SEMESTER-VI

BSC. (HONS.) CHEMISTRY

DISCIPLINE SPECIFIC CORE COURSE -16 (DSC-16): Principles in Qualitative Analysis and Bioinorganic Chemistry

CREDIT DISTRIBUTION, ELIGIBILITY AND PRE-REQUISITES OF THE COURSE

Course title & Code	Credits	Credit distribution of the course			Eligibility criteria	Pre-requisite of the course (if any)
		Lecture	Tutorial	Practical/ Practice		
Principles in Qualitative Analysis and Bioinorganic Chemistry (DSC-16: Inorganic Chemistry -VI)	**04**	**02**	**--**	**02**	Class 12th with Physics, Chemistry, Mathematics	**--**

Learning Objectives

The Objectives of this course are as follows:

- To discuss the principles of qualitative analysis
- To understand the concept of solubility products and the common ion effect on the separation of cations.
- To discuss the importance of metal ions in biological systems.
- To discuss the applications of iron in physiology, including iron transport and storage.

Learning Outcomes:

By the end of the course, the students will be able to:

- Explain the basic principles of qualitative inorganic analysis.
- Discuss the influence of solubility products and the common ion effect on the separation of cations.
- Discuss the identification of interfering anions and their removal.
- Explain and discuss the importance of metal ions in biological systems, through discussions on
  metal-containing enzymes, the sodium-potassium pump.
- Discuss the applications of iron in physiology, including iron transport and storage system.

Unit-1: Theoretical Principles in Qualitative Analysis (Hours: 12)

Basic principles involved in analysis of cations and anions. Solubility product, common-ion effect. Principles involved in separation of cations into groups and choice of group reagents. Interfering anions (fluoride, borate, oxalate and phosphate), need to remove them after Group II and methods of removal. Analysis of insoluble substances.

Unit-2: Bioinorganic Chemistry (Hours: 18)

Metal ions present in biological systems, classification of elements according to their action in biological system. Geochemical effect on the distribution of metals. Sodium / potassium pump, conduction of nerve impulses, Ca-pump, carbonic anhydrase and carboxypeptidase. Excess and deficiency of some trace metals. Toxicity of metal ions (Hg, Pb, Cd and As), reasons for toxicity, Use of chelating agents in medicine, Cisplatin as an anti-cancer drug.

Iron and its application in bio-systems, Haemoglobin, Myoglobin, cytochrome-C-oxidase ; Storage and transfer of iron.

Practical: Credits: 02

(Laboratory periods: 15 classes of 4 hours each)

(A) Qualitative semi-micro analysis of mixtures containing 3 anions and 3 cations. Emphasis should be given to the understanding of the chemistry of different reactions. The following radicals are suggested:
CO_3^{2-}, NO_2^-, S^{2-}, SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, CH_3COO^-, F^-, Cl^-, Br^-, I^-, NO_3^-, BO_3^{3-}, $C_2O_4^{2-}$, PO_4^{3-}, NH_4^+, K^+, Pb^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}, Sn^{2+}, Sb^{3+}, Fe^{3+}, Al^{3+}, Cr^{3+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}

(B) Mixtures should preferably contain one interfering anion, or insoluble component ($BaSO_4$, $SrSO_4$, $PbSO_4$, CaF_2 or Al_2O_3) or combination of anions e.g. CO_3^{2-} and SO_3^{2-}, NO_2^- and NO_3^-, $Cl^-$and Br^-, Cl^- and I^-, Br^- and I^-, NO_3^- and Br^-, NO_3^- and I^-. Spot tests should be done whenever possible.

Essential/recommended readings

1. Svehla, G. (1996), **Vogel's Qualitative Inorganic Analysis**,7th Edition, Prentice Hall.
2. Huheey, J.E.; Keiter, E.A., Keiter; R. L.; Medhi, O. K. (2009), **Inorganic Chemistry Principles of Structure and Reactivity**, Pearson Education.
3. Lippard, S.J.; Berg, J.M. (1994), **Principles of Bioinorganic Chemistry**, Panima Publishing Company.
4. *Biological Inorganic Chemistry* by **RR Crichton** in additional books
5. *Bioinorganic Chemistry- Inorganic Elements in the Chemistry of Life: An Introduction and Guide*, 2nd Edition by **Wolfgang Kaim, Brigitte Schwederski, Alex Klein**
6. Atkins, P.W.; Overton, T.L.; Rourke, J.P.; Weller, M.T.; Armstrong, F.A. (2010), 5th Edition, Oxford University Press.

Note: Examination scheme and mode shall be as prescribed by the Examination Branch, University of Delhi, from time to time.

