

UNIVERSITY OF MUMBAI



Syllabus for Sem V & VI

Program: B.Sc.

Course: CHEMISTRY (Three Units)

(Credit Based Semester and Grading System
with effect from the academic year 2013–2014)

T. Y. B.Sc. CHEMISTRY (Three Units)**Credit Based and Grading System****To be implemented from the Academic year 2013-2014****SEMESTER V****Theory**

| Course | UNIT | TOPICS | Credits | L / Week |
|-----------------|-------------|---|----------------|-----------------|
| US3CH501 | I | 1.1 Colligative Properties of Dilute Solutions (8L) 1.1.1 Dilute solution, colligative properties, Raoult's law, relative lowering of vapour pressure. 1.1.2 Elevation in boiling point of a solution, thermodynamic derivation relating elevation in the boiling point of a solution and the molar mass of the non-volatile solute. 1.1.3 Depression in freezing point of a solution, thermodynamic derivation relating the depression in the freezing point of a solution and the molar mass of the non-volatile solute. 1.1.4 Osmotic pressure, van't Hoff's equation for osmotic pressure, (derivation is expected) and determination of molar mass of the solute. Abnormal molar masses of solutes and van't Hoff factor (calculation of Degree of Association and Degree of Dissociation.) 1.2 Phase Rule (7L) 1.2.1 Gibb's phase rule and terms involved in the equation. 1.2.2 Application of phase rule to ONE component systems (i) water system, (ii) sulphur system 1.2.3 Application of phase rule to TWO component systems, condensed systems, condensed phase rule, eutectic systems (Lead-Silver system), desilverisation of lead. 1.2.4 Introduction to three component system, explanation of phase diagram for three liquids forming one immiscible pair. | 2.5 | 1 |
| | II | 2 Electrochemistry – Electrochemical cells (15L) | | 1 |

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| | | <p>2.1 Lewis concept of Activity and Activity coefficient, Mean ionic activity and mean ionic activity coefficient γ_{\pm} of an electrolyte, expression for activities of electrolytes of different valence type, ionic strength of a solution, Debye-Huckel limiting law (derivation not expected)</p> <p>2.2 Classification of cells: 1.chemical cells without transference 2.Concentration cells with and without transference (derivations of expression for concentration cell EMF are expected) Origin of liquid-liquid junction potential and its elimination using a salt bridge.</p> <p>2.3 Applications of EMF .measurements in the determination of 1. pH of a solution using quinhydrone and glass electrode. 2 solubility and solubility product of sparingly soluble salts using chemical cell and concentration cell method 3. determination of liquid-liquid junction potential .</p> | | |
| | III | <p>3 Chemical Bonding And Solid State Chemistry (15L)</p> <p>3.1 Molecular Symmetry (10L) 3.1.1 Introduction and Importance. 3.1.2 Symmetry elements and symmetry operations. 3.1.3 Concept of a Point Group with illustrations using the following point groups: (i) C_{av} (HCl), (ii) D_{ah} (H_2), (iii) C_{2v} (H_2O), (iv) C_{3v} (NH_3), (v) C_{2h} (trans – trichloroethylene), and (vi) D_{3h} (BCl_3).</p> <p>3.2 Molecular Orbital Theory for Polyatomic Species (5L) 3.2.1 Simple triatomic species: H_3^+ and H_3 (correlation between bond angle and Molecular orbitals). 3.2.2 Other molecules (considering only σ-bonding): i) BeH_2, ii) H_2O.</p> | | 1 |
| | IV | <p>4. Solution Chemistry</p> <p>4.1 Acid-base Chemistry in Aqueous Medium (8L) 4.1.1 Acidity of mono- and polyatomic cations. 4.1.2 Basicity of mono- and polyatomic anions (discussion for 4.1.1 as well as</p> | | 1 |

