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**Department of Chemistry**

**College of Science**

**University of Salahaddin**

**Subject: Chemical Identification (Spectroscopy)**

**Course Book : (Year 4)**

**Lecturer's name: Dr.Rostam R. Braiem**

**Academic Year: 2022-2023**

**Course Book**

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| **1. Course name** | **Chemical Identification (Spectroscopy)** | |
| **2. Lecturer in charge** | **Dr.Rostam R. Braiem** | |
| **3. Department/ College** |  | |
| **4. Contact** | **e-mail:** [**Rostam.braiem@su.edu.krd**](mailto:Rostam.braiem@su.edu.krd)  **:lozanr@yahoo.co.uk**  **Tel: 009647504512915** | |
| **5. Time (in hours) per week** | **For example Theory: 2**  **Practical: 3** | |
| **6. Office hours** | **Thersday 8.5-10.5 am , 11.5-1.5 pm** | |
| **7. Course code** | **Empirical formula,Hydrogen index deffecincy,IR,NMR,UV** | |
| **8. Teacher's academic profile** | **B.Sc. chemistry 1990-1991**  **M.Sc. organic chemistry 1997**  **Ph.D. Organic chemistry (heterocyclic compounds ) 2005** | |
| **9. Keywords** | **Identification,spectrophotometer,** | |
| **10. Course overview:**   * To introduce the rapid development of spectroscopic techniques and To promote a wide spectrum of background knowledge in Spectroscopy among students and research scholars.To provide a deeper understanding of spectroscopy in various other fields of science and technology.To stimulate discussion and exchange of information of various aspects of spectroscopy and To provide a platform for researchers to present their findings. | | |
| **11. Course objective:**  Different spectroscopic instruments used for identification of organic compounds including infra red,proton nuclear magnatic resonance and ultra violet spectroscopy.  After finishing each technique,the students will be able to identify all organic compounds depending on each instruments and collecting data from all to describe the whole structure ,molecular formula and molecular mass of unknown. | | |
| **12. Student's obligation**  Students should complete assigned reading before class begins, so they can contribute their thoughts to new discussions.  They should also finish homework before entering the classroom. Asking questions about unclear material is an important part of the classroom experience. It is not uncommon for students to have similar difficulties, so speaking up will help everyone understand the discussed information.  Teachers can also benefit from a student’s questions. Each student should participate in the classroom. Discussing relevant subjects at appropriate times can spark new conversations and produce valuable debates. | | |
| **13. Forms of teaching**  White board writing,data show ,computer,videos and power point presentation | | |
| **14. Assessment scheme**  This scheme of Assessment is prepared as per 33% choice in short answer questions, essay questions & questions relating to practicals.In order to promote the cause of concept based learning at least 10 % questions must be unseen or of daily life but relating to specified learning outcomes of Curricula & Syllabi. The questions relating to practical will be asked from the practical Note Book as per chapter were detail given in the curriculum and syllabi.  The Practical will be conducted at the end which is mandatory to qualify for award of certificate. | | |
| **15. Student learning outcome:**  1-Knowledge/Remembering: define, list, recognize  2-Comprehension/Understanding:characterize, describe, explain, identify, locate, recognize, sort  3-Application/Applying: choose, demonstrate, implement, perform  4-Analysis/Analyzing: analyze, categorize, compare, differentiate  5-Evaluation/Evaluating: assess, critique, evaluate, rank, rate  6-Synthesis/Creating: construct, design, formulate, organize, synthesize | | |
| **16. Course Reading List and References‌:**  ▪ Key references: 1- Introduction to spectroscopy by Pavia  ▪ Useful references: 2- advanced organic chemistry by Morrison & Boyed | | |
| **17. The Topics:** | | **Lecturer's name** |
