CEUM 2023

THE CENTRAL EUROPEAN NMR SYMPOSIUM
& BRUKER USERS MEETING
/ SOLID-STATE NMR WORKSHOP

BOOK OF ABSTRACTS

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13–15 SEPTEMBER 2023 PRAGUE

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CONFERENCE PROGRAM

CEUM 2023

THE CENTRAL EUROPEAN NMR SYMPOSIUM
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/ SOLID-STATE NMR WORKSHOP

13.9.2023

WED

Central European NMR Symposium – Venue: Faculty of Architecture

8:00–9:00 **Registration**
9:00–9:10 **Conference opening**

Session 1: Chair: Radek Pohl

9:10–9:40 **Lecture 1: Janez Plavec**
Structural and dynamic insights into quadruplexes and their ligand interactions

9:40–10:10 **Lecture 2: Lothar Brecker**
Ordinary' ^{31}P NMR to Study the Stereochemical Course of an ecAGP Catalyzed Phosphoryl Transfer

10:10–10:40 **Lecture 3: Anne C. Conibear**
Chemical biology tools to understand protein posttranslational modifications

10:40–11:10 **Coffee break**

Session 2: Chair: Jan Blahut

11:10–11:40 **Lecture 4: Jan Stanek**
Resonance assignment with ^{1}H detectionand fast MAS: challenges and solutions for large deuterated proteins

11:40–12:10 **Lecture 5: Eike Brunner**
In Situ High-Pressure NMR Spectroscopy of Flexible MOFs

12:10–12:40 **Lecture 6: Jürgen Senker**
Electrolyte-Host materials with Ultrafast Proton Conduction based on microporous frameworks

12:40–13:40 **Lunch**

Session 3: Chair: Václav Veverka

13:40–14:10 **Lecture 7: Jaroslav Havlík**
Application on NMR spectroscopy in plant science and wine research

14:10–14:40 **Lecture 8: Tobias Madl**
Deciphering the complex role and metabolic regulation of arginine methylation by NMR spectroscopy

14:40–15:10 **Lecture 9: Lukáš Trantírek**
In-cell NMR spectroscopy of nucleic acids: Progress, Challenges, and Opportunities

15:10–15:40 **Coffee break**

Session 4: Chair: Jan Sýkora

15:40–16:10 **Lecture 10: Josef Granwehr**
NMR and EPR of battery cells and components

16:10–16:40 **Lecture 11: Radek Marek**
Paramagnetic NMR of ruthenium compounds and their host-guest assemblies

16:40–17:10 **Lecture 12: Tomasz Ratajczyk**
Hyperpolarization of Molecules via Reversible Interaction with Parahydrogen

17:10–18:00 **Poster session**
19:00 **Conference dinner/party**

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14.9.2023 THU

Bruker Users' Meeting – Venue: Faculty of Architecture

9:00–9:10	**Christian Steffen** Welcome
9:10–9:30	**Jens Nowag** Fourier 80 News
9:30–10:10	**Jörg Köhler** Tools for Mixture Analysis in NMR
10:10–10:30	**Daniel Baumann** Magnet News and HelioSmart
10:30–11:00	**Coffee Break**
11:00–11:20	**Michael Hammer** Bruker Solutions for Utilizing NMR in a Regulated Environment
11:20–12:00	**Adriane Consuelo Leal Auccaise** Non exponentiality of spin relaxation processes
12:00–12:20	**Oezlen Yasar** Benchtop ESR
12:20–14:30	**Lunchbreak with Poster Session**
14:30–14:50	**Frank Schumann** News & Updates on Liquid State NMR Probes
14:50–15:10	**Klaus Zick** µ-Imaging and Diffusion Application News
15:10–15:30	**Pinelopi Moutzouri** Pureshift, Gemstone and Sharper
15:30–16:00	**Break**
16:00–16:20	**Sandra Ullrich** Updates from Service
16:20–16:40	**Pavel Kessler** TopSpin News
16:40–17:00	**Björn Heitmann** News from Software Development
17:00–17:10	**Q&A**
17:10–	**Poster Prize**