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| | | <p>4.1.2 to Include Latimer equation and predominance diagrams).</p> <p>4.2 Chemistry in Non-aqueous Solvents (7L)</p> <p>4.2.1 Classification of solvents and importance of non-aqueous solvents.</p> <p>4.2.2 Characteristics and study of liquid ammonia, dinitrogen tetroxide and acetic acid as non-aqueous solvents with respect to (i) acid-base reactions and (ii) redox reactions.</p> | | |
| US3CH502 | I | <p>1. Mechanism of Organic Reactions (15L)</p> <p>1.1. Thermodynamic and Kinetic control of organic reactions: Concept with mechanisms of the following reactions: addition of HX to butadiene; sulfonation of naphthalene. Nucleophilicity/ electrophilicity vs Basicity/acidity.</p> <p>1.2 Mechanism of elimination reactions, with stereochemistry: E1 and E2 reactions: regioselectivity (Saytzeff and Hofmann rules).</p> <p>1.3 Mechanism of reactions of carbonyl compounds with nucleophiles: 1.3.1 Formation of acetals/ketals from aldehydes and ketones. 1.3.2 Reaction of aldehydes and ketones with primary and secondary amines. 1.3.3 Acyl nucleophilic substitution (tetrahedral mechanism): Acid catalysed esterification of Carboxylic acids and base promoted hydrolysis of esters.</p> <p>1.4 Mechanism of rearrangements with examples and stereochemistry wherever applicable. 1.4.1 Migration to electron deficient carbon: Pinacol, Benzylic acid. 1.4.2 Migration to electron deficient nitrogen: Beckmann, Hofmann.</p> <p>1.5 Mechanism of the following reactions with synthetic application: Claisen condensation, Michael addition.</p> | 2.5 | 1 |
| | II | <p>2.1 Heterocyclic Chemistry (8L)</p> <p>2.1.1 Introduction: Electronic structure and aromaticity of furan, pyrrole, thiophene and pyridine.</p> <p>2.1.2 Synthesis: Synthesis of furans,</p> | | |

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| | | <p>pyrroles, and thiophenes by Paal-Knor synthesis. Pyridines by Hantzsch synthesis and from 1,5-diketones.</p> <p>2.1.3 Reactivity: Reactivity towards electrophilic substitution reactions- of furan, pyrrole and thiophene on basis of stability of intermediate; and of pyridine on the basis of electron distribution. Nucleophilic substitution reaction of pyridine on the basis of electron distribution.</p> <p>2.1.4 Reactions of heterocycles: The following reactions of furan, pyrrole and thiophene: Halogenation, Nitration, Sulphonation, Vilsmeier formylation reaction, Friedel-Crafts reaction. Furan: Diels-Alder reaction. Ring opening of furan. Pyrrole: Acidity and basicity of pyrrole-Comparison of basicity of pyrrole and pyrrolidine, Acid catalyzed polymerization of pyrrole. Pyridine: Basicity. Comparison of basicity of pyridine, pyrrole and piperidine. Sulphonation of pyridine, with and without catalyst. Reduction. Oxidation of alkyl pyridines and action of sodamide (Chichibabin reaction). N-methylation of pyridine. Quaternization of piperidine, pyrrolidine and Hofmann elimination of the quaternary salts.</p> <p>2.2. Organic Synthesis (7L)</p> <p>2.2.1 Introduction: Criteria for ideal organic synthesis. Yield and selectivity. Multi- component synthesis – with examples, Mannich reaction, Hantzsch synthesis of pyridines (without mechanism).</p> <p>2.2.2 Illustrative synthesis of industrially important compounds: Ibuprofen (chiral synthesis), paracetamol (green synthesis), L-ascorbic acid (from D-glucose), norfloxacin, thyroxine, vanillin, methyl dihydrojasmonate (Hedione), Bifenox-I, pigment red 242, indigo, 2-hydroxy-3-amino-5-nitrobenzene sulphonic acid.</p> <p>2.2.3 Newer methods of organic synthesis: Introduction to the use of the following in organic synthesis: Ultrasound, microwaves, PTC.</p> | | |
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| | <p style="text-align: center;">III</p> | <p>3. Treatment of analytical data-I and sampling (15 L) 3.1 Treatment of Analytical Data (7L) Types of errors, determinate and indeterminate errors, minimization of errors, constant and proportionate errors, accuracy and precision, measures of dispersion and central tendency: mean, median, average deviation, relative average deviation, standard deviation, variance, coefficient of variation.[Numerical problems expected] 3.2 Sampling (8L) Terms involved, importance of sampling, sampling techniques, sampling of gases, ambient and stack sampling, equipment used, sampling of homogeneous and heterogeneous liquids, sampling of static and flowing liquids, methods and equipments used, sampling of solids, importance of particle size and sample size, samples used, need for the reduction in the sample size, methods of reduction in sample size, collection, preservation and dissolution of the sample.</p> | | <p>1</p> |
| | <p style="text-align: center;">IV</p> | <p>4. Titrimetric analysis-I and UV-Visible spectroscopy. (15L) 4.1 Acid-base Titrations (5L) Construction of titration curves and choice of indicators in the titration of [1] strong acid and strong base, [2] strong acid and weak base, [3] weak acid and strong base, [4] weak acid and weak base. 4.2 Precipitation titrations (4L) Argentometric titrations, construction of the titration curve, Volhard's method, Mohr's method, adsorption indicators, theory and applications. 4.3 U.V. Visible Spectroscopy (4L) Photometers and spectrophotometers, Instrumentation in the case of single and double beam spectrophotometers, Qualitative and quantitative analysis, calibration curve method.</p> | | <p>1</p> |

