DEPARTMENT OF CHEMISTRY

M. Phil Chemistry

M. Phil PROGRAMME

REVISED SYLLABUS

Loyola College (Autonomous)

Chennai- 600 034

MCH 1501: INSTRUMENTAL METHODS OF CHEMICAL ANALYSIS

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 to study a given compound.
4. To learn the separation techniques for organic and inorganic compound mixtures.
5. To learn about various analytical processes.

Unit 1: Electron Absorption Spectroscopy (1+11+1 h)

1.1 Infrared Spectroscopy: FT-IR, basic principles and advantages, quantitative IR methods.
1.2 Raman spectroscopy: Resonance Raman, laser Raman and coherent anti-stokes Raman spectroscopy; Applications of IR and Raman spectroscopy to organic and inorganic compounds.
1.3 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; Woodward-Fieser rules to calculate the λ_{max} of organic compounds.
1.4 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.

Unit 2: Nuclear Absorption Spectroscopy (1+11+1 h)

2.1 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.
2.2 Nuclear Quadrupole Resonance Spectroscopy: effect of magnetic field on the spectra, electric field gradient and molecular structure, structural elucidation of inorganic and coordination compounds.
2.3 Mossbauer Spectroscopy: interpretation of isomer shifts, quadrupole and magnetic interactions, Mossbauer emission spectroscopy, structural elucidation.

Unit 3: Mass spectrometry and Emission Spectroscopy (1+11+1 h)

3.1 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.
3.2 Photo Electron Spectroscopy: Koopman's theorem, PES, XPS, ESCA, and Auger spectroscopy, applications.
3.3 Fluorescence and Phosphorescence spectroscopy: Instrumentation, Applications of organic and inorganic compounds; X-ray fluorescence spectroscopy and chemiluminescence.
3.4 Flame emission spectroscopy: flame photometry, AAS, and ICP-AES.

Unit 4: Electrochemical Techniques and Thermal methods (1+11+1 h)

4.1 Cyclic voltammetry, differential pulse voltammetry: principle, instrumentation and applications.
4.2 Stripping voltammetry: anodic and cathodic stripping voltammetry-principle and applications.
4.3 Principle and applications of chronoamperometry, chronocoulometry, and chronopotentiometry.
4.4 Principle, instrumentation and applications of thermogravimetric analysis, Differential thermal analysis and differential scanning calorimetry.
4.5 Thermochemical analysis and dynamic mechanical analysis: instrumentation.
4.6 Thermometric titrations: principle and applications.

Unit 5: Separation and Analytical Methods (1+11+1 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 analyzers.
5.3 Electron microprobes: SEM, TEM, STM and AFM.
5.4 X-Ray methods of analysis: single crystal and powder X-ray diffraction techniques, EDAX.

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.
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10. D. Ishii, *Micro and Semi-Micro High Performance Liquid Chromatography*, VCH, Weinheim, 1979.
11. P. T. Kissinger and W. R. Heineman Eds., *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed., Marcel Dekker Inc, New York, 1996.
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13. D. A. Skoog, F. J. Holler and T. M. Nieman, *Principles of Instrumental Analysis*, 5th Ed, Harcourt Asia Pte Ltd, India, 2001.
14. Srivastava, *Chemical Analysis: An Instrumental Approach,* S. Chand, New Delhi.
15. F. A. Settle, Ed. *Handbook of Instrumental Technique for Analytical Chemistry*, Pearson Edn, India, 1997.
16. B. K. Sharma, *Instrumental Methods of Chemical Analysis*, 23rd Edn, Goel Publishing, Meerut, 2004.

MCH 1502: SCIENTIFIC RESEARCH METHODOLOGY

Semester: 1 Credits: 6

Category: Major Core (MC) Hours/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 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 Chemical Literature (1+13+1h)

1.1 Research – Purpose, criteria, characteristics, objectives.

1.2 Types of research: fundamental or pure, applied, analytical, descriptive, exploratory, historical, and experimental research.

1.3 Research Design – Need – Features – Inductive, Deductive and Development of models.

1.4 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.

1.5 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.

1.6 Computer search of literature: web of science, SCI, EBSCO, Google Scholar, Thomson Reuters, ISI, ICI, Proquest, Pubmed, SciFinder, , STN International, ICV, Journal home pages.