DISCIPLINE SPECIFIC CORE COURSE – 17 (DSC-17): Polynuclear Hydrocarbons, Photochemistry, Pericyclic Reactions, and Spectroscopy of Organic Compounds

CREDIT DISTRIBUTION, ELIGIBILITY AND PRE-REQUISITES OF THE COURSE

Course title & Code	Credits	Credit distribution of the course			Eligibility criteria	Pre-requisite of the course (if any)
		Lecture	Tutorial	Practical/ Practice		
Polynuclear Hydrocarbons, Photochemistry, Pericyclic Reactions, and Spectroscopy of Organic Compounds (DSC-17, Organic Chemistry-VI)	04	03	--	01	Class 12th with Physics, Chemistry	-

Learning objectives

The objectives of this course are as follows:

- To provide thorough knowledge of the chemistry of polynuclear hydrocarbons .
- To detail the basic principles and applications of pericyclic reactions and photochemistry
- To familiarize students with the various tools and techniques for identifying and characterizing the organic compounds through their interactions with electromagnetic radiations *viz.* UV-Visible, IR and NMR spectroscopy.

Learning outcomes

By studying this course, students will be able to:

- Discuss and use the chemistry of polynuclear hydrocarbons for application in real world problems.
- Discuss and use the pericyclic reactions and photochemistry for research and other applications.
- Use spectroscopic techniques to determine structure and stereochemistry of known and unknown compounds.

SYLLABUS OF DSC-17

Unit-1: Polynuclear Hydrocarbons **(Hours: 6)**

Introduction, classification, structure, nomenclature and uses. Aromaticity of polynuclear hydrocarbons, structure elucidation of Naphthalene and general methods of preparation of naphthalene and anthracene (including Haworth method, Friedel Craft acylation, Diels Alder reaction, Elbs reaction). Relative reactivity of naphthalene and anthracene in comparison to benzene.

Discussion on the following reactions (with mechanism) for Naphthalene and Anthracene: Addition reactions, Oxidation, Electrophilic substitution- Friedel Craft reaction, Chloromethylation, Halogenation, Formylation, Nitration and sulphonation. Reduction reaction and Diels Alder reaction.

Unit-2: **Photochemistry and Pericyclic reactions** **(Hours: 12)**

Photochemistry

Introduction and basic principles of photochemistry, photochemical energy, photolytic cleavage, photochemistry of carbonyl compounds (Norrish type 1, Norrish type 2 and Peterno Buchi reactions)

Pericyclic Reactions

Introduction: Types of pericyclic reactions (Electrocyclic, Cycloaddition and Sigmatropic Rearrangements), Symmetry in σ and π molecular orbitals, Frontier Molecular Orbitals.

Electrocyclic Reactions: Conrotatory and Disrotatory motion in ring opening and ring closing reactions in (4n) and (4n+2) π electron systems, FMO method, Woodward Hoffmann rule.

Cycloaddition Reactions: [2+2] and [4+2] π cycloaddition reactions, Diels Alder reaction (electron rich and electron poor dienes and dienophiles, Stereochemistry, Alder rule of endo addition).

Sigmatropic Reactions: [1,3], [1,5] and [3,3] sigmatropic rearrangements, Cope rearrangement, Claisen Rearrangements.

Unit-3: **Spectroscopy of Organic Compounds** **(Hours: 27)**

UV-Visible Spectroscopy: Types of electronic transitions, λ_{max}, chromophores and Auxochromes, bathochromic and hypsochromic shifts, intensity of absorption, factors affecting λ_{max} values, application of Woodward Rules for calculation of λ_{max} for the following systems: α, β-unsaturated aldehydes, ketones, carboxylic acids and esters; conjugated dienes: alicyclic, homoannular and heteroannular; Extended conjugated systems (aldehydes, ketones and dienes); distinction between *cis* and *trans* isomers by UV; Colour concept, Theory of colour and constitution-Witt's theory, valence bond and molecular orbital theory.

IR Spectroscopy: Fundamental and non-fundamental molecular vibrations; IR absorption positions of O and N containing functional groups; effect of H-bonding, conjugation, resonance and ring size on IR absorptions; fingerprint region and its significance, application of IR in functional group analysis.

^{1}H-NMR Spectroscopy: Basic principles of proton magnetic resonance, chemical shift and factors, influencing it; equivalent and non-equivalent protons (chemical and magnetic equivalence), Spin–Spin coupling and coupling constant; Anisotropic effects in alkene, alkyne, aldehydes and aromatics. Interpretation of NMR spectra of simple compounds containing AX, AX_2, AX_3, A_2X_3 spin systems, special case of 1-nitropropane.