Practicals

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| US3CHP05 | <p><u>Physical Chemistry Practicals</u></p> <p>Chemical Kinetics – 1. To determine the order between $K_2S_2O_8$ & KI by fractional change method.</p> <p>Potentiometry – 2. To determine the solubility product and solubility of AgCl potentiometrically using chemical cell.</p> <p style="text-align: center;">OR</p> <p>3. To determine the solubility product and solubility of AgCl potentiometrically using concentration cell.</p> <p>Colorimetry – To determine the amount of Fe(III) present in the given solution by using salicylic acid by colorimetric titration.(static method) ($\lambda=525$ nm)</p> <p><u>Inorganic Chemistry Practicals</u></p> <p>Inorganic preparations 1. $Tris(en)_2Ni(II)S_2O_3$ 2. Tetra-amminecopper (II)Sulphate</p> <p>Inorganic estimation/analysis 1. Ni complexometrically using Murexide indicator</p> | 1.5 | 4 |
| US3CHP06 | <p><u>Organic Chemistry Practicals</u> Binary Mixture Separation, drying, weighing & Melting Point (No identification) (Solid + Solid) (4 Expts)</p> <p><u>Analytical Chemistry Practicals</u> 1. Estimation of persulphate in the given sample by the method of back titration. 2. Determination of Vitamin C content of a given tablet by titration with sodium hydroxide pH metrically</p> | 1.5 | 4 |

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SEMESTER VI
Theory

| Course | UNIT | | Credits | L / Week |
|----------|------|--|---------|----------|
| US3CH601 | I | <p>1 Molecular Spectroscopy (15 L)</p> <p>1.1 Dipole moment: Dipole moment, polarization of a bond, bond moment, dipole moment and molecular structure.</p> <p>1.2 Rotational Spectrum: Rotational spectrum of a diatomic molecule, rigid rotor, moment of inertia, energy levels, conditions for obtaining pure rotational spectrum, selection rule, nature of spectrum, determination of inter nuclear distance and isotopic shift.</p> <p>1.3 Vibration (IR) spectrum: Vibrational motion, degrees of freedom, modes of vibration, vibrational spectrum of a diatomic molecule, simple harmonic oscillator, energy levels, zero point energy, conditions for obtaining vibrational spectrum, selection rule, nature of spectrum.</p> <p>1.4 Vibration-Rotation spectrum of diatomic molecule vibrating rotor, energy levels, selection rule, nature of spectrum, R and P branches, anharmonic oscillator : energy levels, selection rule, fundamental band, overtones . Application of vibration-rotation spectrum in determining Force constant, determination and significance. Introduction to infrared spectra of simple molecules like H₂O and CO₂</p> <p>1.5 Raman Spectroscopy : Scattering of electromagnetic radiation, Rayleigh scattering, Raman scattering, nature of Raman spectrum , Stoke's lines, anti-Stoke's lines, Raman shift, quantum theory of Raman spectrum, comparative study of IR and Raman spectra, rule of mutual exclusion.(example of CO₂molecule).</p> | 2.5 | 1 |
| | II | <p>2.1 Renewable Energy Sources (5L)</p> <p>2.1.1. Lithium ion cell.</p> <p>2.1.2. Fuel cells; Choice of fuel and oxidant, Bacon's H₂ and O₂ fuel cell.</p> <p>2.1.3. Solar cells, solar energy, photovoltaic effect, semiconductors as solar energy</p> | | 1 |

