LOYOLA COLLEGE (*Autonomous*), CHENNAI-34
Department Of Chemistry

M.Phil. COURSES FROM THE ACADEMIC YEAR 2007-2008

SEMESTER – I					
Course Code	NAME OF PAPER	COURSE		EXAMINATION	
		Hrs/ week	Credits	Hours	Marks
CH-1118 MC	Scientific Research Methodology	6	6	3	100
CH-1119 MC	Instrumental methods of chemical analysis	6	6	3	100
CH-1120 MC	Seminar and Report	2	1	--	100
CH-1154 ES	Synthetic Organic Chemistry	6	6	3	100
CH-1155 ES	Coordination and Supramolecular Chemistry	6	6	3	100
CH-1156 ES	Advanced Coordination Chemistry	6	6	3	100
CH-1157 ES	Chemistry of Nanomaterials	6	6	3	100
SEMESTER – II					
CH-1217 MC	Project work and dissertation	-	17	--	100
Total			36		500

CH –1118 : SCIENTIFIC RESEARCH METHODOLOGY

M.Phil. Chemistry

Semester – I	No. of Credits : 6
Course : Major Core(MC)	No. of hours per week : 6

Objectives

1. *To introduce the purpose and importance of research for future development.*
2. *To know the various indexes and abstracts in science and technology as a source of all information in chemistry.*
3. *To learn the ways of carrying out literature search for current awareness and for the retrospective survey.*
4. *To learn the scientific method of collecting data and to compute statistical parameters to arrive at meaningful conclusions.*
5. *To know the methodology of writing thesis and journal articles.*

Unit 1: Scientific Research and the Chemical Literature (25 h)

1.1 The search for knowledge, purpose of research, scientific method, role of theory, characteristics of research.

1.2 Types of research: fundamental or pure research, applied research, action research, historical research, experimental research.

1.3 Indexes and abstracts in science and technology: applied science and technology index, biological abstracts, chemical abstracts, chemical titles, current chemical reactions, current contents, engineering index, index chemicus, index medicus, physics abstracts, science citation index.

1.4 The Chemical Abstracts

Current awareness searching: CA weekly issues, CA issue indexes.

Retrospective searching: CA volume indexes-general subject index, chemical substance index, formula index, index of ring systems, author index, patent index.

CA Collective indexes: Collective index (CI), decennial index (DI).

Access points for searching CA indexes: index guide, general subject terms, chemical substance names, molecular formulas, ring systems, author names, patent numbers.

Locating the reference: finding the abstract, finding the original document, chemical abstract service source index.

Classical and comprehensive reference works in chemistry: Beilstein's Handbook of Organic Chemistry, Gemelin Handbook of Inorganic Chemistry; compilations of data, synthetic methods and techniques, treatises, reviews.

1.5 Computer search of literature: ASAP Alerts, CA Alerts, SciFinder, ChemPort, ScienceDirect, STN International; Journal home pages.

1.6 A report on literature survey.

Self study

(a) An overview of selected list of compilation of data: *Dictionary of Organic Compounds, Merck Index, CRC Handbook of Chemistry and Physics, Lange's Handbook of Chemistry*.

(b) An overview of selected list of synthetic methods and techniques and general treatises: *Organic Synthesis, Reagents for Organic Synthesis, Comprehensive Organic Chemistry, Encyclopedia of Reagents for Organic Synthesis.*

(c) A brief literature survey from Chemical Abstracts for locating relevant journal articles.

Unit 2: Techniques for Analysing Data (20 h)

2.1 Statistical considerations: population and samples, sampling distributions, interference about the population mean, sampling problems; the conditions of observation-research in natural settings, surveys, laboratory experiments; design of experiments.
2.2 Parametric and nonparametric data; descriptive and inferential analysis.
2.3 Frequency distributions: Graphing frequency distribution-discrete versus continuous scales, bar graphs, frequency polygons; describing frequency distributions-modality and skewness.
2.4 Measures of central tendency: the mode, the median, the mean.
2.5 Measures of variability (dispersion): the total range, the interquartile range, the average deviation, the variance-analysis of variance and covariance; the standard deviation; normal distributions: the normal distribution and the normal probability curve.
2.6 Measures of relative position: standard scores- sigma score (z), standard score (Z or T), and college board score (Z_{cb}); percentile rank.

Unit 3: Correlational methods (5 h)

3.1 Scatter diagrams and linear regression line; Spearman rank order correlation. Pearson's product moment correlation.
3.2 Correlation coefficients: Pearson r-using Pearson r to predict scores; interpreting the magnitude of r-nonlinear relations, restricted ranges.
3.3 Interpreting correlational data: reliability coefficients-internal consistency, test-retest reliability, alternate-forms reliability; validity coefficients-construct validity; regression effects; correlation and casuality-cross-lagged panel analysis.

