60453 - Structural characterization techniques

Información del Plan Docente

Academic Year	2017/18
Faculty / School	100 - Facultad de Ciencias
Degree	543 - Master's in Molecular Chemistry and Homogeneous Catalysis
ECTS	6.0
Year	1
Semester	First semester
Subject Type	Compulsory
Module	---

1.General information

1.1.Introduction

The purpose of this course is to provide the student with a wide variety of structural tools, which generate informations usually complementaries but which can also be overlapped. We tackled here with the study of the nuclear magnetic resonance (NMR) spectroscopy, the mass spectrometry (MS), UV-Vis and fluorescence spectrophotometry, chromatographic techniques and electrochemistry. We propose a double challenge for this course: the knowledge of each individual technique and the ability to integrate the knowledges of the different techniques.

To achieve these goals, we intend the study in-depth of each technique on itself, the study of the information provided by it and how this information is related with the structural determination. In addition, we intend to give an integrated perspective of the whole set of techniques as a global solution for the structural determination and/or the interpretation of a physical phenomenon.

1.2.Recommendations to take this course

To take this course it is highly advisable a previous knowledge of instrumental and spectroscopic methods, as well as a correct understanding of technical and scientific texts in English language. The assistance to the classes and the daily study will help to overcome this course.

1.3.Context and importance of this course in the degree

This course of *Structural Characterization Techniques* is a mandatory course of 6 ECTS, is developed during the first four-month period and belongs to the module *Structural Characterization*. The structural characterization is the cornerstone for the research on synthesis and catalysis. The meaning of this course is to provide the students with the tools to develop this task with maximal rigor. This goal is complemented with the characterization of physico-chemical properties, basis of plausible applications. This a very specialized course, where the knowledge of the different techniques is treated in-depth and strengthened in order to give to the student's skills to be independent when designing new experiments and interpreting the results of each technique.

1.4.Activities and key dates

The scheduled activities will take place during the first semester, in several sessions along the week, taking one hour each session. All information about schedules, calendars and exams is available at https://ciencias.unizar.es/calendario-y-horarios, and in the webpage of the Master http://masterqmch.unizar.es. The presentation of practical works will be done according with the calendar, which will be announced sufficiently in advance.

The contents of the course (classes, practical problems and seminars) can be complemented with the assistance to the CSIC's postgraduate course "**Course of practical use of NMR spectrometers. Basic level**", which will take place along the first semester. This course of 20 hours is of non-compulsory character and, at the end of the course, the students achieve a certificate of competency.

2.Learning goals

2.1.Learning goals

The knowledge of the physical grounds of all techniques introduced during the course, and the type of information provided by each one.

The interpretation of the information provided by the corresponding spectrum or diagram (chromatogram, voltammogram) generated by each technique, and their relationship with the structure of the compound.

For each technique, the knowledge and correct identification of its particular instrumentation, the most relevant parts and components (hardware) and their specific function.

The correct sample handling and preparation, how to perform basic experiments and to design new ones (in the cases where the technique and the software allows to do it) and how to manage the most relevant parameters of each experiment to get a given information.

To achieve an integrated vision of the whole set of techniques, being able to select the specific technique, or the particular combination of them, which are the most adequates for the correct resolution of structural problems.

2.2.Importance of learning goals

The determination of molecular structures is a basic point on research in chemical synthesis and catalysis. Moreover, the determination of the physical and chemical properties of new compounds through the use of different techniques, once the structure is known, allows to establish the structure-properties-applications relationship. Because all these facts, this course deals with a basic and critical key subject for the harmonic development of the others courses. Obviously some techniques can be more important than others depending of the type of research involved on each specific case, and even it could happens than one of them becomes mandatory. Anyway, two or more techniques will be necessary to reach a correct structural determination for most of the cases. As we will see, all techniques here presented are often used in almost all published works on chemical synthesis and catalysis, therefore their correct management (dominio) is very important.