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| | | <p>converters, silicon solar cell</p> <p>2.1.4. Hydrogen : Fuel of the future, production of hydrogen by direct electrolysis of water, advantages of hydrogen as a universal energy medium.</p> <p>2.2 Nuclear Magnetic Resonance Spectroscopy (6L)</p> <p>2.2.1. Nuclear spin, magnetic moment, nuclear 'g' factor, energy levels, Larmor precession, Relaxation processes in n.m.r. (spin-spin relaxation and spin-lattice relaxation).</p> <p>2.2.2. NMR Spectrometer, chemical shift, shielding and deshielding of protons, low resolution n.m.r. spectrum of methanol and ethanol.</p> <p>2.3 Chemical Kinetics (4 L)</p> <p>2.3.1 Collision theory of reaction rates, application of collision theory to 1. uni-molecular reaction and 2. bimolecular reaction (Lindemann theory, derivation expected). Merits and drawbacks of collision theory.</p> <p>2.3.2 Classification of reactions as slow, fast and ultra-fast. study of kinetics of fast reactions by Stop flow method.</p> | | |
| | <p style="text-align: center;">III</p> | <p>3. Coordination Chemistry (15L)</p> <p>3.1 Crystal Field Theory (CFT) (7L)</p> <p>3.1.1.Basic tenets of Crystal field theory and effect of crystal field on central metal valence orbitals.</p> <p>3.1.2 Splitting of <i>d</i> orbitals in octahedral, tetrahedral and square planar complexes.</p> <p>3.1.3 Crystal field splitting energy ($10\Delta_o/10\Delta_o$) for octahedral complexes and factors affecting the magnitude of Δ_o.</p> <p>3.1.4Crystal field stabilization energy (CFSE), calculation of CFSE, for octahedral and tetrahedral complexes with d^1 to d^{10} metal ion configurations.</p> <p>3.1.5 Effect of crystal field splitting on i) Ionic radius and ii) Lattice energy.</p> <p>3.1.6 Theoretical failure of the CFT model.</p> <p>3.1.7Experimental evidence for co-valence in co-ordination compounds.(i) ESR spectrum of $[\text{IrCl}_6]^{2-}$ (ii) NMR spectrum of tris (acetyl acetanato) vanadium complex, (iii) Intensities of <i>d-d</i> transitions, and (iv) Nephelauxetic effect.</p> <p>3.2 Molecular Orbital Theory (MOT) of Coordination Complexes (4L)</p> | | <p style="text-align: center;">1</p> |

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| | | <p>3.2.1 Application to octahedral complexes in case of (i) $[\text{Ti}(\text{H}_2\text{O})]^{3+}$, (ii) Fluoro complexes of Fe(II) and Fe (III) and (iii) Cyano complexes of Fe(II) and Fe (III).</p> <p>3.2.2 Effect of pi-bonding an ligand field splitting parameter in $\text{M}\rightarrow\text{L}$ and $\text{L}\rightarrow\text{M}$ interactions.</p> <p>3.3 Electronic States and Terms for Polyelectronic Atoms (4L)</p> <p>3.3.1 Introduction: electronic configuration and electronic states, Term symbols, coupling of spin momenta (M_s),orbital momenta (M_l)and spin- orbit coupling or Russell-Saunders coupling.</p> <p>3.3.2 Determination of Terms for p^2 electronic configuration (as in a carbon atom).</p> <p>3.3.3 Terms and micro-states for transition metal atoms/ions.</p> | | |
| | <p style="text-align: center;">IV</p> | <p>Some Selected Topics (15L)</p> <p>4.1 Inorganic Polymers (3L)</p> <p>4.1.1 Various methods of classification with examples.</p> <p>4.1.2 Chemistry of borazine with reference to preparation , properties, structures, bonding and applications.</p> <p>4.2 Characteristics and Treatment of Liquid Effluent (06L)</p> <p>4.2.1Characterization of waste: biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), aerobic and anaerobic processes.</p> <p>4.2.2 Removing of solid contaminants, physical and chemical principles such as coagulation, flocculation and sedimentation.</p> <p>4.2.3 Primary,secondary and tertiary of liquid effluents.</p> <p>4.3 Nanomaterials (04L)</p> <p>4.3.1Introduction and importance of nanomaterials.</p> <p>4.3.2 Properties (Comparison between bulk and nanomaterials): (i) Optical properties, (ii) Electrical conductivity, and (iii) Mechanical properties.</p> <p>4.3.3 Forms of nanomaterials: nanofilms, nanolayers, nanotubes, nanowires, and nanoparticles.</p> <p>4.3.4 Chemical methods of preparation: (i) Colloidal route, and (ii) Sol-gel method.</p> <p>4.4 Inorganic Pharmaceuticals (2L)</p> | | <p style="text-align: center;">1</p> |