Unit 4: Using data to make decisions (5 h)

4.1 Nonparametric tests: Chi square test, median test, Mann-Whitney test, Sign test, Wilcoxon matched-pairs signed ranks test.
4.2 Testing statistical significance: the logic of hypothesis testing-the null hypothesis (H_0), the level of significance, two tailed and one tailed tests of significance, degrees of freedom, students distribution (t), homogeneity of variances.
4.3 The alternate hypothesis, the nature of the test, decision errors and their probabilities, hypothesis about frequencies and hypothesis about mean differences.

Unit 5: The Scientific Writing (5 h)

5.1 Research reports, theses, journal articles: format and writing style.
5.2 Requirement of technical communications: eliminating wordiness and jargon-tautology, redundancy, imprecise words, superfluous phrases.
5.3 Steps to publishing a scientific article in a journal: types of publications-communications, articles, reviews; when to publish, where to publish, specific format required for submission, organization of the material.
5.4 Documenting: abstracts-indicative or descriptive abstract, informative abstract, footnotes, end notes, referencing styles, bibliography-journal abbreviations (CASSI), abbreviations used in scientific writing.

Self study

(a) Journals which publish only communications in chemistry.
(b) Journals which publish only reviews.

(c) Standard journal abbreviations of select journals in chemistry.

References

1. R. L. Dominoswki, *Research Methods*, Prentice Hall, 1981.
2. J. W.Best, *Research in Education*, 4th ed. Prentice Hall of India, New Delhi, 1981.
3. H. F. Ebel, C. Bliefert and W.E. Russey, *The Art of Scientific Writing*, VCH, Weinheim, 1988.
4. B. E. Cain, *The Basis of Technical Communicating*, ACS., Washington, D.C., 1988.
5. H. M. Kanare, *Writing the Laboratory Notebook*; American Chemical Society: Washington, DC, 1985.
6. J. S. Dodd, Ed., *The ACS Style Guide: A Manual for Authors and Editors*; American Chemical Society: Washington, DC, 1985.
7. Gibaldi, J.; Achtert, W. S. *Handbook for writers of Research Papers*; 2nd ed.; Wiley Eastern, 1987.
8. Joseph, A. *Methodology for Research*; Theological Publications: Bangalore, 1986.

CH –1119 : INSTRUMENTAL METHODS OF CHEMICAL ANALYSIS

M.Phil. Chemistry
Semester – I — No. of Credits : 6
Course : Major Core(MC) — No. of hours per week : 6

Objectives

1. *To master the basic principles of spectroscopy to apply for structural elucidation.*
2. *To learn the methods of characterizing compounds by spectroscopic techniques.*
3. *To learn the various instrumental methods studying a given compound.*
4. *To learn the separation techniques for organic and inorganic compounds.*
5. *To learn about industrial analytical processes.*

Unit 1: Absorption Spectroscopy (20 h)

1.1 Infrared and Raman Spectroscopy: FT-IR, basic principles, quantitative IR, resonance Raman and laser Raman spectroscopy, applications of IR and Raman spectroscopy to organic and inorganic compounds.

1.2 Electronic Spectroscopy: term symbols, spin-orbit coupling in free ions, electronic spectra of O_h and T_d complexes, charge transfer transition, structural evidence from electronic spectra.

1.3 Nuclear Magnetic Resonance Spectroscopy: spin-spin splitting, application of spin-spin coupling to structural determination, factors influencing the appearance of NMR spectrum-fast chemical reaction, second order spectra, quadrupole nuclei, NMR double resonance; FT NMR, principles, measurement of T_1 and T_2, applications of NMR to ^{19}F and ^{31}P magnetic nuclei; 2D NMR, NOESY and COSY; magnetic resonance imaging; applications of ^{1}H and ^{13}C NMR in structural elucidation; NMR spectra of paramagnetic compounds–scalar and pseudo contact shift.

1.4 Nuclear Quadrupole Resonance Spectroscopy: effect of magnetic field on the spectra, electric field gradient and molecular structure, structural elucidation of inorganic and coordination compounds.

1.5 Electron Paramagnetic Resonance Spectroscopy: hyperfine splitting in isotropic systems; epr spectra of systems with more than one unpaired electrons-Kramer’s degeneracy, zero field splitting, epr of triplet states, anisotropy in *g*-value, anisotropy in hyperfine splitting, nuclear quadrupole interaction; applications of epr to organic and inorganic compounds.

1.6 Mossbauer Spectroscopy: interpretation of isomer shifts, quadrupole and magnetic interactions, Mossbauer emission spectroscopy, structural elucidation.