3.Aims of the course and competences

3.1.Aims of the course

The main goal of this course of *Structural Characterization Techniques* is to provide the student with a set of tools, in the form of techniques, focused to the structural characterization and the measurement of physical and chemical properties, which result mandatory for the research in chemical synthesis and catalysis. The course tackle the study of the most relevant, informative and useful spectroscopic, spectrometric and chromatographic techniques for research in inorganic, organic and organometallic chemistry, and in homogeneous and heterogeneous catalysis. The aim of this course is the study in depth of each technique, from the physical basis to the advanced applications, as well as the specific infrastructure of each one. Moreover, we aim to provide the student with a global perspective of the whole set of techniques and how to combine the information gathered on each one to obtain a single structural determination.

The scope of application of all studied techniques is really wide, because they are basic tools of structural determination and their knowledge is mandatory in all laboratories of chemical synthesis and catalysis. The use of these techniques is global, not only in the domain of the academic research, but also in other areas such as the medicine, the pharmaceutical industry, the food industry, quality control processes and so on.

3.2.Competences

To be able to discriminate, among the different techniques, which is the most adequate to solve an specific problem or, alternatively, which is the combination of techniques providing the maximal information.

To design experiments on each technique optimizing the experimental parameters.

To be able to make a correct interpretation of the experimental data (spectra, chromatograms, voltammograms), finding their relationship with the structure.

To be able to make a critical analysis of the data gathered and determine the accuracy level of the performed characterization.

Capacity to increase autonomally the knowledge on each technique.

Capacity to analyze critically and make assessments about a given structural determination performed using a given technique.

To be able to perform bibliographic searches about particular aspects of the different techniques and summarize clearly the key points of such publications.

4.Assessment (1st and 2nd call)

4.1.Assessment tasks (description of tasks, marking system and assessment criteria)

The evaluation during this course is based on the following activities, weighted as indicated:

1.- A mid-term examination containing theoretical, theoretic-practical questions and problems from the themes 1 to 6 (nuclear magnetic resonance) of the program (**P1**). Students who get a mark higher than 5 points will avoid these themes in the final exam.

2.- Development and exposition of a supervised practical work (**T1**).

3.- There will be a final exam at the end of the term containing theoretical and theoretic-practical questions or problems from the themes 7 to 15 of the program (**P2**). Students who had not been done the control **P1** or who had not get a 5 points mark, must have an additional exam with questions from themes 1 to 5 (**P1'**). The weight of **P1'** over the final mark will be the same than that of **P1** or **P2**.

The final mark will be the best one of the following two marks:

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MARK 1 = 0.35 x (**P1** or **P1'**) + 0.30 x **T1** + 0.35 x **P2**

MARK 2 = 0.5 x (**P1** or **P1'**) + 0.5 x **P2**

The rating of the students in the second annual examination session will consist in a single written exam that cover all themes of theory, problems or laboratory sessions defined as learning activities. The number of official opportunities to which the student has right by registration (2 per year), as well as the consumption of such opportunities, will be regulated by the *Normativa de Permanencia en Estudios de Máster* and *Reglamento de Normas de Evaluación del Aprendizaje* (http://www.unizar.es/ice/images/stories/calidad/Reglamento%20Evaluacion.pdf). The general criteria for the design of the final exams and the qualification system will also be regulated by the Reglamento, as well as the publication of the hour, place and date where the revision of the exams will take place after publication of the qualifications.

5.Methodology, learning tasks, syllabus and resources

5.1.Methodological overview

The learning process defined for this course is based mostly on lectures, where the student is prompted to participate actively, complemented with classes of problem-solving, thematic seminars and tutorials. Although this course has a clear practical and applied orientation, the theoretical bases of each technique is not neglected because they are mandatory for their correct understanding and proper data interpretation.

The structure of the seminars will be that of practice sessions where the students have to tackle real problems and where the methodology for the correct analysis and interpretation of experimental data (for instance, spectra) is presented. Most of the techniques taught in the course are used as self-service in our Institute. Therefore, in order to get an optimal information/time ratio, is compulsory to know the available experiments on each case, how to measure properly and how to extract the information contained on each set of experimental data. During the laboratory sessions, of compulsory attendance, the students will learn the different parts of the hardware of each technique and how it works, in order to gather as much information as possible in an autonomous way. In the case of nuclear magnetic resonance, the students will have the opportunity to attend a practical course of the use of the spectrometer (20 h), at the end of which they will have acquired the basic competences to measure NMR spectra in a totally autonomous way.