Applications of IR, UV and ^{1}H-NMR Spectroscopy for identification of simple organic compounds (spectra to be provided for some representative compounds).

Practical component

Practical: **Credits: 01**

(Laboratory periods: 15 classes of 2 hours each)

1. Systematic qualitative analysis of the given organic compounds containing monofunctional groups (Aryl halides, nitro compounds, amines and amides) and simple

bifunctional compounds like salicylic acid, cinnamic acid, *p*-nitro phenol etc. and preparation of one suitable crystalline derivative.

2. Differentiation between of *o*-/*p*-hydroxybenzaldehyde by IR spectroscopy (Spectra to be provided).
3. Differentiation between of benzoic acid and cinnamic acid by UV spectroscopy (Spectra to be provided).

Essential/recommended readings

Theory:

1. Morrison, R. N., Boyd, R. N., Bhattacharjee, S.K. (2010), **Organic Chemistry**, 7th Edition, Dorling Kindersley (India) Pvt. Ltd., Pearson Education.
2. Finar, I.L. **Organic Chemistry** Volume 1, Dorling Kindersley (India) Pvt. Ltd., Pearson Education.
3. Finar, I.L. **Organic Chemistry** Volume 2, Dorling Kindersley (India) Pvt. Ltd., Pearson Education.
4. Solomons, T.W.G., Fryhle, C.B.; Snyder, S.A. (2017), **Organic Chemistry**, 12th Edition, Wiley.
5. Silverstein R.M. (2005), **Spectrometric Identification of organic compounds**, 7th edition, John Wiley and Sons,
6. Kemp W. (2019), **Organic Spectroscopy**, Third Edition, MacMillan.
7. Pavia, D. (2015), **Introduction to Spectroscopy**, Fifth Edition, Cengage Learning India Pvt. Learning.
8. Scheinmann, F., **Introduction to spectroscopic methods for identification of organic compounds**, Volume 2, Pergamon Press.
9. Ahluwalia, V.K., Parashar, R.K. (2011), **Organic Reaction Mechanisms**, 4th Edition, Narosa Publishing House.
10. Horspool, W.M. (1976) **Aspects of Organic Photochemistry**, Academic Press.
11. Singh J, Awasthi S K, Singh J, **Fundamentals of Organic Chemistry**, Pragati Prakashan Meerut.

Practical:

1. Vogel, A.I. (2012), **Quantitative Organic Analysis**, Part 3, Pearson Education.
2. Mann, F.G., Saunders, B.C. (2009), **Practical Organic Chemistry**, Pearson Education.
3. Furniss, B.S., Hannaford, A.J., Smith, P.W.G., Tatchell, A.R. (2012), **Vogel's Textbook of Practical Organic Chemistry**, Fifth Edition, Pearson.
4. Ahluwalia, V.K., Dhingra, S. (2004), **Comprehensive Practical Organic Chemistry: Qualitative Analysis**, University Press.
5. Ahluwalia, V.K., Aggarwal, R. (2004), **Comprehensive Practical Organic Chemistry: Preparation and Quantitative Analysis**, University Press
6. Pasricha, S., Chaudhary, A. (2021), **Practical Organic Chemistry: Volume–I**, I K International Publishing house Pvt. Ltd, New Delhi
7. Pasricha, S., Chaudhary, A. (2021), **Practical Organic Chemistry: Volume–II**, I K International Publishing house Pvt. Ltd, New Delhi

DISCIPLINE SPECIFIC CORE COURSE-18 (DSC-18): Photochemistry and Spectroscopy

CREDIT DISTRIBUTION, ELIGIBILITY AND PRE-REQUISITES OF THE COURSE

Course title & Code	Credits	Credit distribution of the course			Eligibility criteria	Pre-requisite of the course (if any)
		Lecture	Tutorial	Practical/ Practice		
Photochemistry and Spectroscopy (DSC-18, Physical Chemistry VI)	**04**	**02**	**-**	**02**	**Class XII with Physics, Chemistry and Mathematics**	

Learning Objectives:

The Learning Objectives of this course are as follows:

- To make students understand the laws of photochemistry and their applications
- To understand the basis of molecular spectroscopy
- To study different types of spectroscopic techniques and their applications

Learning Outcomes:

By studying this course, students will be able to:

- Explain low and high quantum yield
- Explain photosensitized reactions
- Apply the concept of quantization to spectroscopy.
- Interpret various types of spectra and know about their application in structure elucidation

SYLLABUS OF DSC-18

Unit-1: Introduction to Molecular Spectroscopy and Photochemistry (Hours: 6)

Interaction of electromagnetic radiation with molecules and various types of spectra; Born Oppenheimer approximation.