Unit 2: Mass spectrometry and Emission Spectroscopy

2.1 Mass Spectrometry: methods of ion generation-molecular ions from volatile samples-EI, CI, PI, FI; molecular ions from non-volatile samples-FAB, ESI, FD, and MALDI; mass analysers-TOF, beam type and ion-trapping.
Tandem mass spectrometry: techniques-multiple tandems, multiple quadrupole devices, Tandem MS with TOF, quadrupole ion trap; applications of MS for structural elucidation of organic and inorganic compounds, mass spectrometry of polymers and biopolymers.

2.2 Photo Electron Spectroscopy: Koopman’s theorem, PES, XPS, ESCA, and Auger spectroscopy, applications.

2.3 Fluorescence and Phosphorescence spectroscopy: X-ray fluorescence spectroscopy and chemiluminescence
2.4 Flame emission spectroscopy: flame photometry, AAS, and ICPAES

Unit 3: Electrochemical Techniques (10 h)

3.1 Cyclic voltammetry, differential pulse voltammetry; principles and applications
3.2 Stripping voltammetry: anodic and cathodic stripping voltammetry-principle and applications.
3.3 Principle and applications of chronoamperometry, chronocoulometry, and chronopotentiometry.

Unit 4: Thermal Methods (10 h)

4.1 Principle, instrumentation and applications of thermogravimetric analysis, Differential thermal analysis, differential scanning calorimetry
4.2 Thermochemical analysis and dynamic mechanical analysis: instrumentation.
4.3 Thermometric titrations: principle and applications.

Unit 5: Separation and Analytical Methods (10 h)

5.1 Chromatography: Gas chromatography, HPLC, supercritical fluid chromatography, and capillary electrophoresis, SEC: instrumentation and applications
5.2 Industrial process analysis, methods based on bulk properties, IR process analysis, oxygen analysis, automated chemical analysers.
5.3 Electron microprobes: SEM, TEM, STM and AFM.
5.4 X-Ray methods of analysis: single crystal and powder X-ray diffraction techniques.

References

01. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* Vol A and B, 5th ed., Wiley Interscience, 1996.
02. R. S. Drago, *Physical Methods in Chemistry*, Saunders, 1977.
03. W. W. Paulder, *Nuclear Magnetic Resonance: General Principles and applications*, Wiley, New York, 1987.
04. A. E. Derome, *Modern NMR techniques for Chemistry Research*, Pergamon Press, 1988.
05. E. Breitmer and W. Voeller, *Carbon-13 NMR Spectroscopy*, 3rd ed, VCH, Weinheim, 1987.
06. Y. Takeuchi and A. P. Marchand, *Applications of NMR Spectroscopy to Problems in Stereochemistry and Conformational Analysis*, VCH, Weinheim, 1986.
07. J. A. Weil, J. R. Bolton, and J. E. Wertz, *Electron Paramagnetic Resonance*, Wiley Interscience, 1994.
08. W. R. Croasmum and R. M. K. Carlson, *Two Dimensional NMR Spectroscopy:* John Wiley, New York, 1985.
09. D. Ishii, *Micro and Semi-Micro High Performance Liquid Chromatography*, VCH, Weinheim, 1979.
10. P. T. Kissinger and W. R. Heineman Eds., *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed., Marcel Dekker Inc, New York, 1996.
11. H. H. Willard, L. L. Merritt, J.A. Dean and F. A. Seattle, *Instrumental Methods of Analysis*, 7th ed, CBS Publishers, New Delhi, 1986.
12. D. A. Skoog, F. J. Holler and T. M. Nieman, *Principles of Instrumental Analysis*, 5th Ed, Harcourt Asia Pte Ltd, India, 2001.
13. Srivastava, *Chemical Analysis: An Instrumental Approach*, S. Chand, New Delhi,
14. F. A. Settle, Ed. *Handbook of Instrumental Technique for Analytical Chemistry*, Pearson Edn, India, 1997.

15. B. K. Sharma, *Instrumental Methods of Chemical Analysis*, 23rd Edn, Goel Publishing, Meerut, 2004.

CH –1154 : SYNTHETIC ORGANIC CHEMISTRY

M.Phil. Chemistry

Semester – I	No. of Credits	: 6
Course : Subject Elective(ES)	No. of hours per week	: 6

Objectives:

01. To know the methods of synthetic strategies and applications

02. *To apply the knowledge of chemical reactions in organic synthesis*

UNIT 1: Preliminary planning and control elements (15 hours)

1.1 Known and unknowns of synthetic systems, analysis of complex and interrelated carbon frame work, precursors, retrosynthetic approach.

1.2 Yield of synthetic reactions, convergent synthesis.

1.3 Functionalisation and interconversion of functional groups- functionalisation of alkanes, alkenes, alkynes, aromatic hydrocarbons, heterocyclic compounds and inter conversion of functional groups

1.4 Formation of Carbon-carbon bonds- general strategy, disconnections and synthons, electrophilic and nucleophilic carbon species.