CONFERENCE PROGRAM

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THE CENTRAL EUROPEAN NMR SYMPOSIUM
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15.9.2023

FRI

Solid-state NMR workshop – Venue: Institute of Organic Chemistry and Biochemistry

8:30–9:00 **Registration**
9:00–9:10 **Workshop opening (Martin Dračínský)**

Session 1: Chair: Olivier Lafon

9:10–9:40 **Lecture 1: Jean-Paul Amoreux**
Recent developments in NMR of quadrupolar nuclei in solids

9:40–10:10 **Lecture 2: Andrea Simion**
Heteronuclear decoupling sequences for fast MAS NMR – from theory to applications

10:10–10:40 **Lecture 3: Jan Blahut**
Proton Ultra-Fast MAS: Promise for Paramagnetic Solids

10:40–11:10 **Coffee break**

Session 2: Chair: Martin Dračínský

11:10–11:40 **Lecture 4: Ulrich Scheler**
Charge compensation, hydrogen bonds and packing in polyelectrolyte complexes

11:40–12:10 **Lecture 5: Jiří Brus**
Structure and dynamics of Chain-Walking Polymerized polyethylenes as seen by solid-state NMR spectroscopy

12:10–12:40 **Lecture 6: Marta K. Dudek**
Establishing hydrogen atom position in molecular crystals with solid-state NMR

12:40–13:40 **Lunch**

Session 3: Chair: Zdeněk Tošner

13:40–14:10 **Lecture 7: Sebastian Wegner**
New Tools and Automation in Solid State NMR

14:10–14:40 **Lecture 8: Christian Bonhomme**
NMR/DNP crystallography, MAS MRI and theory for inorganic materials and biomaterials

14:40–15:10 **Coffee break**

Session 4: Chair: Marta Dudek

15:10–15:40 **Lecture 9: Zdeněk Tošner**
Optimal control methods for multidimensional solid-state NMR of proteins

15:40–16:10 **Lecture 10: Olivier Lafon**
How ultra-high field NMR spectroscopy can contribute to the design of advanced functional materials?

16:10–16:20 **Conclusion remarks (Jean-Paul Amoreux)**

CEUM 2023

THE CENTRAL EUROPEAN NMR
SYMPOSIUM & BRUKER USERS MEETING
/ SOLID-STATE NMR WORKSHOP

ABSTRACTS

SPEAKERS

Structural and dynamic insights into quadruplexes and their ligand interactions

Janez Plavec [1,2,3]

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G-quadruplexes (G4) are unique structures formed by guanine-rich DNA and RNA sequences. They consist of stacked G-quartets, where four guanine bases are held together by Hoogsteen hydrogen bonding. G4 structures are found in various regions of the genome, including telomeres and promoter regions, and they play important roles in gene regulation and genome stability. Their distinctive structure and functional significance make G4 intriguing targets for drug development and potential therapeutic interventions.

NMR spectroscopy is a powerful technique used in studies of ligand interactions with G4 providing detailed information about the structure, dynamics, and thermodynamics of these complexes. By monitoring chemical shifts, NMR can identify specific interactions between ligands and G4, such as hydrogen bonding and stacking interactions. NMR also allows for the determination of binding constants and stoichiometry, providing insights into the binding affinity and mode of ligand binding to G4. This information is crucial for understanding the stability and flexibility of the complexes and can shed light on the mechanism of ligand binding.

NMR can also be used to study ligand-induced changes in G4 topology. Comparing the NMR spectra of the free G4 and the G4-ligand complex, resonance shifts can be detected, indicating changes in the folding pattern of the G4 structure. Through NOE experiments, NMR can reveal the proximity and spatial relationships between the ligand and the G-quartet. Yes, heterocycles can intercalate in G4. Intercalation is the insertion of planar aromatic or heteroaromatic molecules between base pairs of nucleic acids, disrupting the regular stacking arrangement.

[1] K. Peterková, M. Stitch, R. Z. Boota, P. A. Scattergood, P. I. P. Elliott, M. Towrie, P. Podbevšek, J. Plavec, S. J. Quinn, *Chem. Eur. J.* **2023**, 29, e202203250.

