MANGALORE UNIVERSITY
Department of Post-graduate Studies and Research in Chemistry

Ph. D. Degree Programme in Chemistry

The Course Work: The Course Pattern and the Scheme of Examination.

1. The course work shall be of the following pattern. The course contents/ syllabi of papers 1 to 3 shall be decided by the concerned Board of Studies.

Papers	Particulars	Hours of Instruction per week	Duration of Exam.(hrs)	Marks			Credits
				IA	Exam	Total	
Paper 1	Research Methodology	4	3	30	70	100	4
Paper 2	Theoretical Foundations	4	3	30	70	100	4
Paper 3	Recent Developments	4	3	30	70	100	4
Paper 4	Reviewing of Literature and Planning of the Proposed Research Work with a TentativeTitle	16				200	8
						Total	20

2. Thesis on a chosen topic.

The PG BOS in Chemistry proposes the following Course Work for the Ph.D. Programme

i) Paper 1, CH 601: Research Methodology

ii) Paper 2, CH 602: Theoretical Foundations in Chemistry

iii) Paper 3: Recent Developments in one of the following Courses

a) CH 611: Co-ordination Chemistry

b) CH 612: Analytical & Structural Chemistry

c) CH 621: Heterocyclic & Medicinal Chemistry

d) CH 631: Physical Organic & Structural Chemistry

e) CH 632: Electrochemistry

f) CH 633: Polymer Chemistry

iv) Paper 4, CH 651: Reviewing of Literature and Planning of the Proposed Research Work with a Tentative Title

The contents of the papers prepared and approved are as follows

CH 601: Research Methodology

UNIT – I [14 hrs]

Scope of research in chemistry, types of research – basic and applied, frontier areas of research in chemistry, interdisciplinary research, outstanding discoveries and Noble prizes in chemistry during the last two decades. Choosing problem for research consistent with fields of research interests of the students and guide-literature study by a systematic reference work involving the use of books, monographs, periodicals, abstracts, documents, reviews, reports, conference proceedings, patents and dissertations, under the supervision of guide – on-line acquisition of literature (e-journals)

UNIT – II [14 hrs]

Research Problem- Identification, statement of research problem, objectives, design and execution of experiments, collection and interpretation of experimental data, arriving at conclusions. Reporting the results of research – style and format – title, abstract, the text, references, tables, figures, elucidations, quotations and footnote. Writing of research papers and dissertations.

UNIT – III [14 hrs]

Errors and analysis of experimental data – classification of errors – errors in observation, accidental and systematic errors. Significant figures and computation, statistical treatment of errors – curve fitting and regression analysis – tests of statistical significance 7 hrs.

General awareness of computer hardware, CPU, computer memory, I/O devices, information storage, software components, Types of computers, application of computers, programming languages, computer program's, stored program concept, operating systems, DOS and its use, Algorithm, program flow charts. 7 hrs.

UNIT – IV [14 hrs]

Introduction to computer applications and programming in chemistry

Applications of computers in chemistry, Programming examples and use of software packages in chemistry 6 hrs.

Chemical Education: Popularization of science education. Social and educational applications of chemical knowledge. 4 hrs.

The changing face of chemistry: Identification and development of key concepts in chemistry. Preparation of audio-visuals for teaching chemistry 4 hrs.

Reference:

1J. Anderson, Durston and Poole, Thesis and Assignment Writing, Wiley Eastern, 1977
2. A.M. Heiss: Challenge to graduate students, Jossey Bass Inc.
3. J. Topping: Errors of observation and their treatment, Champan and Hall (1972)
4. I.N. Gibra: Probability and Stastistical inference for scientist, prentice Hall (1973)
5. K.V.Raman: Computer in chemistry, TMH N. Delhi (1993)
6. P.N. Arora: Programming with basic for computers, Chand and Co., N. Delhi (1987)
7. Ramkumar: Programming with Fortran – 77 Tata – MeGraw Hill, New Delhi (1989)
8. V. Rajaraman: Computer Progamming in Fortun IV, V. Prentice Hall, N. Delhi (1987)
9. Chemical Abstracts, Monographs and Internet Services.