Unit 2: Descriptive Statistical Data Analysis (1+ 13 +1 h)

2.1 Statistical considerations: population and samples, sampling distributions, inference about the population mean, sampling problems; the conditions of observation-research in natural settings, surveys, laboratory experiments; design of experiments.

2.2 Frequency distributions: Graphing frequency distribution-discrete versus continuous scales, bar graphs, frequency polygons; describing frequency distributions-modality and skewness.

2.3 Measures of central tendency: mean, median, and mode.

2.4 Measures of variability (dispersion): range, interquartile range, average deviation, variance-analysis of variance and covariance; standard deviation; normal distributions: the normal distribution and the normal probability curve.

2.5 Measures of relative position: standard scores-sigma score (z), standard score (Z or T), and College Board score (Zcb), percentile rank.

Unit 3: Correlational methods (1 + 5 + 1 h)

3.1 Scatter diagrams and linear regression line; Spearman rank order correlation. Pearson's product-moment correlation.

3.2 Correlation coefficients: Pearson r, 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: Inferential data Analysis (1 + 6 + 1 h)

4.1 Testing statistical significance: the logic of hypothesis testing-the null hypothesis (H_0), the level of significance, two and one tailed tests of significance, degrees of freedom, The alternate hypothesis, the nature of the test, decision errors and their probabilities, hypothesis about frequencies and hypothesis about mean differences.

4.2 Parametric tests: student's distribution (t), Chi square test (χ^2), homogeneity of variances (ANOVA) and covariances (ANACOVA).

4.3 Nonparametric tests: median test, Mann-Whitney test, Sign test, Wilcoxon matched-pairs signed ranks test.

Unit 5: Scientific writing, Application of results and Ethics (1+13+1h)

5.1 Preparing Research papers for journals, Seminars and Conferences – Design of paper using Template, Impact factor of a journal, citation Index, h-index, i10- index, DOI, ISBN, ISSN.

5.2 Preparation of Project Proposal - Title, Abstract, Introduction – Rationale, Objectives, Methodology – Timeframe and work plan – Budget and Justification - References

5.3 Documenting: abstracts-indicative or descriptive abstract, informative abstract, footnotes, endnotes, referencing styles, bibliography - journal abbreviations (CASSI), abbreviations used in scientific writing.

5.4 Requirement of technical communications: eliminating wordiness and jargon-tautology, redundancy, imprecise words, superfluous phrases.

5.5 Ethics : Environmental Impacts - Ethical Issues – Ethical Committees – Commercialization – copyright – royalty – Intellectual Property rights and patent law – Track Related aspects of intellectual property Rights – Reproduction of published material – Plagiarism – Citation and Acknowledgement – Reproducibility and accountability.

REFERENCES

1. B. L. Garg, R. Karadia, F. Agarwal and U. K. Agarwal, *An Introduction to Research Methodology*, RBSA Publishers, 2002.
2. C. R. Kothari Research Methodology Methods & techniques, 2nd ed. New Age Int. Pub. New Delhi, 2018.
3. S. C. Sinha and A. K. Dhiman, *Research Methodology*, 2nd Vol. Ess Ess Publications, 2002.
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10. J. W.Best, J. V. Kahn, A. K. Jha *Research in Education*, 10th ed. Prentice Hall of India, New Delhi, 2016.
11. P. N. Arora, S. Arora, S. Arora Comprehensive Statistical Methods S. Chand, New Delhi, 2015.

12. H. F. Ebel, C. Bliefert and W. E. Russey, *The Art of Scientific Writing*, VCH, Weinheim, 1988.
13. B. E. Cain, *The Basis of Technical Communicating*, ACS, Washington DC, 1988.

MCH 1601: CHEMISTRY OF MATERIALS

M.Phil. Chemistry

Semester – I No. of Credits : 6

Course : Subject Elective(ES) No. of hours per week : 6

Unit – I Crystals – Diffraction, preparative methods and characterization (10h)

1.1 Crystal structure by Powder X-ray diffractions and by Single Crystal analysis, Reciprocal lattices – Fourier Transforms, Fourier Synthesis of Crystal Structures, Single Crystal Analysis and its Applications, Neutron diffraction – Method and Applications.

1.2 Radius ratio rules- coordination number. Packing arrangement - crystal structure in solids – rock salt, zinc blende, wurtzite, fluorite and anti fluorite, spinel and inverse spinel and perovskite structures.