[2] A. Novotný, J. Plavec, V. Kocman, *Nucleic Acids Res.* **2023**, 51, 2602.

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[6] D. Pavc, N. Sebastian, L. Spindler, I. Drevenšek-Olenik, G. K. Podboršek, J. Plavec, P. Šket, *Nat. Commun.* **2022**, 13, 1062.

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[8] A. Ghosh, M. Trajkovski, M.-P. Teulade-Fichou, V. Gabelica, J. Plavec, *Angew. Chem. Int. Ed.* **2022**, 61, e202207384.

[9] S. Aleksič, P. Podbevšek, J. Plavec, *Biochemistry* **2022**, 61, 2390.

‘Ordinary’ ^{31}P NMR to Study the Stereochemical Course of an ecAGP Catalyzed Phosphoryl Transfer

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The enzyme α-D-glucose 1-phosphate phosphatase from *Escherichia coli* (ecAGP) catalysis a transphosphorylation from α-mannose 1-phosphate (Man1P) to Glc resulting in glucose 6-phosphate (Glc6P). It was necessary to use NMR Spectroscopy for a stereochemical analysis of this phosphoryl transfer in order to thoroughly investigate the mechanism of the ecAGP catalyzed reaction.

For this purpose we prepared (R_P)- and (SP)-[^{16}O,^{17}O,^{18}O]Man1P as complementary substrates.[1] Both compounds were reacted with Glc in the presence of wild-type ecAGP as well as of a H18D mutant, respectively. The formed *P*-chiral Glc6P samples were further converted in two synthetic steps to the corresponding cyclic methyl 4,6-phosphates. Purified products were analyzed by NMR spectroscopy, using in particular ‘ordinary’ ^{31}P NMR spectra as key experiments.[2,3]

The fast ^{17}O relaxation caused large line widths at half height for all ^{31}P NMR signals of the cyclic methyl 4,6-phosphates, which were still containing a ^{17}O-label. However, the different stereoisomers of the also resulting α/β-D-glucopyranose-4,6-[^{16}O,^{18}O]phosphate methyl esters led to 16 isomers, all leading to detectable narrow signals in the ^{31}P NMR spectra. Relative integral values of those 16 signals were caused by different distribution of ^{16}O and ^{18}O in the *P*-chiral phosphate moiety.

These respective isotope patterns were induced by the absolute chirality of initially applied *P*-chiral Man1P as well as by the original *O*-isotopic enrichment. Hence, the relative signal integrals in the ‘ordinary’ ^{31}P NMR spectra allowed conclusions about the stereochemical course of this phosphoryl transfer. These findings were key results in studying the mechanism of wild-type ecAGP as well as of the H18D variant catalyzed phosphoryl transfers, respectively.[4]

[1] P. Malová Križková, S. Prechelmacher, A. Roller, F. Hammerschmidt, *J. Org. Chem.* **2017**, 82, 10310–10318.

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Chemical biology tools to understand protein posttranslational modifications

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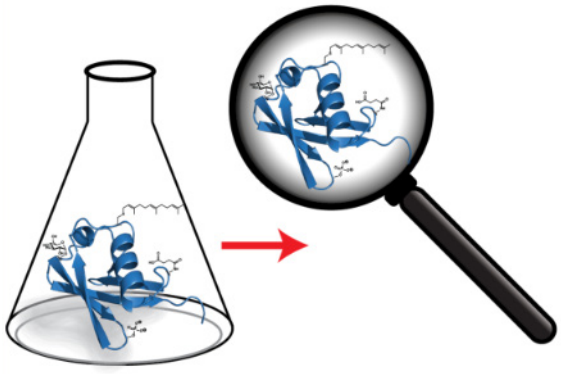
Posttranslational modifications regulate the location, interactions, and destruction of a protein, controlling fundamental cellular processes. However, unravelling precise effects of these modifications on proteins is challenging because of difficulties obtaining proteins bearing site-specific modifications for structural and functional studies. Furthermore, effects of posttranslational modifications on protein structure are seldom investigated, leaving a gap in our knowledge of how posttranslational modifications modulate protein function. In this presentation, I will discuss our work towards an understanding of the structural effects of posttranslational modifications from small model peptides and small proteins, to larger proteins. I will demonstrate how solid phase peptide synthesis provides access to modified peptides for structural studies and how protein semi-synthesis tools can be used to generate site-specifically modified and segmentally isotope labelled proteins for NMR spectroscopy. Illustrating this strategy, I will discuss recent projects in which we used chemical protein synthesis to make specifically modified and segmentally isotope labelled variants of nucleosomal proteins for nuclear magnetic resonance spectroscopy and functional studies. I aim to show how integrating chemical protein synthesis with structural biology allows us to gain new insights into the effects of protein posttranslational modifications on protein structure, dynamics and regulation.