1.5 Regiospecific control elements, use of protective groups, activating groups and bridging elements.

1.6 Streospecific control elements – functional group alterations and transportations.

Self study:

Electrophilic carbon-nitrogen reagents, electrophilic alkenes, Grignard and related organometallic reagents.

UNIT 2: Asymmetric synthesis (10 hours)

2.1 Terminology and analytical methods, Strategy and classification of methods, first, second, third and fourth generation methods. Use of two each of chiral substrates, chiral auxiliaries, chiral reagents.

2.2 Asymmetric catalysis, cataslytic asymmetric alkylation, hydrogenation, reactions catalysed by enzemes and other proteins.

2.3 Organotransition metal chemistry, applications to asymmetric organic synthesis.

2.4 Alkylation of active methylene compounds in asymmetric synthesis.

Self study:

Multistage synthetic routes, aymmetric Diels-Alder reaction, alkylation α to nitrogen.

UNIT 3: Silicon and boron in organic synthesis (10 hours)

3.1 Properties of bonds to silicon, nucleophilic substitution at silicon, 1,2-rearrangements.

3.2 Protection of hydroxy groups as silyl ethers, silyl enol ethers and related silyl ethers, synthesis of alkenes(Peteson olefination).

3.3 Alkynyl-, vinyl- and arylsilanes in organic synthesis, arylsilanes and acylsilanes.

3.4 Typical organic synthesis involving organosilicon compounds.

3.5 Hydroboration, asymmetric hydroboration, reactions of organoboranes-oxidation, protonolysis, amination, halogenolysis, isomerisation.

3.6 Organoboron routes to unsaturated hydrocarbons- synthesis of alkenes, alkynes, diynes, enynes.

3.7 Alkylboranes and boron enolates in organic synthesis, double asymmetric induction.
3.8 Boronic ester homologation.

Self study:

Silyl ketene acetals, regioselective electrophilic attack on alkynylsilanes, applications of boron compounds in asymmetric synthesis.

UNIT 4: Redox reactions in organic synthesis (15 hours)

4.1 Oxidation of hydrocarbons, alcohols, carbon-carbon double bonds, diols, epoxides.
4.2 Enantioselective epoxidation of allylic alcohols, diastereoselective epoxidation, ozonolysis.
4.3 Oxidation of ketones – Baeyer-Villiger oxidation, oxidation with thallium(III) nitrate, selenium reagents and intermediates in organic synthesis, lead tetraacetate.
4.4 Catalytic hydrogenation, selectivity of reduction, homogeneous hydrogenation, reduction by dissolving metals.
4.5 Reduction by hydride transfer reagents – aluminium alkoxides, LAH, sodium borohydride, sodium cycnoborohydride, trialkylborohydrides.
4.6 Electrochemical organic synthesis

Self study:

Wolff-Kishner reduction, desulphurisation of thio-acetons, di-imide, low valent titanium species.

UNIT 5: Selected Organic synthesis (10 hours)

Reagents for organic synthesis and their applications - Synthesis of Z-Heneicos-6-en-11-one, Disparlure, Z-Jasmone, helicenes, annulenes, progesterone, cortisone and peptide synthesis.

Self study:

Wolff-Kishner reduction, desulphurisation of thio-acetons, di-imide, low valent titanium species.

Reference books

1. *R.K.Mackie, D.M.Smith and R.Alan Aitken, Guide book to organic synthesis, III Edition, Longman Group Limited, 1999.*
2. Ireland R.E, Organic synthesis, Prentice Hall India, Goel publishing house, 1990
3. Smith, M.B, Organic synthesis, II Edition, McGraw Hill International, 2002
4. House H.O. Modern Synthetic reactions, W.A. Benjamin Inc, 1972
5. Carruthers, W, Modern Methods of organic synthesis, III edition, Cambridge University Press, 1986.
6. Norman R.O.C., Organic synthesis, Chapman Hall, London, 1980
7. Susan E.Thomas, Organic synthesis, Oxford science publications, 1994.
8. I.L.Finar, Organic synthesis, Longman, 2004.
9. Francis A.Carey and Sundberg, Advanced Organic Chemistry, 5th edition, Tata McGraw-Hill, New York, 2003
10. Smith and Jerry March, March's Advanced Organic Chemistry, John Wiley, 2007.

CH –1155 : COORDINATION AND SUPRAMOLECULAR CHEMISTRY

M.Phil. Chemistry		
Semester – I	No. of Credits	: 6
Course : Subject Elective(ES)	No. of hours per week	: 6

Objectives

1. To quantify bonding parameters in cubic and distorted geometries from electronic spectra.
2. To identify suitable coordination compounds for the construction of supramolecular assemblies and nanostructures.
3. To learn the methodology of constructing supramolecular assemblies with desired peoperties for specific application.
4. To identify complexes suitable for application in medicinal inorganic chemistry.
5. To set research goals in the highly topical areas of research in coordination and supramolecular chemistry.