1.3 Single crystal growth – Low and High temperature, solution growth technique – Gel and sol-gel methods, Hydrothermal. Melt growth – Bridgeman-Stockbarer method, Czochralski method. Flux technique, Physical and Chemical Vapor Deposition method (PVD and CVD). Characterization – TG-DTA, SEM, TEM Analysis. Applications of Single Crystals.

Self study:

Piezoelectric, pyroelectric and ferroelectric crystals

Unit – II Sensors and types of sensors (10 h)

2.1 Definition, types of sensors – optical, mass sensitive, heat sensitive, temperature, electromagnetic, mechanical and electrochemical sensors.

2.2Humidity sensors – relative humidity, requirements of humidity sensors, miniaturisation of humidity sensors – capacitive, resistive, hygrometric, gravimetric and optical. Materials as humidity sensors – metal oxides – single, mixed doped metal oxides, polymers. Sensing mechanism.

2.3 VOC sensors - sources of VOCs, health effects of VOCs, need for detection of VOCs, different materials used as VOC sensors - metal oxides – single, mixed doped metal oxides, polymers. Sensing mechanism.

2.4 Biosensors - definition, principle of detection, types of biosensors - optical and electro chemical biosensors. Nanobiosensors, nanonose, types of nanobiosensors - electrical and electrochemical, nanowires, viral, nanoshell biosensors. Applications – nanobiosensors and cancer – point of care testing.

Self study

Different metal oxides and polymers used as chemical and biosensors and their applications in different fields.

Unit 3 : Catalytic materials (10 h)

3.1 Physisorption and Chemisorption – five types of physical adsorption isotherms, unimolecular and multimolecular adsorption. Specific surface area of catalyst - BET equation. Dubinin-Radushkevich (DR) Theory, t- and α_s- plots. Pore Volume and pore size distribution –Bottle neck theory, open pore theory, determination - Barrett−Joyner−Halenda (BJH) methods, Mercury porosimetry.

3.2 Heterogeneous catalytic oxidation - different oxidation catalysts – metal oxides, supported metal oxides, zeolites, electrophilic and nucleophilic oxidation - mechanism, selectivity in oxidation, structure sensitivity, supported metal oxide catalysts. Liquid phase oxidations – redox molecular sieves, Titanium Silicalite – 1 and metal substituted Titanium Silicalite – 1 and aluminophosphates. Metal complexes encapsulated in molecular sieves for the catalytic oxidation of olefins.

3.3 Catalytic and photocatalytic removal of pollutants from aqueous sources – different catalysts used for the removal of inorganics, organics, and microorganisms. Endocrine disrupting chemicals – need for the catalytic degradation, mechanism, different photocatalysts used – pure, mixed and doped metal oxides.

Self study

Catalytic oxidation of alcohols and aromatic hydrocarbons using various catalysts.

Unit 4 : Nanomaterials (10h)

4.1 Nanostructured materials – bottom-up approach and top-down approach with examples, synthesis – physical methods – inert gas condensation, arc discharge, laser ablation. chemical methods – chemical reduction, electrochemical synthesis, thermolysis method – flame spray pyrolysis, sol-gel method, solvothermal and hydrothermal method, chemical vapor deposition –

reaction types, different kinds of CVD techniques – metalloorganic CVD (MOCVD),plasma enhanced CVD, low pressure (LP) CVD, biological methods – use of bacteria, fungi for nanomateirals synthesis,

4.2 Characterization of nanostructures – lithography techniques – electron beam, dip pen, photo lithography, XRD, SEM, EDX, TEM, AFM, STM and SNOM.

4.3 Nanomachines and Nanodevices - Microelectromechanical Systems (MEMS), Nanoelectromechanical Systems (NEMS) - Fabrication, Naodevices and Nanomachines.

4.4 Nanomaterials in energy storage –solar cells (photovoltaics) rechargeable batteries, supercapacitors, hydrogen production, conversion and storage, photoelectrochemical decomposition of water.

Self study

Nanofabrication by replica molding, solvent assisted micromolding, electrical microcontact printing.