Chemical biology tools to understand protein posttranslational modifications.

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[3] Conibear, A. C.; Rosengren, K. J.; Becker, C. F. W.; Kaehlig, H., *J. Biomol. NMR* 73, 587-599 (**2019**).

[4] Niederacher, G.; Urwin, D.; Dijkwel, Y.; Tremethick, D. J.; Rosengren, K. J.; Becker, C. F. W.; Conibear, A. C., *RSC Chem. Biol. 2,* 537-550 (**2021**).

Resonance assignment with ^{1}H detection and fast MAS: challenges and solutions for large deuterated proteins

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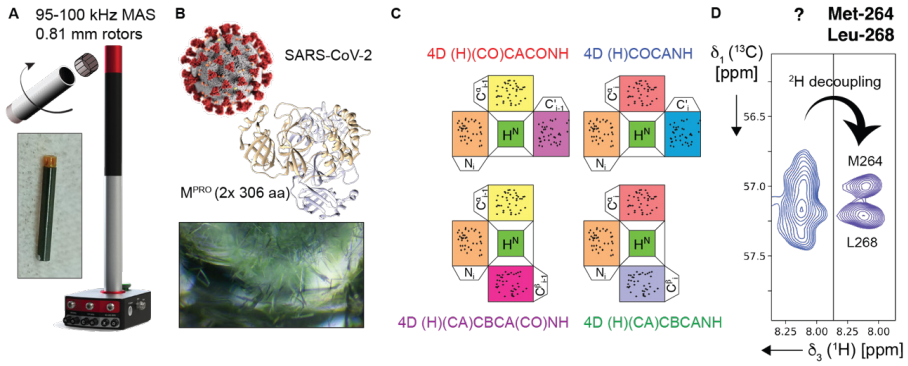
In NMR spectroscopy of proteins, protons play a particular role as sensitive reporters on protein dynamics and protein-protein interactions. Here we leverage recent technological advancements in magic-angle spinning at frequencies up to 100 kHz for systematic resonance assignment in highly deuterated microcrystalline samples.

First, we present the surprising advantages of ^{2}H decoupling for resolution and coherence lifetime of ^{13}C spins. In this respect, we present RF designs for backbone resonance assignment experiments with higher sensitivity and dramatically improved resolution. We demonstrate that four-dimensional variants of the triple-correlations (H-N-CA/CB/CO) disambiguate sequential resonance assignment in challenging systems such as SARS-CoV-2 main protease (2x306 aa). We also discuss the capabilities of automated approaches (e.g. FLYA) to facilitate the spectral analysis in such cases.

Additionally, we will explore specific ^{1}H-labelling of Ile, Leu, and Val residues with linear ^{13}C-chains, and otherwise an extensive ^{2}H- and uniform ^{13}C-enrichment, to establish systematic correlations between methyl and backbone amide ^{1}H resonances. 3D/4D spectroscopy and a *J*-mediated ^{13}C-^{13}C mixing are key to assignment of methyl ^{1}H and ^{13}C chemical shifts [1]. Novel methods for Histidine *side-chain* resonance assignment and determination of protonation & tautomeric state are also presented.



Samoson's 100 kHz MAS technology with < 1 µL rotor volumes (A) is employed to study microcrystalline SARS-CoV-2 main protease (B). Complexity of resonance assignment is addressed with a set of four-dimensional correlation schemes (C) with resolution greatly enhanced by ^{2}H-decoupling (D).