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| | | <p>4.4.1 Gastrointestinal agents viz., (i) antacids (aluminium hydroxide, milk of magnesia, sodium bicarbonate and (ii) cathartics (magnesium sulphate and sodium phosphate). Topical agents viz., (i) protectives and adsorbents (talc, calamine), (ii) antimicrobial agents (potassium permanganate, tincture iodine, boric acid) and astringents (alum).</p> | | |
| US3CH602 | I | <p>1 Spectroscopy (15L) 1.1 Introduction : Electromagnetic spectrum, units of wavelength and frequency. 1.2 UV- Visible Spectroscopy: Basic theory, solvents, nature of UV-VIS spectrum, concept of Chromophore, auxochrome, bathochromic shift, Hypsochromic shift hyperchromic effect and chromophore-auxochrome interactions. 1.3 IR Spectroscopy: Basic theory, nature of IR spectrum, selection rule , fingerprint region. 1.4 PMR Spectroscopy: Basic theory of NMR, nature of PMR spectrum, chemical shift (δ unit), standard for PMR, solvents used. Factors affecting chemical shift: (1) inductive effect (2) anisotropic effect (with reference to C=C, C₆H₆, C=O and benzene ring). Spin- spin coupling and coupling constant. Proton exchange- application of deuterium exchange , Application of PMR in structure determination. 1.5 Spectral characteristics of following classes of organic compounds, including benzene and monosubstituted benzenes, with respect to UV-VIS, IR, PMR: (1) alkanes (2) alkenes and polyenes (3) alkynes (4) haloalkanes (5) alcohols (6) carbonyl compounds (7) ethers (8) carboxylic acids (9) esters (10) amines (11) amides (broad regions characteristic of different groups are expected). 1.6 Problems of structure elucidation of simple organic compounds using individual or combined use of the above spectroscopic technique are expected. (index of hydrogen deficiency should be the first step in solving the problems).</p> | 2.5 | 1 |

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| | II | <p>2.1 Organometallic Chemistry (5L) 2.1.1 Introduction: Carbon-metal bond-Nature, types reactivity. 2.1.2 Organo magnesium Compounds: Grignard reagent :Preparation, structure, and stability, Reaction with compounds containing acidic hydrogen,carbonyl compounds, cyanides and CO₂. 2.1.3 Organolithium Compounds : Preparation using alkyl/aryl halides. Reactions with compounds containing acidic hydrogen, alkyl halides, carbonyl compounds, cyanides and CO₂. Lithium dialkyl cuprates: Preparation and reactions with aliphatic /aromatic/vinylic halides. 2.1.4 Organozinc compounds: Preparation of dialkyl zinc. Reaction with water, acid chlorides and alkyl halides. Reformatsky reaction (with mechanism). 2.2 Chemistry of some Important Biomolecules: (10L) 2.2.1 α-Amino acids: Structure,configuration,Essential amino acids and their abbreviations, classification, Properties: pH dependency of ionic structure and isoelectric point. Methods of preparations: Strecker synthesis, amidomalonnate synthesis, Erlenmeyer azalactone synthesis. 2.2.2 Polypeptides and Proteins: Polypeptides: Peptide bond. Nomenclature and representation of polypeptides. Merrifields solid phase peptide synthesis (example of di- and tri- peptides for nomenclature and synthesis). Proteins: Sources, types,functions,colloidal nature, separation based on isoelectric point, denaturation and functions. Partial and total hydrolysis. General idea of primary, secondary, tertiary and quaternary structures. 2.2.3 Nucleic acids: Selective hydrolysis of nucleic acids.Sugars and bases in nucleic acids. Stuctures of nucleosides an nucleotides in DNA and RNA. Structure of nucleic acids (DNA and RNA): Base pairing in nucleic acids. Importance of nucleic acids-self duplication, protein synthesis.</p> | | 1 |
| | | Treatment of analytical data-II and Titrimetric analysis-II (15L) | | 1 |