CH 602: Theoretical Foundations in Chemistry

Unit – I: Molecular Symmetry and Group Theory:

Molecular Symmetry – symmetry elements and operations

Group theory – Concept of a group, definition of point group. Classification of molecules. Group multiplication tables. Matrix representations of symmetry operations, class similarity transformation, reducible and irreducible representations. The great Orthogonality theorem. Character tables, relationship between representations and wave functions. Group theory and hybrid orbitals. Group theory and MO's. Molecular vibrations – Symmetry types of normal modes of vibrations. Selection rules for fundamental vibrational transitions, symmetry considerations to determine IR active and Raman active lines . [7 hrs]

Infrared and Raman Spectroscopy– Theories and instrumentation, Stretching and bending vibrations, Characteristic group frequencies and their dependence on chemical environment. **UV and Visible Spectroscopy** – Principles, instrumentation and applications. 7 hrs.

UNIT - II [14 hrs]

Resonance Spectroscopy: Nuclear Magnetic resonance – Principles and applications in structure elucidations. Instrumentation, FT NMR. EPR and its applications. 5 Hrs.

Electron spin resonance – Principles, instrumentation and sampling. ESR of organic free radicals in solution, inorganic radicals and transition metals. 3 Hrs.

Mass Spectrometry – Principles, instrumentation, interpretation of mass spectra, fragmentation processes. Techniques of ionization,Maldi mass. 2 Hrs.

Chromatographic Methods: Principles and applications of column, paper, thin layer chromatographic techniques. HPLC GC, GCMS and LCMS 2 Hrs.

Thermal Analysis – TG, DTA and DSC – Principles and applications 2 Hrs.

UNIT – III: [14 hrs]

Composite problems involving the applications of UV, IR, proton and C-13 NMR and mass spectroscopic techniques. Structural elucidation of organic molecules. 6 Hrs.

Reagents and Reaction Mechanisms: Classification of reagent and reactions, nucleophilic, electrophilic substitution reactions, Reactions involving carbonium ions. Carbanions, free radicals, carbenes and nitrenes. Methods of determining reaction mechanisms, kinetic and non-kinetic methods, mechanisms of oxidation – reduction reactions and some important named reactions in organic chemistry 5 Hrs.

Asymmetric Synthesis: The chiral pool, α-amino acids in the synthesis of benzodiazepines, carbohydrates, preparation of tomolal from D-mannitol, Felion-Ahn model and Cram's chelation control 3 hrs.

UNIT – IV: Thermodynamics, Kinetics and Catalysis [14 hrs]

Entropy and Free energy concepts, concepts and terminology in kinetics, time scales, techniques of measurements of concentrations – conventional and fast techniques. Empirical rate equations - methods of determining rate laws. Transition state theory and its pplication to reactions in solution. Activation parameters and their uses. Potential Energy surfaces and their applications. Effect of substituents, LFER, kinetic isotopic effect. Homogeneous & heterogeneous catalysis-mechanism of surface reactions.

REFERENCES:

1.V. Ramkrishnan and M.S. Gopinanthan: Group theory in Chemistry, Vishal (1988)