[1] P. Paluch, R. Augustyniak, M.-L. Org, K. Vanatalu, A. Kaldma, A. Samoson and J. Stanek, *Front. Mol. Biosci.* **2022**, 9:828785.

In Situ High-Pressure NMR Spectroscopy of Flexible MOFs

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Metal-Organic Frameworks (MOFs) exhibit unique properties, for example huge internal surfaces. A particularly important sub-class of MOFs is surprisingly flexible. Such compounds undergo pronounced, adsorption-induced structure transitions and can change their unit cell volumes by more than a factor of two. This process depends on the temperature, gas pressure, and type of adsorbed gas. The underlying mechanisms are complex and not yet fully understood.[1]

In situ studies of host-guest interactions are particularly powerful. Within the present contribution, we describe *in situ* high-pressure NMR studies of gas adsorption (e.g., ^{129}Xe, $^{13}CO_2$) on flexible MOFs. Our homebuilt apparatus enables *in situ* high-pressure NMR studies by the application of variable gas pressures up to about 100 bar at variable temperatures down to 190 K inside the NMR spectrometer. This allows following adsorption/desorption isotherms by observing the signals of the adsorbed gases and to correlate the NMR-derived parameters with volumetric measurements.

The described *in situ* NMR technique could for example be used to characterize gas-induced phase-transitions in various flexible MOFs like DUT-8 (DUT: Dresden University of Technology)[2,3] as well as DUT-49 with its unique negative gas adsorption transitions. [4,5] Gas exchange processes are studied by 2D exchange spectroscopy (EXSY). It is also demonstrated that the chemical shift of ^{129}Xe observed at very high pressure, i.e., close to a relative pressure of 1, correlates well with the average pore size of MOFs [5] and can thus be used as a measure to estimate average pore sizes.

In summary, *in situ* high-pressure NMR spectroscopy in combination with techniques like solid-state NMR spectroscopy and volumetric adsorption experiments provides deeper insight into the unique adsorption and phase transition behavior of flexible MOFs.

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Electrolyte-Host materials with Ultrafast Proton Conduction based on microporous frameworks

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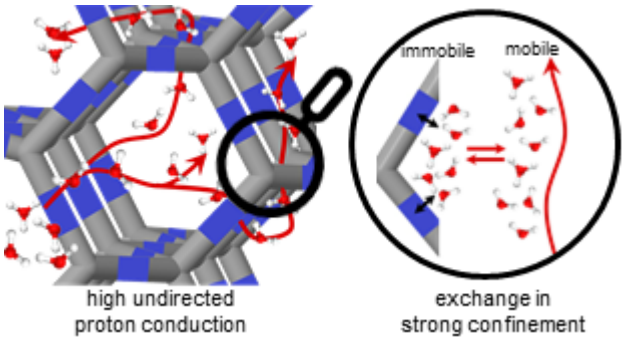
Electrolyte-host systems based on structured materials are promising candidates for separators in electrochemical energy storage and conversion devices [1]. The spatial constraints of the structured hosts enforce a shape to the electrolytes and impose interactions at the electrolyte-host interfaces. If the dimension of the constraints reaches the nanometre scale, confinement effects on the mass and charge transport within the electrolyte emerge. Recent results suggest that the complex interplay between the confinement-induced guest-host interactions and the mobility of the mass and charge carriers can lead to exceptional transport properties [2]. Until now, little is known about the underlying transport mechanisms.

Here, we report on a comprehensive analysis of aqueous electrolyte-host systems based on microporous aromatic frameworks that combine X-ray scattering, multi-nuclear solid-state NMR spectroscopy, NMR diffusometry and electrochemical impedance spectroscopy. We could analyse the structural arrangement at the framework's interfaces and correlate it to the mobility and transport of the electrolyte components within the fluid phases. The outstanding proton conductivities up to 1 S cm^{-1} are explained by a transport mechanism governed by a continuous exchange between interface-bound and mobile electrolyte components and a mass and charge transport through the mobile domains coupled by the nanometre-sized pores. The local order of post-synthetically introduced sulfonic acid groups is essential in establishing continuous percolation paths for the charge carriers.



