

SEMESTER –II

ANALYTICAL TECHNIQUES & SPECTROSCOPY-II

THEORY MODEL PAPER

COURSE CODE: P20/CHE/DSC/204 **Time:2 ½ Hours**
No. Of Credits: 4 **Max Marks: 60**

SECTION-A

I Answer the following **4 x 10 = 40 M**

1. a) Explain the principle of cyclic voltammetry and describe the cyclic-Voltammogram of insecticide parathion (CO3)
   b) Write the principle and application of DTA. (CO4)

OR

2. a) Explain The Principle Of TGA With Examples And Its Applications. (CO5)
   b) Write A Short Note On Pulse Polarography And Square Wave Polarography**.**(CO2)

3. a) Predict The ^{1}h Nmr Spectra Of Amx And Abc Type**.** (Co6)

   b) What Is Noe? Discuss Any Two Of Its Applications. (Co6)

OR

4. a) Explain the simplification of NMR spectra by any two instrumental techniques with one example each. (CO6)
   b) Discuss the applications ^{19}F NMR. (CO6)

5. a) Explain Mclafferty rearrangement using a suitable example (CO8)
   b) Write notes on the mass fragmentation pattern of carbonyl compounds. (CO8)

OR

6. a) Write the principle and applications involved in GC –MS (CO7)
   b) What is Ortho effect and how is it useful in mass spectrometry? (CO7)

7. a)What is Hyperfine splitting? Give the importance of ‘g’ (Lande) factor in ESR.**(CO9)**
   b) Give the salient features of the ESR spectrum of Cu(II)BisSalicylaldimine. (CO10)

OR

8. a) Write short notes on Auger electron spectroscopy. (CO9)

   b) Explain Koopmans theorem.(CO9**)**

SECTION-B

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

9. What is the role of DME in polarography explain with diagram. **(CO1)**

10. Explain different types of Amperometric titration with suitable examples.**(CO3)**

11. What are lanthanide shift reagents? How are they useful in ^{1}HNMR spectroscopy? **(CO6)**

12. What is Magic angle spinning Explain its importance? **(CO6)**

13. Discuss the Retro-Diels-Alder fragmentation pattern with examples. **(CO8)**

14. Write about ESI and MALDI **(CO7)**

15. Describe the principle involved in the XPS/ESCA analysis. **(CO9)**

16. Explain Kramer's degeneracy with an example**(CO10)**