In addition to these activities, students will prepare a supervised assignment. It will deal with the full structural determination of an unknown sample using the combined application of all knowledges acquired during the course in the different techniques. This structural determination will be coordinated, as much as possible, with the synthetic works developed in the couses of *Synthetic Strategies on Advanced Organic Chemistry* and *Molecular Design in Inorganic and Organometallic Chemistry.*

5.2.Learning tasks

The course includes the following learning tasks:

- Interative lectures (3 ECTS).
- Problem-solving sessions and seminars (2 ECTS).
- Laboratory sessions on big machines (NMR, GC, and so on) (1 ECTS).
- Guided assignments of practical orientation.
- Tutorials for reduced groups or individualized.

5.3.Syllabus

The course will address the following topics:

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Topic 1. Basics of the Nuclear Magnetic Resonance (NMR). Excitation: the nuclear spin, behaviour of the nuclear spin on the magnetic field, Larmor frequency, population of the different energy levels, transition energies, the macroscopic magnetization, the electromagnetic pulse, the resonance condition. Relaxation: T1 and T2 relaxation, the correlation time, the spectral density function, the Free Induction Decay (FID) and its mathematical treatment.

- *Problems.* Examples of analysis of NMR spectra: chemical shift and coupling constants involving 1H, 13C, 19F and 31P nuclei.

Topic 2. 1D experiments in NMR. Pulse programs and sequences, important parameters, the pulse-acquisition sequence, 1H and 19F experiments, parameter sets. Optimizing the pulse-acquisition sequence: improving sensitivity. Double irradiation sequences, decoupling programs, advantages and disadvantages, experiments of 13C and 31P. Multipulse sequences, two- and three-channels configuration: the APT (J-modulated) sequence, polarization transfer, SPI, INEPT and DEPT sequences. Dynamic Nuclear Polarization.

- *Assignment:* basic introduction to Bruker systems, routine for 1D experiments (lock, shim, rpar, wobb), measurement of 1H and 19F experiments. The decoupling channel, 31P and 13C, possibilities: power gated versus inverse gated (integration), APT and DEPT135 experiments.

Topic 3. The NOE effect. Origin of the NOE effect, relationship with relaxation and correlation time, steady-state NOE and transient NOE, mixing time, NOE of more than two nuclei, spin diffusion, the kinetics of the NOE, intramolecular distances, the ROE effect, the spin-lock sequence, the heteronuclear NOE.

Topic 4. 2D experiments. Why is necessary to perform 2D experiments? generation of the second dimension, the evolution time. Homonuclear correlation through coupling constant (COSY, COSY-DQF and TOCSY) or through NOE effect (NOESY, ROESY). Use of pulsed-field gradients, advantages, limitations. Heteronuclear correlation through coupling constant (HETCOR, HMQC, HSQC and HMBC) or through NOE effect (HOESY). Diffusion experiments (DOSY). Selective soft pulses: 1D-NOESY.

- *Problems.* Structural determination using chemical shif, coupling constants and NOE effects obtained from 1D and 2D experiments.

Topic 5. Instrumental aspects. The magnet, parts; the coils, how are they built, alloys, what is a quench, field stability and homogeneity, lock and shim systems, cryoshims, shims profiles. The probe, tuning and matching, direct and inverse probes, cryoprobes, nanoprobes. The console, parts, signal generation, routing, amplification, reception, sampling, digitizers, ADC systems, gradients (concept, shape, applications), handling the FID.

- *Assignment:* 2D experiments COSY, NOESY, HSQC, HMBC, optimization

Topic 6. The NMR time scale, NMR dynamics, fluxional molecules, exchange. Determination of reaction rate constants: spin saturation transfer, simulation of dynamic spectra, reaction kinetics.