Sketch of a confinement-driven transport mechanism.

[1] Q. Zhang, E. Uchaker, S. L. Candelaria, G. Cao, *Chem. Soc. Rev.* **2013**, 42, 3127.
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Application on NMR spectroscopy in plant science and wine research

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High-field nuclear magnetic resonance (NMR) spectroscopy has given a great boost to the field of metabolomics in the last two decades. Due to relatively low sensitivity, NMR metabolomics yields a limited set of features in a sample, but provides quantitative information, robustness, accuracy and identification of unknown compounds. A well-curated set of typically 50-70 metabolites obtained from biological samples or extracts by NMR includes molecules of high physiological relevance and can outperform LC-MS datasets with thousands of provisionally identified features when it comes to classification performance or understanding the biological problem. Thus, each of these complementary methods offers distinct advantages for specific research questions. Major fields of application of NMR include analysis of biofluids, food, but also plant stress responses.

In NMR metabolomics, standard operating procedures are being established with standard pulse sequences, as well as data reduction approaches. Despite progress in 2D NMR metabolomics, 1D ^{1}H NMR has become a golden standard, allowing easy peak picking and extraction of quantitative data. Varying matrix and ionic strength of the samples often lead to a drift in chemical shifts so alignment and/or binning are applied. To facilitate the extraction of metabolite tables, numerous GUI software tools are available, however more robust and user-friendly algorithms are needed. A specific field is the plant NMR metabolomics. While the analysis of biofluids has made substantial advancements, benefiting from relatively consistent set of known metabolites, NMR plant metabolomics encompasses a vast array of chemical structures and encounters unique obstacles and specific issues that necessitate further development.

Our laboratory collaborates with plant growers and breeders, applying NMR analysis to aid their breeding programs for ornamental plants such as gerberas, tulips and major food crops. This technique assists in identifying optimal growth conditions, selecting pathogen-resistant varieties or stress mechanisms. Furthermore, our involvement in a national Czech wine competition showcases another practical application of NMR metabolomics. Through our collaboration, we contributed to the development of an extensive database of local wines, encompassing 3 000 spectra. This database enables basic chemical analysis, variety prediction, and monitoring of authenticity of wine batches on the market.

I will present a comprehensive summary of the state-of-the-art approaches and discoveries in wine and plant NMR metabolomics, show examples of our workflows and practical applications and summarise future needs of these research fields.

Acknowledgment: METROFOOD-CZ research infrastructure project (MEYS Grant No: LM2023064; LM2018100) including access to its facilities.

Deciphering the complex role and metabolic regulation of arginine methylation by NMR spectroscopy

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Protein arginine methylation (ArgMet) is an abundantly-occurring post-translational modification of eukaryotic proteins. Next to its well-known function as a histone-mark regulating mRNA transcription, ArgMet controls a plethora of cellular processes, including signaling, RNA processing, ribosome biogenesis, autophagy, and mitochondrial function. Altered methylation patterns have been associated with common diseases like cancer, cardiovascular and neurological diseases, as well as with aging. Nonetheless, the conditions triggering methylation, as well as the physiological function of non-histone ArgMet are largely unknown.

Here, I will present our recent work aiming at revealing the complex regulation of protein-protein, protein-RNA, and protein-metabolite interactions by ArgMet ranging from nuclear import to RNA-binding and condensate formation using a combination of NMR spectroscopy, biophysical and cellular assays [1-5]. Moreover, I will present new insights into how ArgMet is coupled to and regulated by metabolism and how ArgMet is dysregulated in cancers and neurodegenerative diseases [6-7]. We have recently established a sensitive method for global quantitation of methylated arginines (ArgMet) within proteins by NMR spectroscopy [8-9]. Through this, we discovered that a substantial amount of all Arginines in proteins in human cells and tissues are asymmetrically dimethylated, with increased levels (up to 8 % of all arginines) in cancer cells and human cancer tissue. These results suggest that ArgMet is an important, though understudied post-translational modification and an important regulator of biomolecular interactions and function. Given that ArgMet is dysregulated in several human diseases, ArgMet and related processes constitute a promising target for disease therapy.