| MOLECULAR FORMULAS AND WHAT CAN BE LEARNED FROM THEM  ELEMENTAL ANALYSIS AND CALCULATIONS  DETERMINATION OF MOLECULAR MASS   1. Molecular formulas 2. **INDEX OF HYDROGEN DEFICIENCY** 3. INFRARED SPECTROSCOPY   The Infrared Absorption process  USES OF THE INFRARED SPECTRUM  THE MODES OF STRETCHING AND BENDING  **BOND PROPERTIES AND ABSORPTION TRENDS**  The Infrared spectrometer  Dispersive Infrared Spectrometers  **PREPARATION OF SAMPLES FOR INFRARED SPECTROSCOPY**  WHAT TO LOOK FOR WHEN EXAMINING INFRARED SPECTRA  CORRELATION CHARTS AND TABLES  HOW TO APPROACH THE ANALYSIS OF A SPECTRUM (OR WHAT YOU CAN TELL AT A GLANCE)  A SURVEY OF THE IMPORTANT FUNCTIONAL GROUPS, WITH EXAMPLES  HYDROCARBONS: ALKANES, ALKENES, AND ALKYNES  Higher alkenes Alkanes  Alkenes  Alkynes  C-H Stretch Region  C-H Bending Vibrations for Methyl and Methylene  C=C Stretching Vibrations  Alkynes  Conjugation Effects  Ring-Size Effects with Internal Double Bonds. The absorption frequency of internal (endo)  Ring-Size Effects with External Double Bonds  C-H Bending Vibrations for Alkenes  AROMATIC RINGS  D I S C U S S I O N S E C T I O N  C-H Bending Vibrations  ALCOHOLS AND PHENOLS  D I S C U S S I O N S E C T I O N  O-H Stretching Vibrations  C-O-H Bending Vibrations  C-O Stretching Vibrations  ETHERS  D I S C U S S I O N S E C T I O N  Dialkyl Ethers.  Aryl and Vinyl Ethers.  Epoxides.  Acetals and Ketals.  Acetals  CARBONYL COMPOUNDS  Factors that Influence the C=O Stretching Vibration  Conjugation Effect  Ring-Size Effects  α-Substitution Effects  Hydrogen-Bonding Effects  Hydrogen-Bonding Effects  Normal C=O Bands  Conjugation Effects  Cyclic Ketones (Ring Strain  α-Diketones (1,2-Diketones  β-Diketones (1,3-Diketones)  Carboxylic Acids  E. Esters  General Features of Esters  Conjugation with a Carbonyl Group (α,β Unsaturation or Aryl Substitution)  Conjugation with the Ester Single-Bonded Oxygen  Hydrogen-Bonding Effects  Hydrogen-Bonding Effects  α-Halo Effects.  β-Keto Esters  F. Amides  Carbonyl Absorption in Amides  N-H and C-N Stretching Bands.  G. Acid Chlorides  H. Anhydrides  Amines  NITRILES, ISOCYANATES, ISOTHIOCYANATES, AND IMINES  NITRO COMPOUNDS  CARBOXYLATE SALTS, AMINE SALTS, AND AMINO ACIDS  SULFUR COMPOUNDS  PHOSPHORUS COMPOUNDS  Alkyl and Aryl Halides   1. **NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY**   NUCLEAR SPIN STATES  NUCLEAR MAGNETIC MOMENTS  ABSORPTION OF ENERGY  THE MECHANISM OF ABSORPTION (RESONANCE)  THE CHEMICAL SHIFT AND SHIELDING  THE NUCLEAR MAGNETIC RESONANCE SPECTROMETER  A. The Continuous-Wave (CW) Instrument  B. The Pulsed Fourier Transform (FT) Instrument  CHEMICAL EQUIVALENCE—A BRIEF OVERVIEW  INTEGRALS AND INTEGRATION  CHEMICAL ENVIRONMENT AND CHEMICAL SHIFT  LOCAL DIAMAGNETIC SHIELDING  A. Electronegativity Effects  B. Hybridization Effects  C. Acidic and Exchangeable Protons; Hydrogen Bonding  MAGNETIC ANISOTROPY  SPIN–SPIN SPLITTING (n + 1) RULE  THE ORIGIN OF SPIN–SPIN SPLITTING  THE ETHYL GROUP (CH3CH2I)  PASCAL’S TRIANGLE  THE COUPLING CONSTANT  COMPARISON OF NMR SPECTRA AT LOW– AND HIGH–FIELD STRENGTHS  SURVEY OF TYPICAL 1H- NMR ABSORPTIONS BY TYPE OF COMPOUND   1. ULTRAVIOLET SPECTROSCOPY   THE NATURE OF ELECTRONIC EXCITATIONS  THE ORIGIN OF UV BAND STRUCTURE  PRINCIPLES OF ABSORPTION SPECTROSCOPY  INSTRUMENTATION  PRESENTATION OF SPECTRA  SOLVENTS  WHAT IS A CHROMOPHORE?  Alkanes  Alcohols, Ethers, Amines, and Sulfur Compounds  Alkenes and Alkynes.  Carbonyl Compounds  THE EFFECT OF CONJUGATION  THE EFFECT OF CONJUGATION ON ALKENES  CARBONYL COMPOUNDS; ENONES  α,β-UNSATURATED ALDEHYDES, ACIDS, AND ESTERS  Aromatic Compounds  A. Substituents with Unshared Electrons  B. Substituents Capable of p-Conjugation  C. Electron-Releasing and Electron-Withdrawing Effects  D. Disubstituted Benzene Derivatives  E. Polynuclear Aromatic Hydrocarbons and Heterocyclic Compounds  MODEL COMPOUND STUDIES  VISIBLE SPECTRA: COLOR IN COMPOUNDS  WHAT TO LOOK FOR IN AN ULTRAVIOLET SPECTRUM: | | The following lectures during the year of study 2017-2018 |
