CHEM4610: ADVANCED CHEMICAL TECHNIQUES

The University of Manitoba, Faculty of Science, Department of Chemistry

Syllabus for CHEM4610 (2018/2019).

General Course Description:

Advanced Chemical Techniques (CHEM4610) is a 6 credit hour course that spans over 2 terms. This course provides the opportunity to learn about and be exposed to state-of-the-art research instrumentation spanning diverse fields of specialization. All instructors are experts in their respective fields and aim at providing a stimulating environment.

The 4 sections include:

1) Mass Spectrometry 2) Spectromicroscopy 3) Crystallography and 4) Nuclear Magnetic Resonance.

You will learn about instrumentation, data collection and data analysis while applying those techniques to diverse chemical and biochemical problems. Because of the diversity of the topics no single textbook is available/assigned for CHEM4610, instead the individual instructors will provide literature resources specific to their sections. The term work and assignments will be determined by the individual instructors and will be announced in a section specific syllabus at the beginning of each section.

I) GENERAL INFORMATION:

Class time: Mondays and Wednesdays 2:30 p.m. – 3:45 p.m.
Room: 419 Machray Hall and/or 539 Parker Building

II) INSTRUCTOR INFORMATION:

Course Coordinator:
Name: Dr. Mario Bieringer
Office: 520C Parker Building
E-mail: Mario.Bieringer@UManitoba.ca
Phone: (204) 474 6258

Course Instructors:

1) Mass Spectrometry Section:
Dr. Hélène Perreault
550 Parker Building
Helene.Perreault@umanitoba.ca
(204) 474 7418

2) Spectromicroscopy Section:
Dr. Kathleen Gough
378 Parker Building
Kathleen.Gough@umanitoba.ca
(204) 474 6262

3) Crystallography Section:
Dr. Mario Bieringer
520c Parker Building
Mario.Bieringer@umanitoba.ca
(204) 474 6258

4) Nuclear Magnetic Resonance Spectroscopy Section:
Dr. Scott Kroeker
458 Parker Building
Scott.Kroeker@umanitoba.ca
(204) 474 9335

III) EVALUATION

Each section is worth 25%. Evaluation of each section will be communicated by the instructor at the beginning of the respective section.

The following letter grade conversion will be applied for the final grades:

92.0 -100.0%	A+	64.0 - 69.9%	C+
83.0 - 91.9%	A	58.0 - 63.9%	C
76.0 - 82.9%	B+	50.0 - 57.9%	D
70.0 - 75.9%	B	0 - 49.9%	F

IV) COURSE SCHEDULE & TOPICS:

Section 1 (Sep. 5, 2018 – Oct. 22, 2018):
Mass Spectrometry – Dr. H. Perreault
For a long time, mass spectrometry was used for the mass and structural determination of small organic molecules using electron impact and chemical ionization techniques. Nowadays these methods for volatile compounds are still in demand by synthetic, environmental and natural product chemists, but mass spectrometry has evolved much further with the advent of soft ionization techniques permitting the analysis of large, non-volatile biomolecules. This section will discuss instrumental and analytical aspects of several ionization techniques, mass analyzers, sample preparation methods and compilation and understanding of data. From elements to small molecules to large thermolabile biomolecules and polymers, mass spectrometric methods will be described and compared. Virtual lab sessions will guide the students through data compilation and interpretation.

Section 2 (Oct. 24, 2018 – Dec. 5, 2018):
Spectromicroscopy – Dr. K. Gough
Technological advances have lead to the development of many new forms of microscopy, with light from X-ray to IR and terahertz. With mid-IR, any material can be imaged based on molecular vibrations of the chemical components; Raman imaging is possible with lasers from Deep UV to near infrared. Each wavelength regime and spatial resolution necessitates a completely different type of instrument and provides different types of chemical information on a different spatial scale. In this section, students will see infrared spectrochemical imaging from mm to sub-micron length scales, in transmission as well as Attenuated Total Reflection and with polarized light microscopy. Tip-based methods that provide nm-scale resolution for Raman (Tip Enhanced Raman Spectroscopy) and for infrared (near-field IR spectroscopy and imaging with Atomic Force Microscopy based instruments) will be presented. Students will have one lab experience and be provided with a data cube which they will analyze with guidance from the instructor.

Section 3 (Jan. 7, 2019 – Feb. 13, 2019):
Crystallography – Dr. M. Bieringer
An overview of powder and single-crystal X-ray diffraction methods and their use for the determination of solid-state structures will be given. Diffraction is a very versatile method for structure determination of crystalline solids used in all fields of chemistry and biochemistry, material sciences, pharmacy, life sciences, mechanical and electrical engineering and is often used as a tool in archaeology as well. This section will introduce the basic concept of diffraction theory with examples of single crystal diffraction and powder diffraction.

