

INTER AMERICAN UNIVERSITY OF PUERTO RICO
_____ CAMPUS
DEPARTMENT OF _____
CHEMISTRY PROGRAM

COURSE SYLLABUS

I. GENERAL INFORMATION

Course Title: DETERMINATION OF STRUCTURES BY SPECTROSCOPIC METHODS
Code and Number: CHEM 3230
Credit: 3 credits
Academic term:
Professor:
Office hours:
Office telephone:
Email:

II. DESCRIPTION:

Analysis of the information obtained from the main spectroscopic methods (Infrared, one-dimensional and multidimensional nuclear magnetic resonance, Mass and Ultraviolet) to determine the molecular structure of chemical compounds. Requirement; CHEM 2222.

III. TERMINAL AND TRAINING OBJETIVES

1. Determine molecular formulas from elemental analysis, qualitative tests, and the mass spectrum and use them to predict the functional groups in an organic molecule.
 - 1.1. List the steps involved in determining the molecular formula of a substance.
 - 1.2. Review of percentage (%) calculations using volumetry and gravimetry methods.
 - 1.3. Interpret the results of the qualitative and quantitative elemental analysis of an unknown substance, as well as calculate the percentage composition by means of combustion, gravimetric and / or volumetric analysis.
 - 1.4. Calculate the percentage composition from the molecular or structural formula.
 - 1.5. Calculate the empirical formula from the percentage composition.
 - 1.6. Determine the molecular weight of an unknown by means of acid-base titrations, the Rast method, the general equation of gases or from the mass spectrum.
 - 1.7. Determine the molecular formula from:
 - 1.7.1. empirical formula and molecular weight,
 - 1.7.2. percentage composition and molecular weight,
 - 1.7.3. percentage composition and mass spectrum,
 - 1.7.4. mass spectrum and the rule of 13.
 - 1.8. Determine the degree of unsaturation of a molecular formula and use its magnitude to propose possible structures associated with the molecular formula.
2. Determine molecular formulas and fragmentation patterns of halogenated compounds, hydrocarbons, compounds with oxygen, nitrogenous, carbonyl and heterocyclic by means of mass spectrometry, MS.
 - 2.1. Describe the different methods for ionization of a molecule.
 - 2.2. Describe the essential functions of a mass spectrometer.
 - 2.3. Indicate the characteristics of the ionization chamber and the ion analyzer on a mass spectrometer.
 - 2.4. Describe the difference between chemical and electron impact ionization.
 - 2.5. Determine the molecular weight and the number of atoms of sulfur, chlorine, bromine or combinations of these, from the mass spectrum.
 - 2.6. Determine the molecular formula of an unknown:
 - 2.6.1. from the mass spectrum and the rule of 13
 - 2.6.2. from the mass spectrum and the percentage composition of C, H.
 - 2.6.3. from mass spectrum and tables of molecular formulas.
 - 2.6.4. combining infrared and mass spectra.