- *Problems.* Kinetic and dynamic of chemical processes from the NMR
- *Assignment:* pseudo 2D experiments, T1 measurement using the inversion-recovery method, determination of reaction rate constants.
- *Assignment (optional)*: **Course of practical use of NMR spectrometers. Basic level.** Syllabus: basic introduction to Bruker systems, routine for 1D experiments (lock, shim, rpar, atmm), 1H experiments, optimization, heteronuclei (15N, 19F, 31P, 13C, 29Si, 11B, 119Sn, 195Pt, otros); the decoupler, when and why (waltz16, garp), different decoupling sequences and techniques: power-gated, inverse-gated, spin-echo (APT), polarization transfer (DEPT135); 2D experiments: COSY, NOESY, HMQC, HSQC, HMBC, pseudo-2D sequences, T1 determination through inversion-recovery, reaction kinetics

Topic **7.** Mass Spectrometry and hyphenated techniques I. Mass Spectrometry Fundamentals. Ionization systems: EI, CI, ESI, APCI, APPI, MALDI. Analyzers: Magnetic analyzer, Quadrupole mass filter, ion trap, Time of fly analyzer. Understanding mass spectra: Accurate mass measurements, isotopic pattern.

- *Assignment:* obtaining mass spectra: ESI/APCI, MALDI. High and low resolution spectra.

Topic 8. Mass Spectrometry and hyphenated techniques II. Tandem mass spectrometry. Metastable ions and Collision Induced dissociation. Instruments: triple quadrupole analyzer. Ion trap, hybrid spectrometers etc. Aplications of tandem mass spectrometry.

Topic 9. Mass Spectrometry and hyphenated techniques III. Chromatographic methods coupled to mass spectrometry. Instrumentation: GC/MS, HPLC/MS, TLC/MS. Mixture analysis. Specialized analysis methods: Single ion Recording (SIR), Multiple Reaction Monitoring (MRM).

- *Assignment*: GC/MS. HPLC/MS and Tandem mass spectrometry. Analysis of a complex mixture by using HPLC/MS. Fragmentation study of an organic compound in an ion Trap mass spectrometer.
- *Problems*: Interpretation of mass spectra: accurate mass measurements, Isotopic patterns, Tandem mass spectrometry.

Topic 10. Ultraviolet-visible spectroscopy I. General considerations: i) Introduction and principles. ii) UV-Vis spectrophotometers. iii) Solid state studies: diffuse reflectance spectroscopy. Integrating spheres. Kubelka-Munk equation. iv) Chromophore and auxochrome groups. Isosbestic point. v) Different roles of the metal in the absorption of coordination complexes. Special behavior of lanthanides.

- *Problems:* Protocol for UV-Vis spectra measurement. Examples of assignation of absorption bands to different transition types.
- *Assignment*: Measurement of absorption and diffuse-reflectance spectra: software and sample preparation.

Topic 11. UV-Vis spectroscopy II. Applications: i) Colorants: Azo-derivatives, phtalocianines, formazan-derivatives. ii) Vapochromism: structural origins of vapochromism. Tools used for the analysis and description of vapochromism. Suitability of vapochromic complexes for sensoring.

- *Problems:* UV-Vis review questions.

Topic 12. Luminescence I. General considerations. i) Definition and luminescence forms. ii) Light emission origin. iii) Emission and excitation spectra. iv) Spectrofluorometer. v) Lifetime and half-life of a radiative transition. vi) Quantum yield of fluorescence and phosphorescence. vii) Quenching. viii) Fluorophores. ix) Analysis of luminescent compounds.

- *Problems:* Protocols for the measurement of: emission and excitation spectra, lifetimes and quantum yields. Assignation of the transitions responsible for the luminescence in different compounds.
- *Assignment:* Emission and excitation spectra measurements: software and sample preparation.

Topic 13. Luminescence II: Applications. i) Phosphorescent compounds for OLEDs: principles and set-up of an OLED. The role and characteristics of phosphorescent compounds for OLEDs. ii) Fluorescence sensing.