Unit 5 Diversity in nano systems (10h)

5.1 Carbon nanotubes – Synthesis and purification – laser ablation, arc discharge, sol-gel, chemical vapor deposition method. single and multiwalled carbon nanotubes – advantages and disadvantages, filling of nanotubes, mechanism of growth, electron structure. Properties of carbon nanotubes – transport, mechanical and physical properties. Applications

5.2 Semiconductor Quantum dots – synthesis – sol-gel, precipitation, hydrothermal, solid state reaction. Electron structure, optical and electrical properties, NLO properties, photon up conversion and anti stokes processes, electron-phonon relaxation, ZnO, TiO_2– pure and doped quantum dots.

5.3 Nanorods – axial and zig zag rods, synthesis - sol-gel, precipitation, hydrothermal, solid state reaction, chemical vapor deposition (CVD). Electron structure, optical, magnetic and electrical properties, NLO properties.

5.4 Biological Nanostructures - biological building blocks – sizes of building blocks and nanostructures, polypeptide nanowires and protein nanoparticle. Biological Nanostructures – examples of proteins, micelles and vesicles, multilayer films

Self study

Social implications of nanoscience and nanotechnology – from first industrial revolution to the nano revolution, issues, nanopolicies, harnessing the concept for economic and social development.

References

1. V. Raghavan, Material Science Engineering, Prutice Hall of India, New Delhi, 1991.
2. C. Kittel, Solidstate Physics, John-Wiley and Sons, NY, 1996.
3. W. L. Jolly, Modern Inorganic Chemistry, Mc Graw Hill Book Company, NY, 1989.
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7. B. Viswanathan, S. Kannan, R. C. Deka, Catalysts and Surfaces-Characterization Techniques, Narosa Publishing House Pvt. Ltd., New Delhi, 2010.
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12. B. Viswanathan, Nanomaterials, Narosa Publishing House Pvt. Ltd., New Delhi, 2009.
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15. Charles P. Poole, Jr., Frank J. Owens, Introduction to Nanotechnology, Wiley Indis (P) Ltd., New Delhi, 2006.
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18. S. Shanmugam, Nanotechnology, MJP Publishers, Chennai, 2010.

MCH 1602: COORDINATION CHEMISTRY AND BIO-INORGANIC CHEMISTRY

M.Phil. Chemistry

Semester – I | No. of Credits : 6

Course : Subject Elective(ES) | No. of hours per week : 6

Unit 1 Study of Metal Complexes

1.1 Introduction - Types of ligand and synthesis by Schiff base - Template synthesis and condensation - Nomenclature of mono and binuclear complexes - Physical measurements - molar conductivity and molecular weight.

1.2 Bonding in metal complexes - Werner's theory, Sidgwick theory, VB theory - Inner sphere and outer sphere complexes. Crystal Field theory- tetrahedral, octahedral, square planar, cubic, trigonalbipyramidal complexes, (Energy level diagram). CFSE evidences of CF splitting - Spinel, Inverse spinel, Variation of ionic sizes of M^{2+} and M^{3+} of first row transition elements, Jahn-Teller effect.

1.3 MO Theory - MO energy level diagram of σ and π - bonding in octahedral complexes, π - back bonding. Spectrochemical series.

1.4 Magnetic properties- Relation between magnetic susceptibility and the geometry of the coordination complexes.

Unit 2 Reaction kinetics of coordination complexes

2.1 Inert or labile complexes: Thermodynamic and kinetic stability – water exchange reactions. Aquation: acid and base hydrolysis – D, A and SN1CB mechanism. Factors influencing the rate of the reactions in octahedral complexes. Reactions due to ligands.

2.2 Substitution reaction - mechanism - Trans effect – Synthetic applications and mechanism of trans effect. Different types of substitution reactions.

2.3 Electron transfer reactions - Inner sphere and outer sphere mechanisms - Marcus theory.

2.4 Photochemistry: Photo physical processes - Florescence and phosphorescence emission. Photo substitution – Adamson's rules – examples. Charge transfer photochemistry.

Unit 3 Organometallic Compounds

3.1 Alkene, allyl complexes, metallocenes - Ferrocene- Structure and bonding in ferrocene- Chemical reaction of vanadocene, nickelocene - Alkenes metathesis, oligomerization

3.2 Heterogeneized, homogenous catalysis - polynuclear supported catalysis. Wilkinson catalysis, Sharpless epoxidation (Ti-isopropoxide, t-BuOOH), McMurry Coupling ($TiCl_3/LiAlH_4$), Pauson-Khand Reaction - $Co_2(CO)_8$, Dotz Reaction – Chromium Carbene, Heck Reaction – $Pd(PPh_3)_4$.