| **Examinations:**  **Q1) (20Marks)**  **1)** An important amino acid has the percentage composition ( C 32.00%, H 6.71%, and N 18.66%).Calculate the empirical formula of this substance.  Q1) 1-Answer:  C= 32 %  H= 6.71 %  N= 18.66 %  O= 100 – (57.37) = 42.63 %  C = (32/12) = 2.667 moles  H = (6.71/1) = 6.71 moles  N = (18.66/14) = 1.33 moles  O = (42.63/16) = 2.66 moles  C 2.66H 6.71N 1.33O 2.66  (ALL/1.33)  Empirical formula C2H5NO2  **2)** An (11.32-mg) sample was burned in a combustion apparatus. The carbon dioxide (24.87 mg) and water (5.82 mg) were collected and weighed.  (a) Calculate the percentage composition of the unknown solid.  (b) Determine the empirical formula of the unknown solid.  2- answer:  a) CxHyOz + excess O2 → x CO2 + y/2 H2O  11.32mg 24.87mg 5.82mg  Mmole CO2 = (24.87/44) = 0.56 mmoles  Mmole CO2 = mmole of C in original sample  Wt of CO2 = (0,56 x 12) = 6.72 mg  m mole H2O = (5.83 / 18) = 0.323  m mole H2O x (2/1) = 0.64 mmole of H  wt of H = 0.64 x 1 = 0.64 mg  Or:  CO2 C  ……. ………  44 12  24.87 wt.  Wt of Carbon in CO2 = 6.78mg  H2O H  …… ……….  18 1  5.82 wt. H  Wt of Hydrogen in H2O = 0.32 mg  (0.32 x 2) = 0.64 mg of H  % of C = (6.78 / 11.32) x 100 = 59.89 %  % of H = (0.64 / 11.32) x 100 = 5.65 %  % of O = 100 - ( 65.44) = 34.46 %  C = (59.89/12) = 5 moles  H = (5.65 / 1) = 5.65 moles  O = ( 34.46 / 16 ) = 2.15 moles  C5 H 5.65 O 2.35  All divided by( 2.35)  Empirical formula = C 2.3 H 2.6 O 1 (x 3)  Molecular formula = C 7 H 8 O3  **Q2) Give reasons for the following:(30Marks)**  1) Symmetric bonds, such as those of H2 or Cl2, do not absorb infrared radiation?  Bond must present an electrical dipole that is changing at the same frequency as the incoming radiation for energy to be transferred.  2) There are two strong N=O stretch peaks for a nitro group?  With the symmetric stretch appearing at about 1350 cm−1 and the asymmetric stretch appearing at about 1550 cm−1.  3) N-H and O-H streaching can be distinguished from each others by shapes and intensities of peaks?  The N-H absorption usually has one or two *sharp* absorption bands of lower intensity, whereas O-H, when it is in the N-H region, usually gives a *broad* absorption peak.  Also, primary amines give *two* absorptions in this region, whereas alcohols as pure liquids give only one (Fig.).    4) Conjugation of a C=C double bond with a carbonyl group lower frequency of vibration?  Conjugation of a C=C double bond with either a carbonyl group or another double bond provides the multiple bond with more single-bond character (through resonance), a lower force constant *K,* and thus a lower frequency of vibration.    5) As the alcohol is diluted with carbon tetrachloride, a sharp O-H stretching band appears at about 3600 cm−1.  As the alcohol is diluted with carbon tetrachloride, a sharp “free” (non-hydrogen-bonded) O-H stretching band appears at about 3600 cm−1, to the left of the broad band .  **6)** Ketones absorb at a lower frequency than aldehydes ?  Ketones absorb at a lower frequency than aldehydes because of their additional alkyl group, which is electron donating (compared to H) and supplies electrons to the C=O bond.  This electron-releasing effect weakens the C=O bond in the ketone and lowers the force constant and the absorption frequency.    **Q3) (15 Marks)**  Describe the inductive and resonance effect on the carbonyl absorption frequency in esters and amides.  Answer:  Since oxygen is more electronegative than carbon, this effect dominates in an ester to raise the C=O frequency above that of a ketone.  Second, a resonance effect may be observed when the unpaired electrons on a nitrogen atom conjugate with the carbonyl group, resulting in increased single-bond character and a lowering of the C=O absorption frequency.  This second effect is observed in an amide .    **Q4) (20 Marks)**  In each of the following, a molecular formula is given (Index of hydrogen deficiency). Deduce the structure that is consistent with the infrared spectrum.  