2. F. A. Cotton: Chemical Applications of Group theory, Wiley, New York (1993)
3..C. N. Banwell: Fundamentals of Molecular Spectroscopy, Tata MeGraw Hill, 1997
4. Willard, Meritt and Dean: Instrumental Methods of Analysis, MeGraw Hill (1993)
5. R. S. Drago: Physical Methods in Inorganic Chemistry, Affiliated East-West (1977)
6. P. S. Kalsi: Organic Spectroscopy, Wiley Eastern New Delhi (1990)
7. F. W. McLafferty, W.A. Benjamin Meulo: Interpretation of Mass Spectroscopy, 2nd ed
8. R. M. Silverstein, G.C. Bassler and T.C. Monnill: Spectrometric Identification of Organic Compound, Wiley (1991)
9. W. Kemp: Organic Spectroscopy, ELBS, Mac Millan (1991)
10. E. A. Edsworth, David W.H. Rankin and Stephen Cradock: Structural Methods in Inorganic Chemistry, Blackwell Scientific Publications, London, (1991)
11. D.A. Skoog and D.M. West: Principles of Instrumental Analysis, Saunders (1980)
12. Concepts and Models in Inorganic Chemistry- Douglas, Alexander & McDaniel, Wiley (2001).
13. Comprehensive Inorganic Chemistry – Ed. J C Bailar, Pergamon Press, 1982
14. Advanced Organic Chemistry – J March , Wiley
15. Stereochemistry of Organic Compounds – Nasipuri, New Age International.
16. Organic Chemistry – Clayden, Greeves, Warren & P Wotehrs – Oxford Univ. Press.

CH 611: Coordination Chemistry

UNIT-I: [14 hrs]

Synthesis, Purification and Characterization of Coordination Compounds: Metal aqua ions, solvents and ionic liquids, chromatographic methods, crystal growth methods, Newer methods of synthesis- solid state methods, sol-gel, sonochemistry, microwave, assemblies and self-assembly and electrochemical. supramolecular systems.

UNIT-II: [14 hrs]

Physical Methods of Characterization- Case Studies:NMR, ESR, ENDOR, XRD, Raman and FT-IR, Resonance Raman, Photoelectron, Mossbauer, Electrochemical,Optical, MCD, Mass, Solvatochromism, Electronic spin cross-over.

UNIT-III: [14 hrs]

Bio-coordination Chemistry: Electron transfer systems- cytochromes, iron-sulphur proteins, cuprodoxins. Ion recognition and Transport. Dioxygen-binding proteins, heme-peroxidases, copper oxidases, nitrogen fixation, zinc hydrolases, bioorganometallic chemistry of Co & Ni.

UNIT-IV: [14 hrs]

Applications: Catalysis- polymerization, hydrogenation, CO addition, C-C cross coupling, C-heteroatom cross coupling, Lewis acid catalysts, supported metal catalysts, biomedical applications.

Reference:

1. Comprehensive Coordination Chemistry –J.A. McCleverty &T J Meyer Elsevier (2004)
2. Comprehensive Coordination Chemistry, Ed. G Wilkinson, Pergamon (1984).

CH 612: Analytical and Structural Chemistry

UNIT – I: Analytical Techniques [14 hrs].

Introduction: General Description of chromatography, migration rates of solutes. Band broadening, column efficiency and resolution.**Ion exchange chromatography** : Structures of resins, selectivity, capacity of resins, removal of interfering ions, concentration and recovery of trace metals, anion and cation separations and application for the separation of lanthanides and actinides. Techniques of column chromatography, size exclusion chromatography. **Gas Chromatography** : Principles, columns and detectors.

UNIT – II: [14 hrs].

HPLC : Principles, equipment, columns, detectors, choice of column, materials.

Paper chromatography: Theory and principle. Techniques; one, two- dimensional and circular paper chromatography and applications.

TLC: Efficiency of TL plates, selection of stationary &mobile phases

AAS: Theory, working of AAS instruments, analytical applications, interferences.

Emission Spectroscopy: Flame Emission Spectroscopy, plasma emission spectrometry, Principles of flame photometry, evaluation methods in flame photometry, interferences.

Molecular Luminescence Spectroscopy: Theory of fluorescence and phosphorescence fluorimetry in quantitative analysis, instruments, fluorescence and structure, fluorescence quenching, phosphorescence method, applications in quantitative analysis.

UNIT – III: [14 hrs].

Light-Scattering methods: Nephelometry& turbidimetry-theory, effects of concentration, particle size&wavelength on scattering, instrumentation & application.Activation analysis

Thermal methods: Thermogravimetric analysis, Instumentation, factors affecting the results and applications.Differential thermal analysis, simultaneous DTA-TGA curves. Differential scanning calorimetry, applications.