Characteristics of electromagnetic radiation. Lambert-Beer's law and its limitations, physical significance of absorption coefficients. Laws of photochemistry, quantum yield, actinometry, examples of low and high quantum yields, photochemical equilibrium and the differential rate of photochemical reactions, photosensitized reactions, quenching. Role of photochemical reactions in biochemical processes, photostationary states, chemiluminescence.

Unit-2: Rotational, Vibrational , Raman and Electronic Spectroscopy (Hours: 14)

Rotational spectroscopy: Selection rules, intensities of spectral lines, determination of bond lengths of diatomic molecules, isotopic substitution, classification of molecules based on moment of inertia, applications of rotation spectroscopy (e.g. microwave appliances)

Vibrational spectroscopy: Classical equation of vibration, computation of force constant, amplitude of diatomic molecular vibrations, anharmonicity, Morse potential, dissociation energies, fundamental frequencies, overtones, hot bands, degrees of freedom for polyatomic molecules, modes of vibration, concept of group frequencies.

Vibration-rotation spectroscopy: diatomic vibrating rotator, P, Q, R branches.

Raman spectroscopy: Qualitative treatment of Rotational Raman effect; effect of nuclear spin, Vibrational Raman spectra, Stokes and anti-Stokes lines; their intensity difference, rule of mutual exclusion.

Electronic spectroscopy

Franck-Condon principle, electronic transitions, singlet and triplet states, Jablonski diagrams, fluorescence and phosphorescence, dissociation and predissociation, calculation of electronic transitions of polyenes using free electron model.

Unit-3: NMR and ESR (Hours: 10)

Nuclear Magnetic Resonance (NMR) spectroscopy: Principles of NMR spectroscopy, Larmor precession, chemical shift and low-resolution spectra, different scales (δ and T), spin-spin coupling and high resolution spectra, interpretation of PMR spectra of simple organic molecules like methanol, ethanol and acetaldehyde.

Principles of ESR spectroscopy, hyperfine structures, ESR of simple radicals

Practical component

Practical: Credits: 02

(Laboratory periods: 15 classes of 4 hours each)

(A) Colorimetry :

1. Verify Lambert-Beer's law and determine the concentration of (i) $CuSO_4$ (ii) $KMnO_4$ (iii) $K_2Cr_2O_7$ in a solution of unknown concentration

2. Determine the concentrations of $KMnO_4$ and $K_2Cr_2O_7$in a mixture.
3. Study the kinetics of iodination of propanone in acidic medium.
4. Determine the amount of iron present in a sample using 1,10-phenathroline.
5. Determine the dissociation constant of an indicator (phenolphthalein).
6. Study the kinetics of interaction of crystal violet/ phenolphthalein with sodium hydroxide

(B) UV/Visible spectroscopy:

1. Study the 200-500 nm absorbance spectra of $KMnO_4$ and $K_2Cr_2O_7$ (in 0.1 M H_2SO_4) and determine the λ_{max} values. Calculate the energies of the two transitions in different units (J molecule^{-1}, kJ mol^{-1}, cm^{-1}, eV).
2. Study the pH-dependence of the UV-Vis spectrum (200-500 nm) of $K_2Cr_2O_7$.
3. Record the 200-350 nm UV spectra of the given compounds (acetone, acetaldehyde, 2- propanol, acetic acid) in water. Comment on the effect of structure on the UV spectra of organic compounds.

(C) Analysis of the given vibration-rotation spectrum of HCl(g)

Essential/recommended readings

Theory:

1. Banwell, C.N.; McCash, E.M. (2006), **Fundamentals of Molecular Spectroscopy**, Tata McGraw- Hill.
2. Kapoor, K.L. (2015), **A Textbook of Physical Chemistry**, McGraw Hill Education, Vol 4, 5th Edition, McGraw Hill Education.
3. Kakkar, R. (2015), **Atomic & Molecular Spectroscopy**, Cambridge University Press.

Suggested Readings:

1. Engel, T.; Reid, P. (2013), **Quantum Chemistry and Spectroscopy**, Pearson

Practical:

1. Khosla, B.D.; Garg, V.C.; Gulati, A. (2015), **Senior Practical Physical Chemistry**, R. Chand & Co, New Delhi.
2. Garland, C. W.; Nibler, J. W.; Shoemaker, D. P. (2003), **Experiments in Physical Chemistry**, 8th Edition, McGraw-Hill, New York
3. Kapoor, K.L. (2019), **A Textbook of Physical Chemistry**, Vol.7, 1st Edition, McGraw Hill Education.

Note: Examination scheme and mode shall be as prescribed by the Examination Branch, University of Delhi, from time to time.