UNIVERSITÀ
DEGLI STUDI DI MILANO-BICOCCA

SYLLABUS DEL CORSO

Chimica Analitica Strumentale e Laboratorio

2122-3-E2702Q058

Aims

The main objective of the course is to provide the student with the theoretical foundations and fundamental operative tools of a variety of techniques useful in modern analytical chemistry and necessary for the qualitative and quantitative determination of the chemical nature of a sample. The knowledge of the principles and the instrumentation of the main analytical techniques will be introduced together with the ability to choose and manage the best methods suited to the purposes of the analysis. The student will then be able to evaluate the instrumental characteristics of the fundamental analytical approaches, the fields of application, the advantages and disadvantages of the individual analytical techniques and will therefore be able to suggest the choice of the analytical technique considered most suitable for a specific problem. In particular, the student must demonstrate that he has achieved the following educational objectives:

Knowledge and understanding: at the end of the course the student knows the theoretical and practical bases of the most modern instrumental analytical techniques (UV-vis, IR, NMR, AAS, ICP OES spectroscopic techniques, mass spectrometry, chromatographic methods) and – methods of sample pretreatment.

Applying knowledge and understanding. At the end of the course the student is able to: know how to deal with and solve analytical problems; know how to compare different techniques for the same purpose, evaluating the most suitable technique to apply to the context; acquire and know how to use an appropriate chemical lexicon in relation to the topics covered in the course; use the analytical instrumentation, in particular the one used during laboratory experiments (UV-Vis, Spectro-Fluorometer, GFAAS, ICP OES, HPLC-DAD, GC-MS)

Making judgements. At the end of the course the student is able to: choose the most appropriate analytical technique to solve a given analytical problem; write and justify a critical report on the analytical methods used and the information obtained from the analysis of the data

Learning skills. At the end of the course the student is able to: understand the principles of analytical chemistry and their methodological application to solve general analytical problems; predict what type of information will be possible to identify from the analytical data; evaluate the possibility of alternative analytical methods for solving a problem.

Communication skills. At the end of the course the student is able to: describe in a clear and concise written form, as well as to express orally with appropriate chemical language properties, the objectives, the procedure and the results of the analytical experiments; carry out experimental laboratory work and develop an analytical analysis in a tem-working framework.

Contents

Spectroscopy: introduction to spectroscopy, absorption, emission and excitation spectra. Definition, details and limitations of the Lambert-Beer law. Instrumental components of UV-Visible spectrophotometers, FT-IR and spectrofluorometers: instrumentation structure, sources, monochromators, detectors and signal processing. Quantitative and qualitative applications. Fluorescence spectroscopy. Introduction to NIR spectroscopy.

Atomic absorption spectroscopy (AAS), flame AAS, graphite furnace AAS, atomic emission spectroscopy, Inductively Coupled Plasma, ICP OES, ICP MS, Qualitative and quantitative applications.

Chromatography: general principles. Gas-Liquid, Liquid-Liquid, Ionic Chromatography: injectors, columns and detectors. Outline of affinity and exclusion chromatography. Chromatography applications.

Mass spectrometry: general principles, ionization methods (EI, CI, FAB, MALDI, ESI, APCI), analyzers (quadrupole, TOF, ion trap, FT-MS, orbitrap). Qualitative and quantitative applications.

NMR: nuclear spin; nuclear magnetic resonance principle; NMR spectrometer components. Spectroscopy of 1H: chemical shift, chemical shielding, chemical coupling, first order spectra and higher order spectra. Fourier transform. Spectroscopy of 13C. Examples of interpretation of spectra of organic molecules.

Practical sessions in the laboratory, to illustrate the use of the analytical instrumentation described in the course in qualitative and quantitative applications.

Detailed program

Introduction to spectroscopy, equations and properties of electromagnetic radiation. Definition of amplitude, frequency, wavelength and wave number. Overview of the energies associated with the different spectral regions. Interactions between matter and electromagnetic radiation: definitions of absorption and emission. Definition of Transmittance and Absorbance. Definition of the Lambert-Beer law, description of its parameters and definition of the fields of applicability of the law, its specifications and limitations: instrumental deviations from the law for polychromatic radiation and stray light. Experimental and theoretical absorbance and correction with reference solutions. Description of the additive behavior of the absorbance in mixtures. Definition of absorption spectra. Characteristics of UV-visible and IR absorption spectra. Vibrational transitions and model of the harmonic oscillator. Definition of the theoretical number of vibrational deformations.