Electrophoresis: Theory and classification. Factors influencing mobility, macromolecular size and charge, interaction with supporting electrolyte, pH and concentration discontinuities. Factors affecting electrophoretic phenomena, electrolysis, electroosmosis, temperature and supporting media. Instrumentation and methodology.

UNIT – IV [14 hrs].

The Crystal Structure Studies: Diffraction of X-Rays by Crystals, Stages of X-Ray Structure Analysis of Single Crystals, X-Ray Diffractometers for Investigating Single Crystals, Determination of the Crystal Orientation, Unit Cell and Intensities, Characterisation and Data Collection, Structure Solution and Structure Refinement – SHELXS, SHELXL and other programmes, Calculation of Molecular Parameters, Graphical Visualisation, Plotting and other Analysis, Document Preparation and Word Processing, An Introduction to packing of molecules in the crystal structures and Hydrogen Bonding. An introduction to powder diffraction.

REFERENCES :

1. G.D. Christian : Analytical Chemistry, (4th Ed.), (John Wiley),1986.
2. R.A.Day and A.L. Underwood : Quantitative Analysis, 5th Ed. (Prentice Hall, India), 1998.
3. H.H.Wlliard, L.L.Merrit and J.J.Dean, Instrumental methods of analysis,(7th Ed.) 1988
4. B.K.Sharma, Instrumental methods of chemical analysis, Goel publishing House, 2000.
5. Skoog, Holler and Nieman: Principles of Instrumental Analysis, Harcourt Afca,2001

6. Structural Methods in Inorganic Chemistry, Vol I & II, E.A.V.Ebsworth, D.W.H. Ranklin & S.
Cradock, Blackwell Scientific, 1991.
7.A K Tareen and Kutty, Crystallography, University Press, 2002.
8.F.C.Ladd Mark & Palmer, R.A.: Structure Determination by X-Ray Crystallography, 2003.

CH 621: Heterocyclic and Medicinal Chemistry

UNIT – I [14 hrs]

Nomenclature of Heterocyclic Compounds: Trivial or traditional names, Early semisystamatic convention and Hantzch – Widman system.

Nomenclature of polycyclic systems: Trivial names, IUPAC names, Fusion names, Bridged and fused structures, von- Baeyer names, Spiro names and naming of cyclophanes.

Interconversion of Heterocycles and Rearrangements of heterocyclic compounds: Reactions involving interconversion of heterocycles such as furan to pyrazole. Pyrazole to pyridine, Isatin to Quinoline, Isatogens, Quinazolones and Cinnolines. Rearrangements and ring transformation of 1,2,3–Triazoles, Oxazoles, 1,2,3-Oxadiazoles, Pyridazines, Quinozolines and Quinozalin – N-Oxides.

UNIT – II [14 hrs]

A few typical examples of synthesis of non-heterocycles employing isoxazoles, thiazoles, pyran and pyridine derivatives.

Photochemistry of Heterocycles: Photo-oxidation of pyrroles, photochemical reactions of pyrazoles, 1,2,3 and 1,2,4–triazoles, 1,2,3–triazines, 1,3,4–oxadiazoles, mono and disubstituted tetrazoles. Photochemistry of pyridazines and pyrimidines.

UNIT – III [14 hrs]

Concept of prodrugs, analoages, concept of lead molecules, in drug design, factor governing drug design. Drug design through molecular disjunction and through molecular conjuction. Tailoring of drugs through the application of principles of Bio-isosterism.

Structurally specific and non-specific drugs, factors responsible for drug reaching the active site. Thermodynamic activity, Meyer-Overton and Ferguson Theory. Biochemical and Physiological information leading to the development of new drugs. Quantitative analysis of SAR, Fundamentals of QSAR, Objectives of QSAR. Expression of biological activity, parameters related to chemical structure, Hanch analysis & its application in Medicinal Chemistry. Steric feature of drugs, optical isomerism and biological activity.