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In-cell NMR spectroscopy of nucleic acids: Progress, Challenges, and Opportunities

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In-cell NMR spectroscopy represents a unique and powerful tool for the high-resolution characterization of biomolecular structures and interactions under close-to-physiologically relevant conditions. Specifically, for nucleic acids (NA), state-of-the-art in-cell NMR applications enable validation of physiologically relevant conformations of drug targets and characterization of NA-ligand interactions in the intracellular space of living human cells [1–3].

To improve in-cell NMR readout on nucleic acids, various efforts have been made, including extending the time window for data acquisition, adjusting sample preparation to enable in-cell NMR measurements in defined cellular states, and developing novel probes of NA structure/interactions to increase resolution and sensitivity of in-cell NMR spectra.

In this lecture, I will introduce the fundamental principles of in-cell NMR spectroscopy for nucleic acids, discuss the primary technical obstacles that limit the application of the method, and review recent developments in the field. Additionally, I will highlight future research directions in this area of study.

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Paramagnetic NMR of ruthenium compounds and their host-guest assemblies

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Paramagnetic systems are generally considered difficult to characterize by NMR spectroscopy. However, combined experimental and theoretical investigations can provide great details on the molecular and electronic structure of the systems studied. Our systematic analysis will be shown on a series of paramagnetic ruthenium compounds.

The individual physical mechanisms of hyperfine NMR shifts and relativistic effects on NMR shifts will be discussed. The Fermi-contact term associated with the distribution of electron spin density in the molecule [1] and spin-dipolar and paramagnetic spin-orbit terms that give rise to through-space (pseudocontact) shifts in supramolecular host-guest assemblies [2,3] will be interpreted. Method for determining head vs tail host-guest binding between ruthenium guests and cyclodextrin hosts by using NMR spectroscopy will be demonstrated. Finally, an example of the effect of crystal packing on the NMR resonances of paramagnetic ruthenium systems will be discussed [4].

This work has received support from the Czech Science Foundation (grant no. 21-06991S to R.M.)

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Hyperpolarization of Molecules via Reversible Interaction with Parahydrogen

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There is no question that Nuclear Magnetic Resonance (NMR)-based techniques are some of the most important analytical techniques because of their informativity. However, NMR lacks sensitivity, and as a consequence of this, NMR is expensive to purchase and maintain. Therefore, the boosting of the NMR signal is of significant importance.

Hyperpolarization methods can remarkably enhance the NMR signal by several orders of magnitude[1]. Among the most promising techniques for hyperpolarization is Signal Amplification by Reversible Exchange -SABRE (see Figure 1)[1]. In SABRE, a parahydrogen molecule (p-H_2) -a source of hyperpolarization, a to-be hyperpolarized molecule are in transient contact within a labile ternary complex, which is possible due to an appropriate Ir-based catalyst being employed. When the molecule is involved in the labile complex, a high non-Boltzmann nuclear spin polarization is generated in this molecule. Finally, the hyperpolarized molecule is released from the complex.

Here, our results with SABRE hyperpolarization of various molecular systems will be addressed[2-5]. In particular, the utilization of SABRE for the hyperpolarization of oligopeptides will be discussed[3,4]. For example, the hyperpolarization of biorelevant PyFALGEA oligopeptide ligand, which is selective towards the epidermal growth factor receptor, will be discussed[4]. The interplay between hyperpolarization efficiency and the molecular structure of oligopeptides and catalysts will also be presented[4,5].

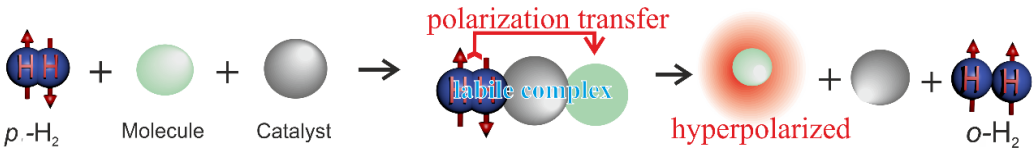

Figure 1. The basic scenario of SABRE.