- 2.7. Recognize, write and justify the structure of molecular ions and the most abundant or characteristic fragments of saturated and unsaturated hydrocarbons, aromatic compounds, compounds with heteroatoms (O, N, S, Si, X) and carbonyl compounds.
 - 2.7. Write the fragments corresponding to the McLafferty rearrangement of alkylbenzenes and compounds with the carbonyl group.
3. Determine molecular structures of hydrocarbons, alcohols, ethers, carbonyl, nitrogen and heterocyclic compounds by means of infrared spectroscopy, IR.
 - 3.1. Describe the components of the electromagnetic spectrum.
 - 3.2. Determine the effect of each of the radiations of the electromagnetic spectrum on organic molecules.
 - 3.3. List the different modes of vibration and bending in a molecule and justify the differences between them. Recognize the overtone and difference bands.
 - 3.4. Apply Hooke's Law to determine the properties of bonds and calculate their absorption frequency.
 - 3.5. List the main components of a Fourier transform IR spectrophotometer.
 - 3.6. Indicate the different techniques to obtain the infrared spectrum of a liquid and a solid.
 - 3.7. Describe the process of energy absorption in IR and its usefulness in infrared spectroscopy.
 - 3.8. Indicate the factors that affect the position, shape and intensity of the absorption of a functional group, with emphasis on the carbonyl group.
 - 3.9. Recognize the characteristic absorptions of alkanes, alkenes, alkynes, benzene compounds, alcohols, ethers, compounds with carbonyl group, amines, nitro compounds, nitriles, isocyanates, mercaptans, sulphones and sulphonates.
 - 3.10. Analyze the IR spectrum of unknown substances and assign the most characteristic absorptions using the correlation tables.
 - 3.11. Write the structural formulas that correlate with the assigned absorptions when analyzing the IR spectrum.
 4. Determine molecular structures of hydrocarbons, ethers, epoxides, carbonyl, nitrogen and heterocyclic compounds by means of nuclear magnetic resonance: $^1\text{H-NMR}$, $^{13}\text{C-NMR}$.
 - 4.1. List the active nuclei for the study in nuclear magnetic resonance and write their orientations or spin states allowed under a magnetic field.
 - 4.2. Relate the dependence of the absorption frequency of the nuclei under study with the type of instrument.
 - 4.3. List and justify the factors that affect the chemical shift, δ .
 - 4.4. Calculate the δ of the H's in alkenes and benzene derivatives using the corresponding tables.
 - 4.5. Apply the $2nI + 1$ rule to predict and justify the multiplicity of peaks corresponding to each class of different nuclei in a molecule.
 - 4.6. Determine the amount of hydrogens (integration) corresponding to each class in the proton NMR spectrum and its relationship to magnetic equivalence.
 - 4.7. Explain the origin of spin splitting between neighboring protons and indicate the relative intensity of the peaks in a multiplet.
 - 4.8. Calculate the coupling constant (J in Hz) between protons from the proton spectrum and use its magnitude to determine stereochemical aspects.
 - 4.9. Predict and recognize the different types of nJ coupling between protons; its dependence on the number of bonds and the dihedral angle.
 - 4.10. Indicate the conditions under which geminal coupling is observed and its relationship with equivalence magnetic.
 - 4.11. Analyze and justify the proton spectrum of molecules in which the $2nI + 1$ rule does not apply, emphasis on the alkenes, aromatic derivatives.
 - 4.12. List and justify the conditions under which coupling with protons of alcohols and amines can be observed.
 - 4.13. Justify the effect of using deuterated water in compounds with acidic hydrogens.
 - 4.14. Identify second order spectra. Analyze the different ways to simplify them by means of displacement reagents, double resonance and / or instruments with a higher working frequency.
 - 4.15. Recognize and analyze proton spectra of molecules with diastereomeric protons and virtual coupling.
 - 4.16. Establish differences between spectroscopic techniques of $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$.
 - 4.17. Recognize and interpret the different spectra of carbon-13: uncoupled, coupled, DEPT.
 - 4.18. Define the term NOE and interpret its numerical value.
 - 4.19. Predict the carbon 13 spectrum of compounds by applying NOE.
 - 4.20. Calculate the δ for the carbons of alkenes and aromatics using the corresponding tables.
 - 4.21. Analyze and justify proton and / or carbon-13 spectra of molecules containing fluorine atoms, deuterium or phosphorus in its structure.

5. Determine and / or correlate molecular structures of ethers, carbonyl, nitrogen and heterocyclic compounds by means of nuclear magnetic resonance in two dimensions.
 - 5.1. Determine which protons are coupled from a homonuclear correlation spectrum (COSY, ^1H - ^1H).
 - 5.2. Determine the number of hydrogens attached to each carbon from heteronuclear correlation spectra (HETCOR, ^{13}C - ^1H).
 - 5.3. Determine which carbons are coupled from the "2-D-INADEQUATE" spectrum.
 - 5.4. Determine the spatial proximity between protons from the "NOE" spectrum