Instrumental components for spectrophotometry: sources, monochromators, filters, sample cells, internal and external reflectance acquisitions, optical fiber, Michelson interferometer and Fourier transformation, detectors (photomultiplier tubes, diode arrays, charge-coupled devices). Single-beam, dual-beam, and multi-channel spectrophotometers. Relative accuracy on absorbance and dynamic range. Specifications for signal acquisition in FT-IR spectrophotometers and definition of the Signal-to-Noise ratio.

UV-visible absorption spectroscopy: qualitative and quantitative applications. Electronic transitions and absorbing species, effect of conjugation on absorption; absorption by charge transfer; quantitative determinations: calibration, limitations and characteristics, operating conditions, advantages and disadvantages; method of standard additions; determination of substances in mixtures with resolved and unresolved peaks; spectrophotometric titrations; determination of the equilibrium constant with Scatchard diagram; determination of the ionization constant of an indicator; study of the stechiometry of a reaction using the continuous variation method (Job) and the molar ratio method.

IR absorption spectroscopy: qualitative and quantitative applications. Factors that determine the increase or reduction of the number of bands in the spectrum; degeneration, coupling and overtone bands; stretching and bending vibrations; factors that determine the intensity and frequency of an absorption band; characteristic regions of the IR spectrum; introduction of the interpretation of IR spectra; background and post processing operations on IR spectra; limitations of the quantitative applications of IR spectroscopy; introduction on NIR (near-infrared) spectroscopy, NIR instrumentation, signal acquisition and industrial applications.

Fluorescence spectroscopy: excitation and emission spectra; relationship between emission spectra and absorption spectra; relationship between emission spectra and excitation spectra; characteristics of fluorescent compounds; relationship between fluorescence intensity and concentration, limits of application to maintain the linear relationships; structure of a spectrofluorometer: sources, monochromators, sample cells, detectors. Applications of fluorescence spectroscopy.

Atomic Absorption Spectroscopy, Atomic Emission Spectroscopy: energy level diagrams, atomic emission spectra, atomic absorption spectra, atomic line widths, line broadening from the Uncertainty effect, Doppler broadening, pressure broadening, temperature effect. Methods of solution sample introduction: pneumatic nebulizers, ultrasonic nebulizers, electrothermal vaporizers, hydride generation techniques. Sample atomization, flame atomization, electrothermal atomization, cold-vapor atomization. Radiation sources: hollow-cathode lamps, electrodeless discharge lamps, source modulation, single-beam instruments, double-beam instruments, spectral interferences, background correction based on D-lamp correction, Zeeman effect, source self-reversal. Chemical interferences (compounds of low volatility, dissociation equilibria, ionization equilibria), matrix modifiers.

Inductively-coupled plasma source. Scheme of ICP OES instrumentation, radial, axial position. Type of detectors. Elements to be analyse, line selection. Interference. ICP MS. Sample preparation.

Introduction to analytical separations and chromatographic separations. Classification of chromatographic methods. Definition of chromatogram. Characteristics of the chromatographic column; distribution constants, retention times, retention factor, selectivity factor. Efficiency of the chromatographic column and its description; definition of plate height and number of theoretical plates. Factors that determine the efficiency of the chromatographic column. Van Deemter's equation. Resolution of the chromatographic column and effect of the factors on the resolution.

Gas-liquid chromatography; introduction to Gas-Liquid chromatography, the separation process in gas chromatography; injection system, columns and their characteristics, capillary and packed columns, liquid stationary phases, flame ionization detectors (FID), thermal conductivity detectors (TCD), electron capture detectors (ECD). Applications of Gas-Liquid chromatography.

Liquid - Liquid Chromatography: characteristics of the chromatograph; sample pumping and injection systems. Types of columns. Characteristics of the stationary phase. The process of elution (isocratic and gradient). Detectors. Ionic Chromatography. Overview of partition, adsorption, size-exclusion and affinity chromatography.

Mass spectrometry: principles of mass spectrometry, electronic ionization, definition of mass spectrum; types of mass spectrometers (quadrupole, flight time, ion trap, orbitrap); components of a mass spectrometer: injection system, ionization methods (EI, CI, FAB, MALDI, ESI, APCI), mass analyzer (quadrupole, TOF, ion trap, FT-MS, orbitrap), tandem mass spectrometry and hybrid analyzers, detector. Interfaces Chromatography - mass spectrometry. Resolution of mass spectrometers and types of mass analyzers. Introduction to atomic mass spectrometry and molecular mass spectrometry. Qualitative applications of mass spectrometry (molecular recognition) and quantitative (hyphenated techniques with chromatographs or ICP-MS).