UNIT – IV [14 hrs]

A detailed discussion including classification, synthesis, test for identification and methods of assay of the following class of drugs. Antipsychotic agents, Anxiolytics. Drugs used in hyperkinetic disorders, Hypertensive drugs, Cardiovascular drugs, Antineoplastic agents and Antiviral agents.

References

1.Text book of Medicinal Chemistry by Burger.
2. Text book of Medicinal Chemistry by Wilson & Gisvold
3. Principles of Medicinal Chemistry- Willium O Poye
4. Medicinal Chemistry- Ashuthosh Kar
5. J.A.Joule and G.F.Smith: Heterocyclic Chemistry, CambridgeUniversity press (1972).
6. A.R.Katritzky and C.J.Rees: Comprehensive Heterocyclic Chemistry, Pergamon (1984).
7. D.H.R.Barton and W.D.Ollis: Comprehensive Organic Chemistry, Vol 14, Heterocyclic Compounds, Pergamon (1979)
8. A.R.Katritzky: Advances in Heterocyclic Chemistry, Vol 15-25, Academic (1971-81).

CH 631: Physical Organic & Structural Chemistry

UNIT -I [14 hrs]

Principles of Reactivity: An overview of kinetic concepts and analysis of kinetic results - rates of simple and composite chemical reactions (simultaneous and consecutive), steady-state treatment, empirical rate equations, methods of determining rate laws. Transition state theory, its limitations and extensions. Applications to reactions in solution. Activation parameters from experimental results, mechanistic significance and their uses. General approaches to reaction mechanism- kinetic & thermodynamic control of reactions. Reactivity-selectivity principles (Hammond's & Curtin-Hammett postulates). 10 Hrs.

Fast Reaction Techniques: Flow, flash photolysis, relaxation and NMR methods. A brief molecular beam studies of reactive collision. Kinetic spectroscopy. 4 Hrs.

UNIT -II [14 hrs]

Potential energy surfaces: – Features & construction. Theoretical calculation of Ea.

Theory of kinetic isotope effects - Primary, secondary and solvent kinetic isotope effects. Tunneling effect. Isotope effects with heavier atoms. 5 Hrs.

Substituent Effects on Reactivity: Inductive effect, electromeric effect, substitutions and the energy of activation. Hammett & Taft equations, LFERs, Deviations from Hammett equation.Dual-parameter correlations- σ_1- & σ_R- scales: Swain-Scott & Edward equations, Winstein Grunwald relationship, Isokinetic relationship. 5 Hrs

Solvation and Solvent Effects: Cage effect, effects of ionic strength, dielectric constant and solvation on rates of reactions (ion-ion, ion-dipole& dipole-dipole reactions). 4 Hrs.

UNIT -III [14 hrs]

Homogeneous catalysis: Electronic and structural effects on acidity and basicity. Acidity functions - Hammett acidity function and its applications. Industrial catalysts: catalyst carrier, promoter, inhibitor & catalyst poison. 4 Hrs.

Reactions at Surfaces: Mechanisms of surface reactions- kinetic effects of surface heterogeneity & interactions – surface inhibition and activation energies –surface exchange reactions– TST of surface reactions–unimolecular & bimolecular reactions. 5 hrs.

Micelles: Surface active agents-micellisation, CMC, micellarcatalysis.

Pharmaco kinetics: Pharma concentration time curve, protein binding and drugs, drug dissolution rate, pharmacokinetics applied to one-component open model (calculation of elimination rate constant & metabolism constant). 5 hrs

UNIT – IV [14 hrs]

The Crystal Structure Studies: Diffraction of X-Rays by Crystals, Stages of X-Ray Structure Analysis of Single Crystals, X-Ray Diffractometers for Investigating Single Crystals, Determination of Crystal Orientation, Unit Cell and Intensities, Characterisation and Data Collection, Structure Solution and Structure Refinement – SHELXS, SHELXL and other programmes, Calculation of Molecular Parameters, Graphical Visualisation, Plotting and other Analysis. Document Preparation and Word Processing. An Introduction to packing of molecules in the crystal structures and Hydrogen Bonding. An introduction to powder diffraction.