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| | <p style="text-align: center;">III</p> | <p>3.1 Treatment of Analytical Data (6L): Distribution of random errors, Gaussian curve, students' t, confidence limits and confidence interval, criteria for rejection of result: 2.5d rule, 4.0 rule and Q test, F test, testing for significance, null hypothesis, method of averages, least squares method. Numerical problems expected]</p> <p>3.2 Complexometric Titrations (5L): General introduction, EDTA titrations, advantages and limitations of EDTA as the titrant, absolute and conditional formation constants of metal EDTA complexes, construction of titration curves, types of EDTA titrations, methods of increasing the selectivity of EDTA as a titrant, metallochromic indicators, theory and applications.</p> <p>3.3 Redox Titrations (4L): General introduction, theory of redox indicators, criterion for choosing an indicator for a redox titration, construction of the titration curves in the case of (1) Fe (II) Vs. Ce(IV) (2) Fe (II) Vs. dichromate, use of diphenyl amine and ferroin as redox indicators.</p> | | |
| | <p style="text-align: center;">IV</p> | <p>Concepts in Quality and miscellaneous methods (15L)</p> <p>4.1 Total quality management (5L) : concept of quality, quality control, quality assurance total quality management, ISO series, Good laboratory practices</p> <p>4.2 Mass Spectrometry (2L): Basic principles, introduction of components only</p> <p>4.3 Thermal Methods (5L): Classification of thermal methods, thermogravimetric analysis, basic principles, instrumentation factors affecting the TG curve, applications</p> <p>4.4 Introduction to Radio Analytical Techniques (3L): Classification of the techniques, introduction to neutron activation analysis and its applications.</p> | | <p>1</p> |

Practicals

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| US3CHP07 | <p><u>Physical Chemistry Practical</u></p> <p>Potentiometry –</p> <p>1. To determine the strength of the given strong acid (HCl) by potentiometric titration using quinhydrone electrode (Calculation of pH from E_{cell} and the plot of (a) $\frac{\Delta E}{\Delta V}$ against V (b) pH against V graphs are expected).</p> <p style="text-align: center;">OR</p> <p>2. To determine pKa value of the given weak monobasic acid (CH_3COOH) by e.m.f. measurements.</p> <p>Conductometry –</p> <p>3. To determine the amount of dibasic acid (Oxalic acid) by conductometric titration against strong base.</p> <p style="text-align: center;">OR</p> <p>4. To determine the relative strength of monochloroacetic acid and acetic acid conductometrically.</p> <p><u>Inorganic Chemistry Practical</u></p> <p>Inorganic preparations</p> <p>1. Tris-(acetylacetonato) iron (III) 2. Bis-(Dimethylglyoximato) nickel (II)</p> <p>Inorganic estimations/ Analysis</p> <p>1. Acidity of a water sample.</p> | 1.5 | 4 |
| US3CHP08 | <p><u>Organic Chemistry Practical</u></p> <p>Organic Preparations: Drying, Weighing & Melting Point (No Purification)</p> <p>1. Aniline/p-toluidine → N-Acetyl derivative 2. Salicylic acid/nitrobenzene/ Acetanilide → Nitro derivative 3. β- naphthol → Methyl Ether derivative (Using dimethyl sulphate) 4. Methyl salicylate/ethyl benzoate → Acid derivative (Hydrolysis)</p> <p><u>Analytical Chemistry Practical</u></p> <p>1. Determination of chemical oxygen demand of a water sample. 2. Determination of percentage purity of a sample of common salt using a cation exchanger. 3. Determination of acetic acid content of a vinegar sample by potentiometric titration with sodium hydroxide using quinhydrone.</p> | 1.5 | 4 |