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

Unit 4 Electronic and Molecular Structure

4.1 Electronic spectroscopy – Term symbol- Orgel and Tanaub-Sugano diagram. Evaluation of D_q^{av}, D_qxy and D_q^z values in cobalt (II) octahedral complexes and tetragonaly distorted cobalt (II) octahedral complexes.

4.2 Infrared and Raman Spectroscopy – Structural diagnosis by IR and Raman spectra. IR spectra assignments of prominent functional groups of coordinated ligands in metal complexes, differentiation of isomers. Resonance Raman Spectroscopy – Principle and any two applications.

4.3 Photoelectron and X-ray photoelectron spectroscopy – principle and applications.

4.4 Application of Nuclear Magnetic Resonance Spectroscopy – fluxional behaviour (temperature variation, NMR spectral studies), Nuclear Quadrupole Resonance Spectroscopy; relationship between electric field gradient and molecular structure, applications in inorganic and coordination complexes.

4.5 Mossbauer Spectroscopy: Significance of Isomer shift and quadrupole splitting, application 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.

4.6 Study of chiral coordination compounds by ORD and CD.

<u>Unit 5</u> Bioinorganic chemistry

5.1 Metal storage, transport and bio-mineralisation - Ferritin, trans ferritin, siderophores, sodium potassium balance, sodium potassium balance, Essential and trace metal ions

5.2 Transport proteins: oxygen carriers – haemoglobin - structure, oxygenation and stereochemistry - Bohr effect. Biological redox system: Cytochromes - classification of cytochrome a, b and c, cytochrome- P450. Iron -sulphur proteins - Rubredoxins and ferredoxins, Chlorophylls and photosynthesis.

5.3 Metallo enzymes- zinc enzymes - carboxy peptidase, peroxidase, superperoxide dismutase and copper proteins - haemocyanin, plastocyanin, stellacyanin, azurin.

5.4 Nitrogen fixation via nitride formation, reduction of dinitrogen to ammonia. Photosynthesis- Photosystem I and Photosystem II.

5.5 Chelate therapy- anticancer activity of platinum complexes, mechanism of anitcancer activity of cis DDP, non-activity of trans DDP. Radioisotopes - diagnosis and treatment of radiopharmaceuticals.

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.

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04. A. E. Derome, *Modern NMR techniques for Chemistry Research*, Pergamon Press, 1988.

05. J. E. Huheey, E. A. Kieter and R. L. Keiter, *Inorganic Chemistry*, 4th ed., Harper Collins, New York, 1993.

06. F. A. Cotton, G. Wilkinson, C. Murillo and M. Bochman, *Advanced Inorganic Chemistry*, 6th ed., John Wiley, New York, 1999.

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.

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11. P. T. Kissinger and W. R. Heineman Eds., *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed., Marcel Dekker Inc, New York, 1996.

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13. Keith F. Purcell, John C. Kotz: *An Introduction to Inorganic Chemistry*, Saunders College, 2010.

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MCH 1603: MACROCYCLIC, DENDRITIC AND SUPRAMOLECULAR CHEMISTRY

M. Phil. Chemistry — Credits: 6

Paper-III (Elective Subject) — No. of hours/week: 6

Objectives

1. *To understand the chemistry of macrocyclic compounds, dendrimers and supramolecular compounds*
2. *To identify suitable methodology for the construction of macrocyclic and dendrimer molecules.*
3. *To learn the methodology of designing and developing supramolecular assemblies with desired properties for specific application.*

Unit 1: Macrocyclic Compounds (1+10+1)

1.1 Definition, structure and stability of macrocyclic compounds. Host-Guest chemistry

1.2 Synthesis of macrocyclic ligands by condensation, addition and by coordination template effects.

1.3 Compartmental Ligands: design and synthesis of macrocyclic and nonmacrocyclic binucleating ligands and their complexes.

1.4 Polyaza macrocycles and macrocycles with pendant arms.

1.5 Metal free synthesis of macrocycles; macrocyclic contraction.

Unit 2: Supramolecular Assemblies (1+14+1)

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

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

2.3 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.