Section 4 (Feb. 25, 2019 – Apr. 8, 2019):
Nuclear Magnetic Resonance Spectroscopy – Dr. S. Kroeker
The sensitivity of NMR spectroscopy to local electronic environments has made it an indispensable tool for the structural elucidation of solids and molecules in solution. This module will outline the basic physics which makes NMR possible, moving on to practical aspects of typical NMR experiments, including spectral acquisition, processing and interpretation. Internal interactions between nuclei and local fields will be presented in detail, as they form the basis for its widespread utility in chemistry, with a focus on magnetic shielding, and dipolar and quadrupolar couplings. Special techniques for sensitivity and resolution enhancement in solid phases will be demonstrated. Case studies illustrating the applicability of multinuclear NMR spectroscopy in various fields will be highlighted.

V) ACADEMIC INTEGRITY POLICIES:
Academic Dishonesty:
The University of Manitoba treats plagiarism and cheating as serious academic offenses.

- The complete documentation regarding cheating, plagiarism and fraud be accessed in the calendar at: http://umanitoba.ca/student/resource/student_advocacy/cheating_plagiarism_fraud.html
- Additional documentation is available on the Faculty of Science website http://umanitoba.ca/science/undergrad/resources/webdisciplinedocuments.html

PART I: Fall 2018: weeks 1 - 6

Section A (Sept. 5 – Oct. 22, 2018)

Mass Spectrometry – Dr. H. Perreault

Mass spectrometry has long been used for the structural determination of small organic molecules using electron impact and chemical ionization techniques. Nowadays these methods are still in demand by synthetic and natural product chemists, and two lectures will describe how empirical formulae and structures can be obtained for volatile molecules. But mass spectrometry has evolved much further with the advent of soft ionization techniques permitting the analysis of large, non-volatile biomolecules. Most biomedical labs are equipped with mass spectrometers, and LC-MS analytical workflows will be highlighted. This section will also discuss instrumental and analytical aspects of several ionization techniques, mass analyzers, hyphenated techniques, and interpretation of data. During three class periods ("virtual" labs), students will learn the interpretation of different types of mass spectrometry data. They will then make short presentations on the data analyzed.

Marking scheme: 90-min final test: 50%; Student presentations: 40%; attendance 10%.

Textbook: not mandatory. One recommended book for readings is Boyd, Basic, Bethem, "Trace Quantitative Analysis by Mass Spectrometry", Wiley, 2008, 724 p.

Class notes: will be provided prior to each class.

PART II: Fall 2018: weeks 7 - 12

OVERVIEW OF COURSE CONTENT FOR VIBRATIONAL SPECTROMICROSCOPY, SECTION 2 OF CHEM 4610

Instructor: Professor Kathy Gough Room 378 email: Kathleen.Gough@umanitoba.ca Phone: 474-6262

The following topics are covered in the posted material that accompanies the lecture presentations, as well as lab tours (scheduled for week 1, owing to conflict with conference) and both assignments. Questions on the tests will be based on this material.

1. Theory of excitation – properties of light and of molecular vibrations that lead to allowed transitions (*by this, I am referring to the Morse oscillator potentials, vibrational energy levels, and changes in molecular dipoles, both permanent,* μ*, and induced,* $\mu = \alpha E$)
   a. IR absorption
   b. Raman scattering

2. Instrumentation and specialized accessories (*several schematics are included in presentations and posted materials; be familiar with the paths of light, why and how the optics are designed this way*)
   a. Michelson Interferometer for FTIR: How it works; Advantages, Signal to Noise
   b. Optics and optical paths for IR microscope, single pixel raster scan *versus* focal plane array (FPA)
   c. Attenuated Total Reflection FTIR; polarization contrast; FTIR tomography
   d. Optics and optical paths for Raman microscope, CCD detector
   e. Relationship between wavelength and spatial resolution (diffraction limits)

3. Important differences between Fourier Transform and dispersive spectrometers
   a. With FTIR, raw data is recorded in one domain (displacement of moving mirror, spatial domain) then FT to create standard absorption spectrum (wavenumber, or frequency domain). Factors discussed include mirror path, spectral resolution, apodization functions and post-collection modifications to raw data.
   b. Advantages of FT over dispersive instruments, for IR and NIR wavelength range, compared to visible laser Raman, which is also a dispersive instrument.