Unit 1: Electronic Structure and Geometry of Coordination Compounds (15 h)

1.1 Electronic spectroscopy: crystal field spectra of O_h and T_d complexes, effect of distortion on the spectra, structural evidence from electronic spectra, evaluation of Δ_o and Δ_t values in Co(III) and Ni(II) O_h and T_d complexes, quantification of covalency-nephelauxetic ratio.

1.2 Tetragonal distortion in octahedral complexes and evaluation of D_q^{xy} and D_q^{z} in tetragonally distorted octahedral Co(III) complexes.

1.3 Nuclear magnetic resonance spectroscopy: application of spin-spin coupling to inorganic structural determinations, NMR spectra of quadrupolar nuclei, NMR of paramagnetic transition metal complexes: scalar shift and pseudocontact shift, scalar shift and covalency.

1.4 Electron spin resonance spectroscopy: hyperfine and zero field effects on the epr spectra of coordination compounds, ligand field interpretation of the *g*- and *A*-tensors, nuclear qudrupole interaction.

1.5 Mossbauer spectroscopy: quadrupole and magnetic interactions, isomer shift and site symmetry of metal ions in coordination compounds, Mossbauer emission spectroscopy and applications.

Self study

(a) Causes of tetragonal distortion in transition metal complexes and their effect on the electronic spectra.
(b) Effect of quadrupole nuclei on spin-spin splitting and hyperfine splitting.
(c) Causes of anisotropy and anisotropic *g*-values.

Unit 2: Supramolecular and Dendritic Chemistry
(15 h)

2.1 Supramolecular assemblies and architectures: nature of supramolecular interactions, homo- and heteropolymetallic polypyridyl systems; supramolecular host-guest compounds.

2.2 Templates and self assembly: biochemical self-assembly, self-assembly in synthetic systems, self-assembling coordination compounds, catenanes and rotaxanes.

2.3 Supramolecular devices: photoinduced elelctron and energy transfer, photo- and electrochemical sensors, light conversion and energy transfer devices, molecular electronic devices (molecular switches, wires, and rectifiers), molecular machines.

2.4 Dendrimers and metallodendrimers: synthetic methodology-divergent and convergent methodologies; types of metallodendrimers, characterization techniques.

2.5 Dendrimer encapsulated metal nanoclusters: silver and gold nanoclusters and nanoparticles, quantum dots, quantum size related photochemical properties, dendrimer encapsulated catalysis.

Self study

(a) Terpyridine and bipyridine-appended spacers, phenazene based spacers.
(b) Different kinds of supramolecular assemblies constructed by covalent-, coordination-, and hydrogen bonding.

Unit 3: Electrochemistry and Photochemistry (12 h)

3.1 Intercomponent energy and electron transfer in supramolecular assemblies: role of bridging ligands.
3.2 Applications of cyclic voltammetry, and differential pulse voltammetry to the study of coordination compounds and metallosupramolecular assemblies: computation of electrochemical parameters and evaluation of reversibility of the redox processes.
3.3 Spectroelectrochemistry: optically transparent electrodes and cells, chronoabsorptometry.
3.4 Solar and renewable energy: light-to-chemical energy conversion in lamellar solids and thin films, solar energy conversion by dye-sensitized photovoltaic cells and by coordination compounds anchored onto semiconductor surfaces.
3.5 Photochemistry of lanthanide complexes: A-ET-E processes, NIR-to-visible photon upconversion, nonlinear optical behavior, exciton multiplication and relaxation dynamics in quantum dots and applications; optical fiber lasers and amplifiers containing lanthanide complexes.

Self study

(a) Causes of electrochemical irreversibility and coupled chemical reactions.
(b) Photochemistry of Ru(II) and Os(II) polypyridyl complexes and Jablonski diagram.
(c) Emission properties and applications of lanthanide emitters.

Unit 4: Bioinorganic and Medicinal Inorganic Chemistry (10 h)

4.1 The supramolecular chemistry of life: photosynthesis-biological photosynthesis, chemical approaches to artificial photosynthesis (light harvesting dendrimers and multiporphyrin arrays); Rhodopsin (a supramolecular photonic device); biochemical self-assembly.
4.2 Contrast enhancing agents for medical diagnostics: thoeory of MRI imaging, Gd-based contrast agents-synthesis and structural features; optical contrast agents-Ag and AuNPs; metal complexes as photosensitizers.
4.3 Metal complexes for radiotherapy: diagnostic radiopharmaceuticals, non-technitium for diagnostic imaging, Tc-labelled small molecules and peptides as diagnostic radiopharmaceuticals.
4.4 Targeted cancer nanotherapy: magnetic nanoparticles and cancer therapy; gold nanoparticles-tunable optical properties and in vivo cancer detection and therapy.