6. Apply ultraviolet-visible spectroscopy (UV-Vis) to predict electronic transitions, the degree of conjugation of polyenes, nitrogenous compounds and with carbonyl group.
 - 6.1 Understand the nature of an electronic excitation in UV-Vis and the principles of this spectroscopy of absorption.
 - 6.2. Predict the number of molecular orbitals in a molecule based on its structure and represent them in terms of their energies.
 - 6.3. Describe the most favorable electronic transitions from the energy diagram and the molecular orbitals of organic molecules.
 - 6.4. Indicate the characteristics of the solvents used in UV-Vis and justify their effect on the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi_{(n+1)}^*$ transitions.
 - 6.5. Calculate the λ_{max} of conjugated dienes, aldehydes or ketones and benzoyl derivatives, applying the empirical rules.
 - 6.6. Apply the Lambert-Beer law and the UV spectrum to determine the absorption intensity and assign the type of electronic transition.

7. Determine structural formulas from:
 - 7.1. Mass spectra, IR and ^1H -NMR.
 - 7.2. Mass spectra, ^1H -NMR and ^{13}C -NMR.
 - 7.3. Mass spectra, IR, ^1H -NMR and ^{13}C -NMR

8. Elucidate and / or confirm structures of organic compounds combining the spectra of: mass, IR, NMR (^1H , ^{13}C and two dimensions) and ultraviolet-visible.

IV. COMPETENCES

This course addresses the following proficiency in the profile for the BS in Chemistry.

1. Predict the behavior of matter in the face of energetic radiation and determine its molecular structure based on the analysis of spectra.

V. CONTENT

1. ELEMENTARY ANALYSIS AND MOLECULAR FORMULAS

- 1.0 Determine the percentage composition from a molecular or structural formula.
- 1.1 Qualitative analysis by sodium fusion to determine the elements in an unknown compound.
- 1.2 Determine the percentage composition by combustion and volumetry or precipitation.
- 1.3 Determination of Molecular Weight applying the Rast method and acid-base titration, from a mass spectrum.
- 1.4 Perform calculations to determine the empirical formula (FE) and the molecular formula (FM).
- 1.5 Determine and interpret the Hydrogen Deficiency Index (HDI) from the FM.
- 1.6 Determination of the Molecular Weight and the molecular formula from the Mass spectrum and the composition of carbon and hydrogen.

2. MASS SPECTROMETRY

- 2.1 Interaction between radiation energy and matter.
- 2.2. Different methods to ionize organic compounds and differences or advantages between them.
- 2.3. The mass spectrum: molecular ion and structure, base peak, isotopic peaks ($M + 2$, $M + 4$, etc.).
- 2.4. Identification of halogens and nitrogen in an organic compound from the mass spectrum.

- 2.5. Determine molecular formulas from the mass spectrum and the partial percentage composition or by applying the rule of 13.
- 2.6. Most common fragmentations (alpha cleavage, retro Diels-Alder and McLafferty rearrangement) and fragmentation mechanism for compounds saturated with heteroatoms, unsaturated hydrocarbons and carbonyl compounds.
- 2.7. Determine the structure of an unknown based on the fragments observed in the mass spectrum

3. INFRARED SPECTROSCOPY

- 3.1. Electromagnetic spectrum and relationship of each component with energy, frequency and wavelength.
- 3.2. Infrared absorption process- Effect of substituents and symmetry on alkenes and alkynes.
- 3.3. Different modes of molecular vibration. Why do various absorptions appear in the spectrum?
- 3.4. Hook's Law- Effect of resonance, ring tension and hydrogen bonds in the position of the absorption of the carbonyl group in aldehydes, ketones, carboxylic acids, esters, amides, acyl chlorides, anhydrides, amines, nitriles, nitro compounds, sulfones and isocyanates.
- 3.5. Instrument: Basic components, accessories and how the spectrum is obtained.
- 3.6. The infrared spectrum: what is it? How is it analyzed? Position, shape and intensity of the absorption bands. Correlation table.
- 3.7. Correlation of infrared absorption bands and functional groups to match, correlate, predict the spectrum.
- 3.8. Calculate the HDI, propose functional groups, analyze the IR spectrum and determine the molecular structure of an unknown.
- 3.9. Determine the molecular and structural formula by combining the infrared and mass spectra and using correlation tables.