- *Problems:* Luminescence review questions

Topic 14. Electrochemical techniques I. Basic concepts: electron-transfer and energy levels, concentrations and potential (Nernst's equation), kinetics of the electron-transfer reactions (Butler-Volmer's equation), mass transport (Fick's laws).

Topic 15. Electrochemical techniques II. Potential step voltammetry (Cottrell's equation), lineal voltammetry (Randles-Sevick's equation), cyclic Voltammetry (chemical reversibility).

- *Assignment:* Basic introduction to potentiostat/galvanostat E&G, sample preparation, CV waves (Vi, Vf, Vs, scan rate).

5.4.Course planning and calendar

Further information concerning the timetable, classroom, assessment dates and other details regarding this course, will be provided on the first day of class or please refer to the bulletin board and the Faculty of Science website (https://ciencias.unizar.es).

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The submission of assignments will be done according to the calendar, which will be announced in advance.

The students will be provided with diverse teaching material either at reprography or through the University's virtual platform https://moodle2.unizar.es/add.

5.5.Bibliography and recommended resources

BB Bard, Allen J**.** Electrochemical methods: fundamentals and applications / Allen J. Bard, Larry R. Faulkner . **-** 2nd ed. New York [etc.]: John Wiley & Sons, cop. 2001

BB Claridge, Timothy D. W., eauthor**.** High-resolution NMR techniques in organic chemistry / Timothy D.W. Claridge. . Third edition. Amsterdam; London: Elsevier, [2016] 264 4 ò016

BB Determinación estructural de compuestos orgánicos / E. Pretsch ... [et al.] Barcelona [etc.]: Masson, 2003

BB Friebolin, Horst. Basic one- and two-dimensional NMR spectroscopy / Horst Friebolin. **-** 5th completely revised and enlarged ed. Weinheim [etc.]: VCH, cop. 2011

BB Herbert, Christopher G**.** Mass spectrometry basics / Christopher G. Herbert, Robert A.W. Johnstone Boca Raton [etc.]**:** CRC Press , cop. 2003

BB Schmidt, Werner. Optical spectroscopy in chemistry and life sciences / Werner Schmidt Weinheim: Wiley-VCH, cop. 2005

BB Zerbe, O. Applied NMR Spectroscopy for Chemists and Life Scientists. 1st Wiley-VCH, Weinheim, Germany 2014

BC Berger, Stefan. 200 and more NMR experiments: a practical course / Stefan Berger, Siegmar Braun . Weinheim: Wiley-VCH, cop. 2004

BC Claridge, Timothy D. W. High-resolution NMR techniques in organic chemistry [Recurso electrónico] / Timothy D.W. Claridge . 2nd ed. Amsterdam; London: Elsevier, cop. 2009

BC F. G. Kitson, B. S. Larsen, C. N. McEwen. Gas Chromatography and Mass Spectrometry. A Practical Guide. Academic Press 1996

BC K.L. Busch, G. L. Glish, S. A. McLuckey. Mass Spectrometry/Mass Spectrometry, Techniques and Applications of Tandem Mass Spectrometry. Wiley VCH 1988

BC Laboratory techniques in electroanalytical chemistry / edited by Peter T. Kissinger, William R. Heineman. 2nd ed. rev, and expanded New York [etc.]: Marcel Dekker, cop. 1996

BC Lakowicz, Joseph R**.** Principles of fluorescence spectroscopy / Joseph R. Lakowicz. 3rd ed. (corrected at 4th printing 2010) New York: Springer, 2010

BC Pregosin, Paul S. NMR in organometallic chemistry / Paul S. Pregosin. Weinheim: Wiley-VCH, 2012

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BC R. E. Ardrey. Liquid Chromatography-Mass Spectrometry: An Introduction. Willey-VCH 2003

BC Requena Rodríguez, Alberto. Espectroscopía / Alberto Requena Rodríguez, José Zúñiga Román. Madrid [etc.]: Pearson/Prentice Hall, cop. 2004