Self study

(a) Antenna effect and funneling of electronic energy in supramolecular assemblies.
(b) Generation of ^{99m}Tc chelates.

Unit 5: Synthesis of Novel Coordination Compounds and Supramolecular Assemblies (8 h)

5.1 Templates and self-assembly: synthesis of Schiff base macrocycles and macrocyclic binucleating ligands by coordination template effects, self-assembling coordination compounds-design principles, molecular cubes, squares and boxes; self-assembly of metal arrays; catenanes and rotaxanes.
5.2 Polyazamacrocycles and macrocycles with pendant arms.
5.3 Construction of polynuclear supramolecular assemblies and nanostructures.

Self study

(a) Design of Robson-type compartmental Schiff base macrocycles derived from 2,6-diformyl-4-methylphenol and 2,6-diformylpyridine.
(b) Methods of self-assembling coordination compounds.

References

1 Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; Harper and Row: New York; 1983.
2 Cotton, F. A.; Wilkinson. G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley Interscience: New York; 1988.
3 Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; Saunders: Philadelphia, 1976.
4 Lever. A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier Publishing Company: Amsterdam; 1984.
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8 Sawyer, D. T.; Sobkowiak, A.; Roberts, Jr., J. L. *Electrochemistry for Chemists*, 2nd ed.; Wiley Interscience: New York; 1995.
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12 Lindoy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: Cambridge; 1989.
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15 Bosman, A. W.; Janssen, H. M.; Meijer, E. W. “About Dendrimers: Structure, Physical Properties, and Applications”; *Chem. Rev.* **1999**, *99*, 1665.
16 Newkome, G. R.; He, E.; Moorefield, C. N. “Suprasupermolecules with Novel Properties: Metallodendrimers”; *Chem. Rev.* **1999**, *99*, 1689.
17 Jurisson, S. S.; Lydon, J. D. “Potential Technetium Small Molecule Radiopharmaceuticals”, *Chem. Rev.* **1999**, *99*, 2205.
18 Anderson, C. J.; Welch, M. J. Radiometal Labeled Agents (Non-Technetium) for Diagnostic Imaging”, *Chem. Rev.* **1999**, *99*, 2219-2234.
19 Ali, H.; van Lier, J. E. “Metal Complexes as Photo- and Radiosensitizers”, *Chem. Rev.* **1999**, *99*, 2379.
20 Majoral, J.-N.; Caminade, A.-M. “Dendrimers Containing Heteroatoms”, *Chem. Rev.* **1999**, *99*, 845.
21 Bunzli, J.-C. G; Piguet, C. “Lanthanide-Containing Molecular and Supramolecular Polymetallic Functional Assemblies”, *Chem. Rev*. **2002**, *102*, 1897.
22 Kuriki, K.; Koike, Y. “Plastic Optical Fiber Lasers and Amplifiers Containing Lanthanide Complexes”, *Chem. Rev*. **2002**, *102*, 2347.
23 Parker, D.; Dickins, R. S.; Puschmann, H.; Crossland, C.; Howard, J. A. K. “Being Excited by Lanthanide Coordination Complexes: Aqua Species, Chirality, Excited-State Chemistry, and Exchange Dynamics”, *Chem. Rev*. **2002**, *102*, 1977.

CH – 1156: ADVANCED COORDINATION CHEMISTRY

M.Phil. Chemistry
Semester – I No. of Credits : 6
Course : Subject Elective(ES) No. of hours per week : 6

Objectives:

03. *To give the students an advanced insight into coordination chemistry*
04. *To make them familiarize with the structural, spectral and the reactivity of the coordination complexes*
05. *To introduce the features of organo-metallic and bio-inorganic metal centers and complexes*

1. Synthesis of Novel Coordination Compounds 5 hrs

a. Synthesis of macrocyclic ligands by schiff base condensation and by coordination template effects. Preparation of crown ethers
b. Compartmental Ligands: design and synthesis of macrocyclic and nonmacrocyclic binucleating ligands and their complexes.
c. Synthesis of triple decker sandwitches and cluster compounds

2. Determination of Electronic and Molecular Structure 25 hrs

a. Electronic spectroscopy – Evaluation of D_q^{av}, $D_q$xy and D_q^z values in cobalt(II) octahedral complexes and tetragonaly distorted cobalt(II) octahedral complexes Evaluation of D_q values in the nickel(II) octahedral complexes.
b. Infrared and Raman Spectroscopy – Structural diagonosis by IR and Raman spectra. IR spectra assignments of prominent function groups of coordinated ligands in metal complexes, differentiation of isomers. Resonance Raman Spectroscopy – Principle and any two applications.
c. Photoelectron and X-ray photoelectron spectroscopy – principle and applications.
d. Application of Nuclear Magnetic Resonance Spectroscopy – fluxional behavior (temperature variation, NMR spectral studies), Nuclear Quadrupole Resonance Spectroscopy; relationship between electric field gradient and molecular structure, applications in inorganic and coordination complexes.
e. Mossbauer Spectroscopy: Significance of Isomer shift and quadrupole splitting, applications to Fe and Sn complexes. Magnetic interactions, Method and two examples of single crystal X-ray analysis of coordination complexes. Significance and applications of EXAFS studies.
f. Study of chiral coordination compounds by ORD and CD