First partial exam

4. NUCLEAR MAGNETIC RESONANCE (NMR) -BASIC CONCEPTS.

- 4.1. Active nuclei and spin states or possible orientations against a magnetic field.
- 4.2. Phenomenon by which energy absorption occurs and which makes it easier to observe the spectrum.
- 4.3. Fundamental equation in NMR.
- 4.4. Calculate the population density according to the instrument and the type of nucleus applying the Boltzmann equation.
- 4.5. Shielding, chemical and magnetic environment.
- 4.6. Chemical shift, internal reference, inductive, hybridization, anisotropy, acidity and hydrogen bonding effects, use of deuterated water.
- 4.7. Instrument and its basic components-Solvents and sample preparation.Proton spectrum-
- 4.8. Graph, scale and correlation table.
- 4.9. Number of signals, multiplicity or number of peaks for each signal, application of the $n + 1$ rule and use of Pascal's triangle.
- 4.10. Integration of the signals in the proton spectrum, $^1\text{H-NMR}$. Calculation and interpretation or prediction.
- 4.11. First order $^1\text{H-NMR}$ spectra for the correlation and determination of simple organic structures (alcohols, ethers, alkyl halides, amines, low-complex alkenes and alkenes, carbonyl compounds, benzene derivatives).
- 4.12. Match, correlate or calculate the IDH and determine molecular structures with the spectrum by assigning each signal based on integration, multiplicity and chemical shift.
- 4.13. Determine the structure of an unknown from mass spectra, IR and $^1\text{H-NMR}$.

5. CARBON-13, $^{13}\text{C-NMR}$ NUCLEAR MAGNETIC RESONANCE.

- 5.1. Differences with $^1\text{H-RMN}$.
- 5.2. Chemical shift, scale, and correlation table
- 5.3. Simple spectrum and hydrogen coupled.
- 5.4. Calculate the chemical shift for benzene carbons.
- 5.5. NOE effect in C-13 NMR.
- 5.6. DEPT spectrum, importance and advantages with respect to the trailer.

- 5.7. Prediction and analysis of carbon-13 spectra for compounds with fluorine, phosphorus and deuterium.
- 5.8. Determine unknown structures by combining mass, IR, proton, and C-13 spectra.

6. NUCLEAR MAGNETIC RESONANCE - NMR ADVANCED CONSIDERATIONS.

- 6.1. Coupling constant (J) and spin-spin coupling mechanism.
- 6.2. Identify the different types of coupling in saturated alicyclic compounds, cyclohexanes alkenes, alkynes and benzene derivatives.
- 6.3. Spin splitting tree in alkenes and calculations of the J from the proton spectrum.
- 6.4. Coupling in molecules with chiral centers. Rule failures (n + 1) due to non-equivalence magnetic within a group.
- 6.5. Protons in oxygen: Alcohols, Alcohol / water and acid / water mixtures.
- 6.6. Protons in nitrogen: Amines, quadrupole broadening.
- 6.7. Effect of solvent on chemical shift.
- 6.8. Virtual coupling in molecules with carbon chains of 5 or more carbons.
- 6.9. Use of shift reagents.
- 6.10. NOE and *decoupling* to simplify proton spectra.

Second partial exam

7. NUCLEAR MAGNETIC RESONANCE IN TWO DIMENSIONS

- 7.1 Review of the DEPT experiment
- 7.2 The COZY experiment
- Pulse sequence
 - How is it obtained
 - How the spectrum is analyzed and interpreted
- 7.3 The HETCOR experiment
- Pulse sequence
 - How is it obtained
 - How the spectrum is analyzed and interpreted
- 7.4 NOE spectrum
- 7.5 The INADEQUATE experiment and its usefulness and spectrum characteristics
- 7.6 Correlate structures with the COSY, HETCOR and INADEQUATE spectra.