4. Advanced techniques based on Surface and Tip-Enhancement of signal
   a. Near-Field Infrared spectroscopy and imaging
   b. Surface and Tip Enhanced Raman Scattering (SERS and TERS)
   c. Spatial resolution with Near-field techniques

5. Applications: Interpretation of spectra, drawn from examples in class and lab-based assignment
   a. Recognition of vibrations that can be affected by orientation relative to plane polarized light
   b. Recognition of functional group patterns and analysis of spectrochemical images

6) EVALUATION 2 Assignments: **40%** *Test Part A:* **30%** (24 hr take home) *Part B:* **30%** (in-class, last day)

This section is worth 25% of your total grade; the numerical score will be sent to the course coordinator. Numerical conversion for the final grade will be as per original general overview:

92-100%	A+	64-69%	C+
83-91%	A	58-63%	C
76-82%	B+	50-57%	D
70-75%	B	0-49%	F

PART III: Winter 2019: weeks 1- 6

CHEM4610: ADVANCED CHEMICAL TECHNIQUES: DIFFRACTION

The University of Manitoba, Faculty of Science, Department of Chemistry

Syllabus for CHEM4610-Diffraction (2018/2019)

I) GENERAL INFORMATION:

Class time:	Mondays and Wednesdays:	2:30 p.m. – 3:45 p.m.
Room:		418 Machray Hall
Class dates for the Diffraction Section:		Jan. 7th, 2019 – Feb. 13th, 2019

II) INSTRUCTOR INFORMATION:

Course Instructor:

Name: Dr. Mario Bieringer **E-mail:** Mario.Bieringer@UManitoba.ca
Office: 520c Parker Building **Phone:** (204) 474 6258
Office hours: by appointment

III) Literature:

*See **UMLearn** site.*

IV) ADDITIONAL RESOURCES:

*See **UMLearn** site. The **UMLearn** site provides the bulk of the information for CHEM4610 Diffraction.*

V) COURSE EVALUATION:

In-class tests and quizzes:	10%
Take home assignments:	2 x 20%
Final written and oral exam:	50%

Notes:

- The in-class tests and quizzes will not be announced. Students should be prepared for in-class testing for every class.
- Assignments will be distributed in class.
- There are no make-up assignments. Assignments not handed in on time will receive a grade of zero.
- The final exam will be written on **Tuesday March 5th, 2019 from 6:00 pm till 8:00 pm**.
- The oral exams will be scheduled for the period **March 11th till March 14th, 2019**.
- Oral exams are on a voluntary base. Oral exam grades lower than the written final exam grades will not be counted. Each oral exam will take approximately 20 minutes. Students interested in an oral exam need to request an oral exam appointment no later than Wednesday **March 8th, 2019** by e-mail Mario.Bieringer@UManitoba.ca.

VI) EXPERIMENTAL COMPONENTS:

This is a lecture course but the material will be easier to understand using hands-on examples. A number of facilities will be visited during the lecture times and measurements will be carried out for the assignments. Those measurements will require students to mount samples and participate in the data collection.

VII) IMPORTANT DATES:

Assignment #1:	distribution date:	Monday, January 21st, 2019
	due date:	Wednesday**, January 30th, 2019**
Assignment #2:	distribution date:	Monday, January 28th, 2019
	due date #1:	**Monday February 4th, 2019 (proposal submission)**
	due date #2:	**Friday, February 15th, 2019 (final submission)**
Final Exam:		**Tuesday, March 5th, 2019**: 6:00 pm – 8:00 pm (539 Parker Bldg.)
Oral Exam:		Deadline to schedule oral exams: **March 8th, 2019** Oral exam period: **March 11th till March 14th, 2019**

VIII) LITERATURE:

E-books:

1. Title: Powder diffraction [electronic resource] : theory and practice
   Author: Billinge, S. J. L. Publisher Cambridge : Royal Society of Chemistry, c2008. Edition Publishing Date 2008 Call Number Internet Access Holdings 1 copy available at Electronic Resources in INTERNET Online Access http://ebook.rsc.org/?DOI=10.1039/9781847558237

2. Title: X-Ray diffraction crystallography [electronic resource] : introduction, examples and solved problems
   Author: Waseda, Yoshio. Publisher Berlin ; Heidelberg ; New York : Springer, c2011. Edition Publishing Date 2011 Call Number Internet Access Holdings 1 copy available at Electronic Resources in INTERNET Online Access http://dx.doi.org/10.1007/978-3-642-16635-8

Additional E-book:

3. Title: Fundamentals of powder diffraction and structural characterization of materials [electronic resource] 2nd ed.
   Author: Pecharsky, Vitalij K. Publisher New York : Springer, c2009. Edition Publishing Date 2009 Call Number Internet Access Holdings 1 copy available at Electronic Resources in INTERNET Online Access http://dx.doi.org/10.1007/978-0-387-09579-0

IX) LECTURE MATERIAL:

1. Description of crystalline solids: periodicities, unit cells, crystal systems, Bravais lattices, fractional coordinates and Miller indices
2. Symmetry of crystalline phases: symmetry elements, symmetry operators, relation between crystal systems and symmetry elements, space groups (emphasis of 'International Tables of Crystallography Volume A", systematic absences of refletions
3. X-ray diffraction: electromagnetic spectrum, X-ray generation (Bremsstrahlung and characteristic emission lines), Bragg's law, determination of unit cell dimensions, reciprocal lattice, Ewald's sphere in 2 and 3 dimensions (diffraction limit), structure factor equation and peak intensities.
4. Single Crystal Diffraction: single crystal diffractometer and single crystal diffraction data analysis, structure solution and electron density maps, structure refinements, understanding crystal structure reports, $RbBe_4(BO_3)_3$
5. Powder Diffraction: single crystal and powder diffraction relation in direct space, powder X-ray diffractometer, X-ray filters, monochromators, single crystal vs. powder in reciprocal space, diffraction angles, peak density as a function of symmetry, peak intensities, peak width and the Scherrer equation
6. Powder Diffraction Data Analysis: phase identification, ICDD, phase mixtures and quantification, typical experimental goals for powder diffraction, comparsion of powder and single crystal results, application of powder diffraction, information from powder data
7. Powder Diffraction Experiments: sample mounts, instrument geometries, peak shape functions, Rietveld method, Crystal structure representation with VESTA
8. Beyond High-Resolution Diffraction: Rietveld refinement example, SAXS (small angle X-ray scattering), comparison of USAXS, SAXS, WAXS and high-resolution PDF experiments
9. Rietveld Software: FullProf, examples of input and output files, examples of powder pattern simulations and Rietveld refinements.
10. Advanced Diffraction: high temperature diffraction, synchrotron based X-ray diffraction, powder neutron diffraction

X) **Academic Integrity:**

POLICIES:
The following is an excerpt from the online Undergraduate Calendar 2017-2018 of the University of Manitoba;

Academic Integrity Academic Integrity

The University of Manitoba takes academic integrity seriously. As a member of the International Centre for Academic Integrity, the University defines academic integrity as a commitment to six fundamental values: honesty, trust, fairness, respect, responsibility and courage.

To help students understand the expectations of the University of Manitoba, definitions of types of prohibited behaviours are in the Student Academic Misconduct Procedure umanitoba.ca/student/studentdiscipline/academic_misconduct and provided below.

"Academic Misconduct" means any conduct that has, or might reasonably be seen to have, an adverse effect on the academic integrity of the University, including but not limited to:

(a) Plagiarism – the presentation or use of information, ideas, images, sentences, findings, etc. as one's own without appropriate citation in a written assignment, test or final examination.

(b) Cheating on Quizzes, Tests, or Final Examinations – the circumventing of fair testing procedures or contravention of exam regulations. Such acts may be premeditated/planned or may be unintentional or opportunistic.

(c) Inappropriate Collaboration – when a student and any other person work together on assignments, projects, tests, labs or other work unless authorized by the course instructor.

(d) Duplicate Submission – cheating where a student submits a paper/assignment/test in full or in part, for more than one course without the permission of the course instructor.

(e) Personation – writing an assignment, lab, test, or examination for another student, or the unauthorized use of another person's signature or identification in order to impersonate someone else. Personation includes both the personator and the person initiating the personation.

(f) Academic Fraud – falsification of data or official documents as well as the falsification of medical or compassionate circumstances/documentation to gain accommodations to complete assignments, tests or examinations.

Over the course of your university studies, you may find yourself in situations that can make the application of these definitions unclear. The University of Manitoba wants to help you be successful, and this includes providing you with the knowledge and tools to support your decisions to act with integrity. There are a number of people and places on campus that will help you understand the rules and how they apply to your academic work. If you have questions or are uncertain about what is expected of you in your courses, you have several options:

Ask your professor, instructor, or teaching assistant for assistance or clarification.