REFERENCES :

1. Physical Chemistry, 5th ed., - Atkins (ELBS) 1995
2. Chemical Kinetics - K.J.Laidler (Pearson Education) 1987.
3. The Physical Basis of Organic Chemistry, H.Maskill, Oxford University Press.

4. Physical Organic Chemistry, N.S.Isaacs, ELBS/Longman.
5. Catalysis - J.C. Kuriacose (Macmillan India Ltd.) 1991.
6. Micelles, Theoretical and applied aspects, V.Moroi, Plenum.
7.A K Tareen and Kutty, Crystallography, University Press, 2002.
8.F.C.Ladd Mark & Palmer, R.A.: Structure Determination by X-Ray Crystallography (2003.

CH 632: Electrochemistry

UNIT-I 14 hrs.

Electrochemistry- fundamentals, definitions and concepts. Electrical conductivity and interionic interactions. Electrode potentials and double layer structure at phase boundaries. Electrode potentials and electrical current.
Fundamentals, study and implications of Ion-ion and ion-solvent interactions.

UNIT-II 14 hrs.

Methods for the study of Electrode/electrolyte interface. Electro catalysis and reaction mechanism. Theory of electro deposition. Ionic liquids-Fundamentals, models and applications. Corrosion-General aspects, types, preventive methods, measurement and theory of corrosion. Corrosion failures, metallic and non metallic coatings. Corrosion failures

UNIT-III 14 hrs.

Conversion and storage of Energy(Battery and fuel cells),
Photo-electrochemistry: Semiconductors as electrodes and applications.
Bio-electrochemistry and Biosensors- fundamentals, importance, communication in biological systems. Ion sensitive electrodes: Fundamentals and applications.

UNIT-IV 14 hrs.

Electrochemical material science- Introduction, nano-particles, nano tubes, semiconductor electrochemistry, materials characterization, electrical conductivity. Environmentally Oriented Electrochemistry- Pollution control, waste management and in separation.
Industrial electrochemistry-fundamentals and synthesis of chemical compounds.
Analytical applications of electrochemistry: Cyclic voltammetry, Ploarography, potentiostat, electrogravimmetry, coulometry and amperometry.

Reference

1. Modern Electrochemistry, Vol.1,2A &2B, Bockris & Reddy (Plenum, New York)1998.
2 Chemical and Electrochemical Energy Systems, Narayan & Viswanathan.
3. Industrial Electrochemistry, Peltcher and Walsh (Chapman & Hall, Cambridge) 1990.
4. Electrochemistry, Carl H. Hamann, Andrew Hammett and Wolf Vielstich, (Wiley-VCH Weinheim) 2nd ed., 2007.
5. Chemical Abstract and Internet services.

CH 633: Polymer Chemistry

Unit I 14 hrs

Conventional and specialized methods of polymer preparation: -Details of free radical, ionic and coordination polymerization considering the examples of common industrial polymers. Few new specialized techniques – Metathesis, Group transfer polymerization etc.

Chemical modification of polymers.

Unit II 14 hrs

Properties and behaviour of polymers-solid state properties and behaviour of polymers in solution. Techniques of Analysis and Characterization-Physical, Analytical, microscopic and

spectroscopic methods of characterization.

Unit III 14 hrs

Engineering and Specialty polymers: Blends, composites, IPN systems, conducting polymers, liquid crystalline polymers: Structural requirements, Preparation, Properties and applications.

Unit IV 14 hrs

Degradation and stability. Modes of Degradation, Polymer waste disposal techniques, Biodegradable plastics.Pharmaceutical and Medical Applications of polymers.

REFERENCES :

1. Text book of Polymer Science : F.W. Billmeyer (Wiley)
2. Contemporary Polymer Chemistry-H.R.Allcock and F.W.Lampe (Prentice Hall)
3. Polymer Science:V.R.Gowariker, N.V.Viswanathan & T.Sreedhar(Wiley Eastern)
4. Polymer science and Technology, J.R.Fried (Prentice Hall).