3. Study of paramagnetic and Antiferro magnetic compounds 5 hrs

a. Magnetic behavior of coordination compounds; Magnetic susceptibility and the geometry of the complexes. Anomalous behavior, Antiferro magnetic interactions, spin-crossover systems
b. Electron paramagnetic Resonance Spectroscopy – ligand field interpretation of the g- and A-Tensors, Nuclear spin interactions, Hyperfine and zerofield effect on the spectrum. Application to Cu(II) and Mn(II) complexes.

4. Kinetics of coordination complexes 15 hrs

a. Inert and labile nature: Thermodynamic and kinetic stability – water exchange reactions. Aquation: acid and base hydrolysis – D, A and SN1CB mechanisms. Factors influencing the rate of the reactions in octahedral complexes. Attack on ligands.

b. Trans effect – Synthetic applications. Kinetics of hydrolysis and ligand exchange in square planar complexes.

c. Inner sphere and outer sphere mechanisms.

d. Photochemistry: Photo physical processes - Florescence and phosphorescence emission. Photo substitution – Adamsons rules – examples. Charge transfer photochemistry

e. Organo metallic chemistry: Allyl complexes, metallocenes, COT – preparation and properties. Alkenes metathesis, oligomerization Heterogenaized homogenous catalysis - polynuclear supported catalysis. Sharpless epoxidation (Ti-isopropoxide, t-BuOOH), McMurry Coupling ($TiCl_3/LiAlH_4$), Pauson-Khand Reaction - $Co_2(CO)_8$, Dotz Reaction – Chromuim Carbene, Heck Reaction – $Pd(PPh_3)_4$,

f. Electrochemical methods of studying coordination compounds: Applications of – AC and DC polarography and cyclic voltammetry to coordination compounds. Electrochemical synthesis of complexes. Coupled chemical reactions; EC, CE and ECE mechanisms

5. Inorganic Biochemistry 10 hrs

a. Ferritin and transferritin, carboxypeptidaseA, carbonic anhydrase, Blue copper protein, SOD.

b. Electron transfer agents (bio-redox agents): cytochromes and iron-sulphur proteins.

c. Nitrogen fixation and the role of metal ions. Photosynthesis - Photosystem I and Photosystem II

d. Essential and trace elements in biological systems, Chelate therapy.

References:

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CH – 1157: CHEMISTRY OF NANOMATERIALS

M.Phil. Chemistry	
Semester – I	No. of Credits : 6
Course : Subject Elective(ES)	No. of hours per week : 6

Objectives

1. To tackle rational synthesis to control size and shape of both organic and inorganic nanostructures.
2. To connect structure to function by design and extending function to dynamics of nanostructures.
3. To think about new functions for devices based on nanostructures.
4. To know the different kinds of nanoarchitectures and their synthesis and functions.
5. To understand the growing interest in using nanostructures for advanced medicine.

Unit 1: Fabrication and Patterning Nanostructures (15 h)

1.1 Preparation of nanostructures: nucleation and particle growth-sol process, sol-gel process, chemical precipitation, hydrothermal synthesis, pyrolysis, vapor deposition.

1.2 Techniques of nanofabrication: photolithography, scanning beam lithography, scanning probe lithiography.

1.3 Nanofabrication by molding, embossing, and printing: hard pattern transfer elements-step-and-flash imprint lithography, nanoimprint lithography; soft pattern transfer elements-replica molding, solvent-assisted micromolding; electrical microcontact printing; nanotransfer printing.

1.4 Self-assembly for nanofabrication: nontemplated self-assembly, templated self-assembly, self-assembled monolayers (SAMs) of thiolates on metals-preparation of SAMs, mechanisms of assembly, SAMs as surface layers.

1.5 Surface modification of nanoparticles, characterization techniques-SEM, TEM, HRTEM, AFM, SAXS, LDI-MS, STM.

Self study

(a) Nanostructures of different shapes and their images.

(b) Growth mechanisms of nanostructures of different shapes.

Unit 2: Nanoarchitectures (10 h)

2.1 Nanotubes based on amphiphilic molecules: methods for nanotube formation-chiral self-assembly, packing-directed self-assembly, amphiphilic polymer assembly, molecular sculpting, template processes; synthesis of hybrid tubular structures-template-directed synthesis.

