

## **CHEM386 – Further Analytical Chemistry (15 credits, optional module, second term/year three)**

Module leader: Dr. Konstantin Luzyanin

Module teaching staff: Dr. Konstantin Luzyanin, Dr. Cate Cropper, Dr. Jonathan Iggo

### **Module description and aims**

To provide the students with a knowledge of the principles of structural elucidation and application of various spectroscopic and spectrometric analytical techniques for identification and structural characterization of small molecules. This module will include the fundamental principles of selected instrumental analytical techniques (solution NMR spectroscopy, mass-spectrometry, separation and hyphenated techniques) in the context of their application for structural analysis in synthetic organic chemistry and catalysis.

### **Learning outcomes and skills**

Having successfully completed this module students will be able to:

- 1) Apply the principles of structural elucidation for identification and characterization of organic compounds
- 2) Demonstrate awareness of the theoretical concepts and application of NMR spectroscopy, mass-spectrometry (MS), chromatography (GC/HPLC), and hyphenated techniques GC/HPLC-MS in the context of structural elucidation in synthetic chemistry and catalysis
- 3) Devise an appropriate method or a multi-technique approach in order to establish the structure of organic compounds and/or confirm their authenticity
- 4) Improve their confidence in scientific communication and presentation of data to subsequently enhance their employability skills.

Having successfully completed this module students will acquire the following skills:

- 1) Students will develop their chemistry-related cognitive ability and skills, relating to intellectual tasks, including problem solving as required by the Chemistry subject benchmark statement
- 2) Students will improve their confidence in scientific communication and develop presentation skills of analytical data.

### **Syllabus**

#### Introduction to structural elucidation (lectures 1-3) - Luzyanin

Principles of structural elucidation; main methods of structural elucidation; limits of application; absolute and relative methods; reliability and validation of analytical methods. Methods for determination of elemental composition and identification of structure.

#### Application of mass-spectrometry for structural elucidation (lectures 4-7) - Luzyanin

1. Fundamentals of mass-spectrometry. Ion sources, detectors and limits of applicability of selected mass-spectrometry approaches. Mass-spectrometry and elemental composition
2. Application of mass-spectrometry in structural elucidation in synthetic chemistry and catalysis

#### Application of solution NMR spectroscopy for structural elucidation (lectures 8-17) – Iggo, Cropper, Luzyanin

1. Fundamentals of NMR spectroscopy; sensitivity and resolution; isotope selection; methods to improve sensitivity and resolution
2. Principles of 1D NMR methods and techniques. 1D direct detection methods; principles of decoupling, polarization transfer, and NOE. Selected 1D NMR methods useful for structural elucidation
3. Principles of 2D NMR methods and techniques. 2D direct and indirect detection methods. Classifications of 2D NMR methods. Selected 2D NMR methods useful for structural elucidation
4. Solution multinuclear NMR measurements. Recognition of structural fragments by 1D and 2D NMR: analysis of chemical shifts, coupling patterns, and skeletal structure. Data processing and spectral interpretation.
5. Determination of relative and absolute configuration and conformation by NMR. Intra- and intermolecular interactions, fluxionality.
6. Application of NMR spectroscopy for structural elucidation in organic chemistry and catalysis

#### Application of separation sciences and hyphenated techniques as an aid for structural elucidation (lectures 18-23) - Luzyanin

1. Fundamentals of chromatography

- Liquid Chromatography: modes of separation, instrumentation, HPLC vs UHPLC. Method development for LC: optimising separation conditions, selecting an appropriate column and detector for the given analysis. LC detectors: UV (photodiode array versus single wave UV), fluorescence, refractive index, electrochemical methods of detection.
- Gas Chromatography: modes of separation, instrumentation. Method development for GC: optimising separation conditions, selecting an appropriate column and detector for the given analysis. GC detectors: flame ionisation detector, thermal conductivity detector.
- Introduction to hyphenation (GC/MS, HPLC/MS, MS/MS). GC Interfaces: Electron Impact Ionization (EI) and Chemical Ionization (CI). HPLC Interfaces: Electrospray ionization (ESI), Atmospheric Chemical Ionization (APCI) and Atmospheric Pressure Ionization (API).
- Applications of chromatography and hyphenated techniques as an aid for structural elucidation in chemical and pharmaceutical analysis.

#### Additional techniques and tools in structural elucidation (lectures 24-25) - Cropper

- Application of UV/vis and IR spectroscopy. Alternative techniques for assignment of relative and absolute configuration of organic compounds. Deuteration and studies of kinetic isotopic effect.
- Database use and search

#### Combined approaches for structural elucidation and their application in different research fields (lectures 26-32) – Luzyanin, Cropper

- Principles of multi-technique approaches for structural elucidation. Three-stage strategy: determination of molecular formula, identification of functional groups, and elucidation of connectivity.
- Application of combined approaches for structural elucidation in synthetic organic chemistry; validation of results

#### **Recommended texts**

S. A. Richards and J. C. Hollerton, Essential practical NMR for organic chemistry, Wiley, 2011. Print ISBN: 9780470710920, Online ISBN: 9780470976401

R. M. Granger, H. M. Yochum, J. N. Granger, and K. D. Sienerth, Instrumental analysis, Oxford University Press, USA, 2018. ISBN: 9780190865337

#### **Additional texts**

E. H. Evans and M. E. Foulkes, Analytical chemistry: a practical approach, Oxford University Press, 2019. ISBN: 9780199651719D

T. Claridge, High-resolution NMR techniques in organic chemistry, 3rd edition, Elsevier, 2016. Print ISBN: 9780080999869, Online ISBN: 9780080999937

E. Breitmaier, Structure elucidation by NMR in organic chemistry: a practical guide, 3rd revised edition, Wiley, 2002. Print ISBN: 9780470850060, Online ISBN: 9780470853061

R. G. Linington, P. G. Williams, J. B. MacMillan, Problems in organic structure determination: a practical approach to NMR spectroscopy, CRC Press, Taylor & Francis Group, 2015. ISBN: 9781498719629

J. A. Iggo and K. V. Luzyanin, NMR spectroscopy in inorganic chemistry, 2nd edition, Oxford University Press, 2019. ISBN: 9780198794851

M.-M. Cid (Editor) and J. Bravo (Editor), Structure elucidation in organic chemistry: the search for the right tools Wiley, 2015. Print ISBN: 9783527333363, Online ISBN: 9783527664610

#### **Format of delivery and assessment**

Delivery: 32 h lectures, 4x2 h workshops on problem solving in small groups, and 110 h of self-directed learning.

Assessment: 1 written examination (70% mark), 4 problem(case)-based learning workshops with summary presentation in small groups (4 x 5% each; one of them is peer-assessed by students and staff/demonstrators using feedback forms; three are assessed by demonstrators/staff only), 1 written course work (10%).