2.4 Self-assembling structures-design principles, molecular cubes, squares and boxes; self-assembly of metal arrays; catenanes, rotaxanes and calixarenes.

Unit 3: Dendrimers and Metallodendrimers (1+11+1)

3.1 Evolution of dendrimers, synthetic methodology, divergent and convergent methodologies, types of metallodendrimers, characterization techniques.

3.2 Light harvesting dendrimers and photoactive metallodendrimers.

3.3 Dendrimer encapsulated metal nanoclusters: silver and gold nanoclusters and nanoparticles, quantum dots and their chemical and photochemical properties.

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

Unit 4: Bioinorganic and Medicinal Supramolecular Chemistry (1+12+1)

4.1 Contrast enhancing agents for medical diagnostics: theory of MRI imaging, Gd based contrast agents-synthesis and structural features; optical contrast agents-Ag and AuNPs; metal complexes as photosensitizers.

4.2 Metal complexes for radiotherapy: diagnostic radiopharmaceuticals, nontechnitium for diagnostic imaging, Tc-labelled small molecules and peptides as diagnostic radiopharmaceuticals.

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

Unit 5: Supramolecular Nanostructural devices (1+15+1)

5.1 Molecular scale machines-interlocked macromolecules.

5.2 Chemically-,electrochemically-,and photochemically controllable supramolecular complexes, molecular shuttles, and catenanes.

5.3 Artificial molecular rotors: rotor behavior in non-interacting systems; interacting rotors; rotors in solution-propellers, gears, and cogwheels; rotation in sandwich and nonsandwich porphyrins; light-driven- and chemically driven molecular rotors.

5.4 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.

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

References

1. J. W. Steed, J. L. Atwood, *Supramolecular Chemistry,* John Wiley & Sons Ltd.: New York; 2000.
2. J.-M. Lehn, *Supramolecular Chemistry, Concepts and Prespectives,* VCH: Weinheim; 1995.
3. Izatt, R. M.; Christensen, J. J. Eds. *Synthesis of Macrocycles. The Des'gn of Selective Complexing Agents, Progress in Macrocyclic Chemistry, Vc I.* 3; Wiley-lnterscience: NY, 1987.
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MCH 1604: CORROSION SCIENCE

Semester: 1 **Credits : 6**

Category: Elective Subject (ES) **Hours / week: 6**

Objectives

1. To introduce the purpose and importance of corrosion inhibition in research.

2. To understand the properties and applications of various metals and metal alloys in corrosion research and industries.

3. To learn the ways of characterizing the surface of corrosion metal and metal alloys by various techniques.

4. To explore the various applications of corrosion inhibition efficiency and by learning the basic concepts involved.

Unit1:Introduction to Corrosion (1+8+1h)

1.1 Corrosion- Definition - Causes,effects and Cost of corrosion - Direct and Indirect Costs- economic losses - Human life and safety -Factors influencing corrosion- Factors associated with the metal environment- Material factors , Stress factors ,Time factors .Titanic corrosion.

1.2Classification of corrosion-Chemical or Dry corrosion- Electrochemical or Wet corrosion

1.3Expression of Corrosion rates- conversion and determination.

1.4 Forms of corrosion-General attack corrosion or uniform attack- Galvanic or two metals corrosion,Types of corrosion- Crevice , Pitting , underground soil , intergranular , stress - seasonal cracking of alloys -caustic embrittlement - corrosion fatigue- Selective leaching- Erosion Corrosion-Stress corrosion cracking- Filiform corrosion -Flow assisted Corrosion (FAC) De - alloying -Fretting corrosion - High temperature corrosion.

Unit 2: Thermodynamics of corrosion: (1+10+1 h)

2.1 Introduction-calculation of ΔG and other related thermodynamic parameters - Free energy of corrosion reaction-Standard electrode potentials- Nernst equation- Kinetics of corrosion-Introduction-Ohmic polarization -Corrosion kinetic data.

2.2 Theories of corrosion- Electrochemical theory- Electrochemical Process-Wet or Electrochemical Corrosion-Dry or chemical corrosion - Differential aeration corrosion-Water line corrosion- Fence corrosion-Pitting corrosion.

2.3Mechanism of oxidation corrosion – direct atmospheric effect. Electro chemical corrosion - hydrogen evolution- presence and absence of oxygen.