2.2 Carbon nanotubes: assembly in carbon soot, molecular structure, nanotube morphology.

2.3 Control of dimensions: outer diameter, inner diameter, length, wall thickness.

2.4 Nanorods: axial rods-modules and rods, singly- and doubly-linked axial rods; zig-zag rods-oligoenes, oligothiophenes, oligopyrroles, co-oligomers of axial and zig-zag modules.

2.5 Mechanical properties and technological applications of nanoarchitectures.

Self study

Inorganic and organic building blocks for the synthesis of various nanoarchitectures.

Unit 3: Devices Based on Nanostructures (10 h)

3.1 Molecular scale machines-interlocked macromolecules, polyrotaxanes.

3.2 Chemically-, electrochemically-, and photochemically controllable supramolecular complexes, molecular shuttles, and catenates.

3.3 Artificial molecular rotors: rotor behavior in non-interacting systems; interacting rotors; rotors in solution-propellers, gears, and cogwheels; rotation in nonsandwich porphyrins; rotations of molecular carousels (sandwich complexes); light-driven- and chemically driven molecular rotors.

3.4 Optical and electrical properties of nanoparticles: semiconductor quantum dots, quantum size effects and electron transition, NLO properties, photon upconversion and anti Stokes processes, electron-phonon relaxation.

3.5 Lanthanide-containing supramolecular devices: polymetallic functional assemblies-A-ET-E processes, NIR-to-visible photon upconversion, nonlinear optical behavior, exciton multiplication and relaxation dynamics, optical fiber lasers and amplifiers, electroluminescent materials.

Self study

(a) Template assembly of interlocked molecules.

(b) Lanthanide-*d*-metal and lanthanide-*s*-metal containing edifices.

Unit 4: Metallodendrimers, Nanoreactors, and Nanocatalysis (10 h)

4.1 Dendrimers and metallodendrimers: evolution of dendrimers, synthetic methodology-divergent and convergent methodologies, types of metallodendrimers, characterization techniques.

4.2 Light harvesting dendrimers and photoactive metallodendrimers.

4.3 Dendrimer encapsulated metal nanoclusters: silver and gold nanoclusters and their chemical and photochemical properties.

4.4 Nanoreactors: molecular nanoreactors-molecular capsules and boxes, micelle-based systems, vesicle-based systems; macromolecular nanoreactors-polymersomes as nanoreactors, polymer micelles as nanoreactors, unimolecular nanoreactors.

4.5 Nanocatalysis: homogeneous catalysis-cross-coupling reactions, electron-transfer reactions, hydrogenation reactions, oxidation reactions; heterogeneous catalysis-reactions catalyzed by supported transition metal nanocatalysts.

4.6 Dendrimer-encapsulated catalysis-dendrimers with catalytically active cores, dendrimer nanoreactor, catalytically-active dendrimer-encapsulated MNPs.

Self study

Techniques of growing dendrimer-encapsulated AuNPs and AgNPs.

Unit 5: Nanostructures in Biology and Medical Technology (15 h)

5.1 Biomacromolecular nanoreactors: protein cages, viruses-rod-shaped and cage-structured viruses.

5.2 Nanostructure-based detection methods: optical detection of nucleic acids, proteins, biologically relevant small molecules, metal ions; electrical- and electrochemical detection of nucleic acids; magnetic relaxation detection of nucleic acids, proteins, viruses.

5.3 Biological molecular machines: Myosin-structural aspects and chemomechanical properties; ATP Synthases-structure and chemomechanical propertiers of F_1-ATPase and F_0-ATPase rotors; purple photosynthetic bacteria-structure, light harvesting functions.

5.4 Fluorescence imaging: single-molecule fluorescence spectroscopy, confocal and two photon microscopy, fluorescent proteins, imaging studies of protein localization, imaging of cell signaling.

5.5 Targeted cancer nanotherapy: magnetic nanoparticles and cancer therapy; gold nanoparticles-tunable optical properties and in vivo cancer detection and therapy.

References

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CH –1217 : PROJECT WORK AND DISSERTATION

M.Phil. Chemistry
Semester – II   No. of Credits : 17
Course : Major Core(MC)

Objectives

1. *To introduce the purpose and importance of research for future development and sustenance.*
2. *To learn the ways of carrying out literature search for current awareness and for retrospective survey and to plan and carry out experimental work.*
3. *To know the methodology of writing thesis and journal articles.*

The student is counseled regarding facilities available and the professors offering guidance. The student chooses the topic of project and the guide at the beginning of the semester. University rules are followed if the student needs extension of time to submit the dissertation.

Evaluation of the project report:

The controller of examination appoints an external examiner from the panel suggested by the department. The guide also functions as a co-examiner. Viva-voce is conducted.

Quality of work done and written report	50 marks
Oral presentation	25 marks
Viva-voce	25 marks
Total marks	100 marks