Get support from the Academic Learning Centre: umanitoba.ca/student/academiclearning or Libraries: umanitoba.ca/libraries

Visit the Academic Integrity site for information and tools to help you understand academic integrity: umanitoba.ca/academicintegrity

Make an appointment with the Student Advocacy office. This office assists students to understand their rights and responsibilities and provides support to students who have received an allegation of academic misconduct: umanitoba.ca/academicintegrity/

PART IV: Winter 2019: weeks 7 - 12

CHEM 4610 Advanced Chemical Techniques: Nuclear Magnetic Resonance Spectroscopy

Department of Chemistry, Faculty of Science, University of Manitoba

General Information
Class time: Monday/Wednesday 14:30-15:45
Location: 418 Machray
First class: 25 February 2019
Last class: 8 April 2019
Laboratory demonstrations: 6 March 2019 and 27 March 2019

Instructor
Prof. Scott Kroeker
458 Parker Building
204-474-9335
Scott.Kroeker@umanitoba.ca
home.cc.umanitoba.ca/~kroekers/

Course website: universityofmanitoba.desire2learn.com

Textbook: **Nuclear Magnetic Resonance** (2nd edition). P.J. Hore. New York: Oxford University Press (2015)

Additional References:

Understanding NMR Spectroscopy. J. Keeler. Chichester: Wiley and Sons (2010)

Spin Dynamics: Basics of Nuclear Magnetic Resonance. Malcolm H. Levitt. Chichester: Wiley (2008)

Modern NMR Techniques for Chemistry Research. Andrew E. Derome. New York: Elsevier (1987)

Solid-State NMR: Basic Principles and Practice. D.C. Apperley, R.K. Harris, P. Hodgkinson. New York: Momentum Press (2012) [*online access*]

Introduction to Solid-State NMR Spectroscopy. M.J. Duer. Oxford: Blackwell (2004)

NMR of Quadrupolar Nuclei in Solid Materials. R.E. Wasylishen, S.E. Ashbrook, S. Wimperis. Chichester: Wiley and Sons (2012)

Solid-State NMR in Materials Science: Principles and Applications. V.I. Bakhmutov. Boca Raton: CRC Press (2012) [*online access*]

Multidimensional Solid-State NMR and Polymers. K. Schmidt-Rohr, H.W. Spiess. San Diego: Academic Press (1994)

Advances in Biological Solid-State NMR: Proteins and Membrane-Active Peptides. A. Naito, F. Separovic. Cambridge: RSC (2014) [*online access*]

Evaluation
Grade assessment of this section will be based on the following components:

- assignment 1 (distributed 11 March 2019) 25%
- assignment 2 (distributed 25 March 2019) 25%
- section test (8 April 2019) 50%

Assignment distribution and due dates are tentative. There will be no make-up assignments. Late assignments will not be accepted for marking without prior permission from instructor; such permission may be granted at the discretion of the instructor at a penalty of 10% per day. Extensions must be arranged well in advance of the due date.

The final test will be held on 8 April 2019, time and location to be determined.

Academic integrity

The University of Manitoba treats plagiarism as a serious academic offense, subject to severe penalty. Please see *Statement on Academic Dishonesty* (below) and consult the general calendar or the University website for more detailed information: umanitoba.ca/faculties/science/undergrad/resources/webdisciplinedocuments.html

Course Content

Nuclear magnetic resonance spectroscopy is a versatile technique for probing structure and dynamics in many disciplines. Its prominent role in Chemistry derives from its unique sensitivity to local structure, making it a powerful approach to structural elucidation. This module will begin with the theory essential to understanding practical experimental and interpretive aspects of NMR spectroscopy. Dr Davidson will present several lectures on the implementation and analysis of one- and two-dimensional pulse sequences as applied to molecules dissolved in solution. The latter half of the course will focus on the orientation dependence of NMR interactions. Experiments designed to contend with this anisotropy and provide high-resolution NMR spectra of solids will be examined in detail, with special consideration of sensitivity enhancement methods for solid phases. Emphasis will be placed on the multinuclear capacity of NMR in the characterization of a wide variety of samples including organometallic compounds, complex inorganic materials and biological macromolecules.

Topical outline:

- Overview of nuclear magnetic resonance spectroscopy
    - Basic theory
    - Shielding
    - Coupling
    - Relaxation
- Vector description of NMR (Davidson)
- Practical aspects of experimental NMR, including laboratory demonstration (Davidson)
- Two-dimensional NMR: practical aspects, examples and interpretations (Davidson)
- Orientation-dependence of internal interactions:
    - Magnetic shielding
    - Dipolar interactions
    - Quadrupolar coupling
- High-resolution techniques for solids
    - Magic-angle spinning
    - Multiple quantum MAS
- Sensitivity enhancement methods
    - Cross-polarization
    - Dynamic nuclear polarization
- Case studies and special topics
- Solid-state NMR laboratory demonstration