2.4 Factors influencing corrosion: Primary factors related to metal -Nature of the Metal -Nature of the corroding environment- overvoltage - areas of anodic / cathodic Purity of metal - physical state of metals - passive nature of metal - solubility, Volatility of corrosion products

2.5Surface state of the metal--Nature of the corrosion product - Hydrogen over voltage -pH of the medium - Temperature - Presence of oxidizing agents Humidity nature of the corroding environment - influence of pH - formations of cells - polarization of electrodes.

Unit 3: Theories of inhibition: (1+8+1h)

3.1 Inhibitors - definition – classification of inhibitors - Putilova -Deano - anodic, cathodic and mixed.

3.2 Phosphates and Phosphonates - HEDP, ATMP, ethyl phosphonic acid, 2-carboxyethyl phosphonic acid.

3.3 Adsorption theory and molecular structure - hydrogen over potential and film formation theory - synergistic effect - corrosion inhibition in neutral gaseous environments - chromate, molybdates, nitrite, phosphate, silicate, cations, organic inhibitors carboxylate and tannins.

Unit 4: Methods of evaluation of corrosion efficiency: (1+10+1h)

4.1 Introduction- Methods used in corrosion inhibition study-Weight loss method-Synergism parameter (S_I)- Analysis of variance (F – Test)- Influence of immersion period on inhibition efficiency of L-Try – Zn^{2+} system- Influence of pH on the inhibition efficiency of L-Try – Zn^{2+} system-- Influence of sodium dodecyl sulphate (SDS) on the inhibition efficiency of L-Try – Zn^{2+} system.

4.2 Potentiodynamic polarization study - Potentiodynamic polarization measurements corrosion current, corrosion potential, cathodic and anodic polarization.Charge AC transfer resistance, impedance measurement - double layer capacitance – Nyquist plot, Bode plot, impedance value - Cyclic voltammetry.

4.3 Rate of corrosion-Potential measurement - electrochemical series - redox reactions-emf measurement and corrosion current - anodic and cathodic behavior of metals -passivity - testing of virgin metals - alloy - Pourbaix and Evans diagrams.

4.4 Surface analysis- XRD, SEM, EDX, TEM, AFM.

Unit 5: Prevention and control ; (1+8+1h)

5.1 Methods of corrosion prevention and control- Active, Passive, Permanent and Temporary corrosion protection.

5.2 Classification of corrosion control method - corrosion control by modification of environment- Paints - Component and their function.

5.3 Protection from corrosion -Surface treatments-Applied coatings- Anodization- Biofilm coatings Modification of environment - deaeration - dehumidification - inhibitors - protective coatings - preparation of materials forcoating -metallic and non-metallic - organic coatings -special paints -varnish, enamel and lacquers**.**

5.4 Metallic coating, Electroplating - Mechanism of Cathodic protection- Sacrificial anodicand Impressed current cathodic protection method.

5.5Corrosion removal-Design -selection of materials - pure metals and alloys annealing – Controlled permeability frame work elimination ofgalvanic action.

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Journal of Bio- and Tribo-Corrosion

Editors-in-Chief: M.M. Stack; M.T. Mathew; Y. Tian
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11 M.M. Stack; M.T. Mathew; Y. Tian Journal of Bio- and Tribo-Corrosion

MCH 1605: PHYTOCHEMSITRY

M.Phil. Elective Subject Credits: 6

Hours Per Week:6

Objectives:

1. To learn the basic and new approaches to natural product chemistry
2. To know the pharmaceutical and pharmacological applications of natural products
3. To understand the chemistry of natural products with the aid of biotechnological tools and analytical techniques.

Unit 1: ORIGIN OF PRIMARY AND SECONDARY METABOLITES (1+8+1 Hours)

1.1 Types and definition of metabolites, Acetate pathway: polyketides, Shikimate pathway: phenylpropanoids, Mevalonate pathway: terpenoids and steroids

1.2 Basic concepts of primary metabolites: carbohydrates, proteins, lipids, and nucleic acids (classification, molecular structure and nomenclature)

1.3. Basic concepts of secondary metabolites: alkaloids, terpenoids and steroids, tannins, lignins,coumarin phenolic compounds and flavanoids. (classification, molecular structure and nomenclature)

1.4 Phyto harmones: auxin, gibberallin, cytokinin, micro RNAs, brassinolide, abscisic acid, tannins, lignins, phenolic compounds and flavanoids (structure and functions)