8. ULTRAVIOLET-VISIBLE SPECTROSCOPY

- 8.1. Location of the ultraviolet and visible regions in the electromagnetic spectrum. Wavelength range.
- 8.2. Origin of the UV band structure.
- 8.3. Diagram of molecular orbitals, electronic transitions and selection rules in saturated compounds, vinyl ethers, carbonyl compounds, and conjugated molecules.
- 8.4. Instrument, solvent and sample preparation, spectrum presentation and solvents.
- 8.5. Chromophore and effect of auxochromes.
- 8.6. Effect of conjugation and application of empirical rules to calculate λ_{max} : Woodward-Fieser, Woodward for enones and those of benzoyl derivatives.
- 8.7. Important Applications of Ultraviolet Visible Spectroscopy.

Final Exam: Topics 1-8

VI. EVALUATION

Evaluation criteria	Value	% of the final grade
Partial Exam 1	125	20
Partial Exam 2	150	25
Written and oral presentation	200	15
Weekly Quizzes	150	15
Final exam	125	25
Total	700	100

Each exam will include two parts: I. Theory, II. Problems using the printed textbook.

VII. EDUCATIONAL RESOURCES

A. Textbook

Introduction to Spectroscopy, 5th Edition, **2015** by Donald L. Pavia, Gary M. Lampman and George S. Kriz, James R. Vyvyan, Brooks/Cole (Cengage Learning), Print ISBN: 9781285460123, 128546012X

- eText ISBN: 9781305177826, 1305177827

Silverstein, R. M, Webster F. X. , Kiemle, D, J., Bryce D. L. *Spectrometric Identification of Organic Compounds*, 8th Edition, Wiley, **2015**.

B. Complementary books or collections

1. Pouchert, Charles J.; The Aldrich Library of **FT-IR**. II ed. Vol 1-2-3.: Sigma-Aldrich Co, 1997. Ref. QD 96 .15 P66. ISBN 0-946133-39-X
2. Robinson J.W.; Practical Handbook of Spectroscopy Vol III. CRC Press 1991. **QD 95. P73 1991.**
3. Pouchert, Charles J., The Aldrich Library of NMR Spectra, Edition 11. Vol 1-2, Co. 1983 Aldrich Chemical Co., **Ref QD 96 - N8 P 68 1983.**
4. Tsukerblat B. S.; Group Theory in Chemistry and Spectroscopy. Academic Press 1994. **QD 455.3 . G7558 1994.**

C. Electronic resources

1. Program to predict C-13 proton spectra http://www.nmrdb.org/new_predictor
2. Database for MS, IR, proton and C-13 NMR
http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng;
<http://webbook.nist.gov/>

IX. SPECIAL NOTES

- 1 .Auxiliary services or special needs

All students who require auxiliary services or special assistance must request them no later than two weeks after the start of the course or as soon as they become aware that they need them, through the corresponding registry, in the office of the professional counselor with _____.

2. Honesty, fraud and plagiarism

Dishonesty, fraud, plagiarism and any other inappropriate behavior in relation to academic work constitute major infractions sanctioned by the General Student Regulations. Major offenses, as provided in the General Student Regulations, may result in suspension from the University for a defined period of more than one year or permanent expulsion from the University, among other sanctions.

3. Use of electronic devices

Cell phones and any other electronic device that could interrupt the teaching and learning processes or alter the environment conducive to academic excellence will be disabled. Urgent situations will be addressed, as appropriate. The handling of electronic devices that allow accessing, storing or sending data during evaluations or exams is prohibited.

4. Compliance with the provisions of Title IX:

The Federal Higher Education Law, as amended, prohibits discrimination on the basis of sex in any academic, educational, extracurricular, athletic activity or in any other program or employment, sponsored or controlled by an institution of higher education regardless of whether it is carried out. inside or outside the institution's premises, if the institution receives federal funds.

In accordance with current federal regulations, an Assistant Title IX Coordinator has been appointed in our academic unit who will provide assistance and guidance in relation to any alleged incident that constitutes discrimination based on sex or gender, sexual harassment or sexual assault. You can contact the Assistant Coordinator at extension, or email. _____.

The Normative Document entitled Norms and Procedures to Address Alleged Violations of the Provisions of Title IX is the document that contains the institutional rules to channel any complaint that is presented based on this type of allegation. This document is available on the website of the Inter American University of Puerto Rico (www.inter.edu).

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