a) C7H9N  b) C5H12O  Answer:  a)  C7H9N  Cn H 2n+2 n=7  C7 H 2x7 + 2  C6 H 16  Correlation of nitrogen  (Addition of one hydrogen)  C7 H17 N  HDI = (17-9)/2  = 4  Aromatic compound  In IR spectrum there are two bands in rang of amines in region above 3400 cm -1 means the compound is aromatic carring  primery amines,there is also peak for aliphatic and aromatic C-H stretching below and above 3000 cm -1 and also strong bands of C=C aromatic starching.  From data and spectrum the compound is substituted methyl aniline (m-Methylaniline)  **b)**  C5H12O n=5  C n H 2n+2  C5 H 12  Since the compound contain only oxygen,there is no need for correlation  HDI = (12-12)/2 =0  The compound contain no double bonds,so its aliphatic compound.  From the spectrum there is only C-H stretching for aliphatic below 3000 cm -1, also strong band in region of alcohols from 3000 to 3500 cm -1 ,strong and broad band indicate precence of H- bonding in the molecule.also the strong band in 1050 cm -1 indicate that its primery alcohol.  : From above information we can say that the compound is  (2-Methyl-1-butanol)      **Q5) (15Marks)**  Choose the structure that best fits the infrared spectrum shown.  Answer:  A) The firs compound cyclohexanone,There is no any strain inside the ring,so its band will locate in original region 1735 cm -1.  This compound not fixed with the spectrum.  B) In the second compound ,there is only small amount of strain in the molecule which arise the frequency about 30-35 cm -1 ,to approximately 1760 cm -1,because only one carbon abstracted from the ring.  This compound also will not fixed with the spectrum.  C) The third compound will fixed with the spectrum ,because in cyclobutanone there is a large amount of strain which increase the frequency to about 1780 cm-1.  This compound is exactly fixed with the decreasing size of rings.    D) This compound also not fixed with obtained soectrum because in cuclopropanone there is a large amount of strain inside the ring that arise the frequency to above 1800 cm -1.   ------Good Luck------- | | |  |  |  |  | | --- | --- | --- | --- | | **1. Course name** | **Identification of organic compound** | | | | **2. Lecturer in charge** | **Dr.Rostam Rasul ,Dr.Fwad.Mr.Sirwan.Mrs.Shaza and Mr.Haval** | | | | **3. Department/ College** | **Chemistry /science** | | | | **4. Contact** | **e-mail:rostam.braiem@su.edu.krd**  **Tel: (optional)** | | | | **5. Time (in hours) per week** | **practical:3** | | | | **6. Office hours** | **All days(9Am-1Pm)** | | | | **7. Course code** |  | | | | **- I awarded B.Sc. in Chemistry (College of Science) in 1990**  **Salahaddin University.**  **- M.Sc. in 1995 (Salahaddin University-Erbil).**  **- Assist. Lecturer from 1995 till 2012.**  **- Lecturer from 2012 till now.**  **- I was published 6 scientific papers.**  **- I was attended in conference (salahaddin university ) in 1997.** | | | **9. Keywords** | **Aldehyde , ketones ,chemical test ignition test** | | | | **10. Course overview:**  ▪ learning students how to be identified organic compound and to introduced to organic compound by using some method one of them is physical properties (color ,odor, ignition test, melting point and boiling point), another method for physical properties using solubility ( solubility method in water, ether, dil. NaOH, dil. NaHCO3, dil. HCl, Conc. H2SO4 and Conc. H3PO4 ) while the chemical properties include detection of general and special functional groups for( alcohol, phenol, mono and dicarboxylic acid, ester, ether, amide, aryl and alkyl halide, anhydride, amino acid, carbohydrate, amine, aldehyde and ketones) finally method, is identification organic compound by spectrum technique (I.R.,HNMr) | | | | | **11. Course objective:**  - Gaining experiences how to select a suitable technique and method for identification of organic compounds.  - Combining all information that the student are obtained through their working for three weeks with melting point table to know the unknown.  - Comparing the tow techniques(manual and spectra)to be shore that the unknown is the correct one. | | | | | **12. Student's obligation**  The students should have presence in all lectures and Labs.  - Every lecture the first 10 min should be debate about the previous experimental laboratory and the interested student (participant in the debate) take marks.  - The students have round trip to the central laboratories or factories (generally in the 2nd semester). | | | | | **13. Forms of teaching**  Using data show and power point in addition to the white board (Students should be use course references). | | | | | **14. Assessment scheme**  -Tow term examination through the academic year (for theoretical /practical) (7 Marks total).  - The students after all unknown will be fill forms (5 Marks).  - Five Quizzes through each semester (2 Marks).  - Attendances in the laboratory lecture (1 Mark)  ‌ | | | | | **15. Student learning outcome:**  - Students know how dependent on therirselves to identify the unknown.   * Students can easily come in for work in the private sectors, e.g. Organic Lab., etc. * Today due to the technology students can learn more about the modern instruments e.g. (I.R. U.V. Spectrophotometery) | | | | | **16. Course Reading List and References‌:**  ▪ Key references: The systematic identification of organic compound eighth edition (By: Shriner Hermann Morrill Curtir)  ▪ Usefull references: Sheets of identification of organic compounds(Dr.Rustum,Bushra,Naween and Shelan )  ▪ Magazines and review (internet): [www.wekepedia](http://www.wekepedia), [www.science](http://www.science). | | | | | **17. The Topics:** | | | **Lecturer's name** | | In this section the lecturer shall write titles of all topics he/she is going to give during the term. This also includes a brief description of the objectives of each topic, date and time of the lecture  Each term should include not less than 16 weeks | | | **Dr.Rostam Rasul ,Dr.Fwad.Mr.Sirwan.Mrs.Shaza and Mr.Haval**  ex: (3 hrs)  ex: 2017-2018 | | **18. Practical Topics (If there is any)** | | |  | | 1st  week:-theoretical part  Physical properties for organic compounds:  Color, odor, ignition test, melting point and boiling point  2nd  week:  Sodium fussion test, salvation presses  3rd  week:  Solubility  In ( water, ether, NaOH, NaHCO3 , HCl, H2SO4, H3PO4)  4th week:  All functional groups  5th  week: Practical part  unknown -1  M.P. and solubility  6th week: unk. 1  Sodium fusion, ignition test  7th week: unk. 1  Functional groups  8th week: unk. 1  Filling form  Repaid the same steps for all unknowns during the academic year | | | Shaza  (3 hrs)  Shaza  (3 hrs)  Sirwan  (2 hrs)  Sirwan  (3 hrs) for each lab.  (3 hrs) for each lab.  (3 hrs) for each lab.  (3 hrs) for each lab. | | **19. Examinations:**  Q1// Describe chemical test that would serve to distinguish between;   1. N-methyl aniline & N,N-dimethyl aniline. 2. 1-pentyne &1-pentene. 3. Glucose & sucrose.   Q2*ll* Complete the following reactions;     1. Phenol +HNO2 2. P-nitro toluene + ferrous hydroxide + H2O 3. Butanol + Xanthat reagent 4. Chloro propane + NaI/ acetone 5. NaSCN + HNO3   Q3// A) when solvation process occur ?  B) Define 1) sharp M.P. 2) Lassaignes’ test 3) Ignition test .  Q4// Explain and compare the solubility of following compounds;   1. Iso compounds solubility differs widely from that of normal isomers. 2. 3-pentanol & 1-pentanol in water. 3. Phenol & 2,4-dinitro phenol in dilute (NaOH and NaHCO3) | | | | | **20. Extra notes:**  **1) This course is suitable for the 4th year students (B.Sc.), it’s very difficult for the 2nd and 3rd years B.Sc.**  **2) This course is useful in different fields to get works in private sector.** | | | | | **21. Peer review پێداچوونه‌وه‌ی هاوه‌ڵ**  This course book has to be reviewed and signed by a peer. The peer approves the contents of your course book by writing few sentences in this section.  *(A peer is person who has enough knowledge about the subject you are teaching, he/she has to be a professor, assistant professor, a lecturer or an expert in the field of your subject).*  ئه‌م کۆرسبووکه‌ ده‌بێت له‌لایه‌ن هاوه‌ڵێکی ئه‌کادیمیه‌وه‌ سه‌یر بکرێت و ناوه‌ڕۆکی بابه‌ته‌کانی کۆرسه‌که‌ په‌سه‌ند بکات و جه‌ند ووشه‌یه‌ک بنووسێت له‌سه‌ر شیاوی ناوه‌ڕۆکی کۆرسه‌که و واژووی له‌سه‌ر بکات.  هاوه‌ڵ ئه‌و که‌سه‌یه‌ که‌ زانیاری هه‌بێت له‌سه‌ر کۆرسه‌که‌ و ده‌بیت پله‌ی زانستی له‌ مامۆستا که‌متر نه‌بێت.‌‌ | | | | |