1.5. Examples of isolated compounds, (5 each for each secondary metabolite by survey from research articles) their plant origin, and their medicinal uses: Natural products in cancer therapy: antibiotics (dactinomycin), vinca alkaloids(vincristine and vinblastine) biological response modifiers (interleukin-2, alpha, beta and gama interferons , enzymes, epipodophyllotoxins(etoposide and teniposide), palitaxel

Unit 2 : BIOSYNTHESIS (1+10+1 hours)

2.1. Biosynthesis of sucrose in the cytosol, starch, (degradation of starch), Fructose, Cellulose and alkaloids (nicotine and cocaine), phenolics and flavanoids

2.2 Formation of alkaloids from amino acids: cocaine, (-)-hyoseyamine, senecionine, pseudopelletierine, (-)- sparteine, Mescaline, (s)-reticuline, (+)-tubocurarine

2.3 Formation of trans cinnamic acid, Isoterpenoids: isophenyl diphosphate and Isopentenyl pyrophosphate

2.4 Polyketides in Fungi: orsellinic and 6-methylsalicylic (6-MSA) acids, polycyclic aromatics such as citrinin , alternariol , islandicin ,deoxyherqueinone , and norsolorinic acid Generic polyketide assembly pathway reactions catalyzed by iterative fungalpolyketide synthases. the assembly sequence for the squalesatin tetraketide intermediate

2.5 Coenzyme Biosynthesis of Iron/Sulfur Clusters: inorganic cofactors

Unit 3: SECONDARY METABOLITES IN CHEMICAL BIOLOGY (1+12+1 Hours)

3.1 *In-vitro* production of secondary metabolites: screening and selection of highly productive cell lines
3.2 Plant ABC transporters in the cellular transport of alkaloids, terpenoids, phenol, wax-Modulation of ABC transporter by plant secondary metabolites
3.3 Organ cultures as a source of pharmaceuticals, hairy root culture for pharmaceuticals, production of foreign proteins in transgenic plants , vaccines
3.4 Manipulation of nutrients to improve yield, Elicitation: stimulators of secondary metabolites, permiabilisation, *in situ* product removal
3.5 Immobilisation of plant cells for the production of secondary metabolites, Scale up cell cultures, Natural Products produced from plant cell culture

Unit 4: PRODUCTION AND RETROSYNTHESIS OF SECONDARY METABOLITES (1+12 +1 Hours)

4.1 Metabolic Path ways: Approaches to increase production
4.2 Strategies using genetic manipulation, role of genetic Engineering in biosynthesis of flavonoid, anthocyanin, alkaloids, terpenoids and carotenoids
4.3 Synthesis of grevillin, and 2-methyoxystypandrone, Production of tajixanthane and shamixanthane
4.4 synthesis of carminic acid, Conversion of confertifolin into warburganat, Biochromophoric molecules: a systematic investigation of alphanitrocarbonyl compounds using steroids as substrates
4.5 Stork's reserpine synthesis, Enantioselective routes to yohimbine systems, Synthesis of bis-tetrahydrofuran from monensin A

Unit 5: PHYTOCHEMICAL TECHNIQUES (1+10 +1 hours)

5.1 Extraction procedures, types of extractions, solvent choice
5.2 Phytochemical screening of phytochemicals
5.3 General methods of quantification of secondary metabolites alkaloids, terpenoids, tannins, lignins, phenolic compounds and flavanoids.
5.4 Indian Pharmacopeia : Pharmacognostic procedures (fluorescent behaviour, ash values of various types, presence of elements) islolation of peperine, aspirin, lycopene, hesperdin, trimyristin, stigmasterol
5.5 Chromatography, electrophoresis, and Spectroscopy for phytochemical analysis: TLC, Column Chromatography, HPLC, HPTLC, GC-MS study of any two new molecules specifically, Configuration of ethylidene of alkaloid dehydrovoachalotine, *in-vivo* NMR spectroscopy, Mass spectrometric fragmentation patterns for natural products, spectrometric identification of molecules $C_6H_{12}S_2$, $C_{10}H_{14}O$, General methods of structural elucidation of

natural products alkaloid, terpenoid, flavanoid and steroid, electrophoretic evaluation of quality of high molecular weight DNA isolated from plant material.

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