Background. Physical bases of nuclear magnetic resonance, concept of nuclear spin, spin quantum number, main magnetic field, Larmor frequency, population of spin levels. Laboratory reference system, rotating reference system, radiofrequency pulse, 90° pulse, Free Induction Decay (FID). Diagram of an NMR spectrometer. Sample preparation, tuning, shimming. Choice of deuterated solvent. Acquisition of FID and Fourier transform.

^{1}H NMR Spectroscopy. Definition of chemical shift and determining factors: diamagnetic contribution and contribution of magnetic anisotropy. Spin-orbit interaction. Concept of spin system. Multiplets of the 1st order and relative intensity (Pascal triangle). Homotopic, enantiotopic and diastereotopic atoms. Magnetic equivalence concept. Exercises for the determination of spin systems generated by organic compounds.

^{13}C NMR spectroscopy. Chemical shift of the various functional groups, coupling with protons, decoupled spectra. Finally some lessons will be entirely dedicated to the interpretation of NMR spectra of organic molecules.

Practical lab sessions include the following six activities: determination of caffeine in coca-cola by high-performance liquid chromatography (HPLC), spectrophotometric determination of the ionization constant of an indicator, spectrofluorimetric determination of B2 vitamin in milk, determination of copper in wine by atomic absorption spectroscopy (AAS), metal determination in coffee sample by ICP OES, separation of a pesticide mixture by GC-MS.

Prerequisites

Basic knowledge on the theoretical and operational foundations of analytical chemistry. Basic manual skills and operational skills in practical laboratory experiences.

Teaching form

The course is divided into a part of lectures and frontal exercises, in which the theoretical background on the topics are given. During the course, the students follow six different practical experiences in the laboratory, where they learn directly the use of the analytical instrumentation described in the course for qualitative and quantitative applications. On the e-learning page of the course, the slides of the lessons are constantly updated and additional contents are available for further information on specific topics.

The lessons and the laboratory activities will take place in presence: the students will be divided into 2 shifts of 6 groups each of numbers compatible with the maximum capacity of the laboratory in which the experiences will be carried out. Each student will realize all the 6 foreseen experiences.

Textbook and teaching resource

The teachers provide the slides of the course lectures and some scientific articles for the deepening of specific topics through the e-learning platform. In addition to this material provided by the teachers, the following textbooks are recommended:

-D.A. Skoog, F.J. Holler, S.R. Crouch, “Chimica Analitica Strumentale” (EdiSES);

-D.C. Harris, “Chimica Analitica Quantitativa” (Zanichelli); -

R.M. Silverstein, F.X. Webster, D.J. Kiemle, D.L. Bryce, “Identificazione spettrometrica di composti organici” (Casa ed. Ambrosiana).

For each laboratory experience, a laboratory sheet is provided through the e-learning platform. It describes the experience in a synthetic way; furthermore, additional information material is provided, which includes a detailed document with a description of the theoretical foundations and operational methods of the experience, scientific articles for a deepening of the experience and the operating instructions of the instruments.

Semester

First semester

Assessment method

The exam consists of an oral examination in which the topics described in the lectures and the laboratory experiences are discussed. In addition to knowledge on the fundamentals presented in the course, students' skills and aptitudes are also assessed to adapt the theoretical foundations of analytical instrumental chemistry to particular operational and practical conditions; the expositive ability and adequacy of the student's language are also assessed.

In addition, two intermediate tests (with multiple choice tests in the informatic lab) are carried out at half of the course and at the end of the course; each trial includes 30 questions; the first test includes questions on the topics presented in the first part of the course, the second test includes questions on topics presented in the second part of the course and on laboratory experiences; students who obtain positive results in both tests (at least 20 questions answered correctly) may take a reduced oral exam, in which the laboratory reports and their connection to the fundamental topics of the course are discussed. The starting mark in the reduced oral exam consists of the average number of correct answers provided in the two intermediate tests.

For admission to the oral examination it is necessary to have delivered the all the reports of the 6 experiences within the established deadline.

Students who fail an exam can repeat it at the successive exam date.

It is possible to take the exam in English.

Office hours

Teachers are always available to receive students in their offices (or by Webex platform) upon an e-mail request.