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Non-exponentiality of spin relaxation processes

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Investigations of Nuclear Magnetic Resonance relaxation process lead to highly valuable, often unique, information about molecular dynamics and structure. There are different „versions" of relaxation experiments. One of them is NMR relaxometry that enables measuring relaxation rates over a broad range of resonance frequencies (typically up to 40MHz for ^{1}H). The price for varying the resonance frequency and, hence, probing dynamical processes of much different time scales in a single experiments, is low resolution. On the opposite side, high resolution relaxation studies are performed at a high (but single) resonance frequency. In this case one can identify the pools of hydrogen (or other NMR active) nuclei contributing to the specific relaxation components, however, the price to pay is the accessible time scale of dynamical processes being limited to fast motion. Combination of both approaches gives an extremely powerful experimental tool. However, to fully profit from the experimental potential, an appropriate theoretical analyses of the results obtained is needed. At this stage one faces the subject of non-exponentiality of relaxation processes.

By nature, relaxation processes are single-exponential only in rare cases of simple systems. The reason for that is the physical origin of the non-exponentiality. One of them is dynamical heterogeneity of the system – molecular fractions showing different mobility (such as water and macromolecular fractions in solutions of biomolecules) and/or the presence of different molecular groups (such as methyl groups undergoing their own motion superposed on the overall molecular tumbling). The second reason stems however from the quantum-mechanical mechanism of relaxation – mutual spin interactions between NMR nuclei of different resonance frequencies (such as ^{1}H and ^{19}F or ^{1}H and ^{13}C). Although this effect is well-known already for decades, it is often forgotten (neglected). To give an example – analysing ^{1}H and ^{19}F relaxation data for systems including both nuclei, the bi-exponentiality of the relaxation, originating from ^{1}H-^{19}F dipole-dipole interactions, is often not the matter of concern. The picture is even more complicated when the participating nuclei possess quadrupole moments (such as ^{14}N). The subject of non(exponentiality) of relaxation processes will be revisited and illustrated by examples.

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CEUM 2023

THE CENTRAL EUROPEAN NMR
SYMPOSIUM & BRUKER USERS MEETING
/ SOLID-STATE NMR WORKSHOP

ABSTRACTS

SOLID-STATE NMR WORKSHOP

Recent developments in NMR of quadrupolar nuclei in solids

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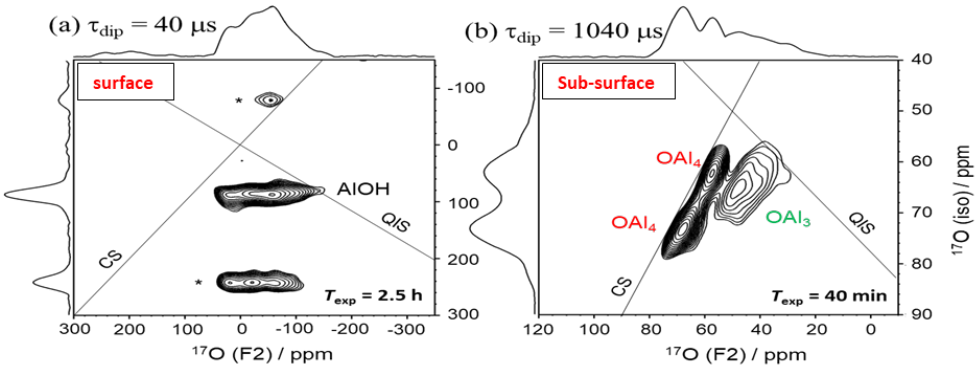
Over 74% of NMR active nuclei have a spin $I \geq 1$ and are subject to quadrupole interactions. Nevertheless, the observation of these nuclei in solids often remains more challenging than with spin-1/2 nuclei since: (i) the spectral resolution is decreased by the second-order quadrupolar broadening, (ii) the larger size of the density matrix complicates the spin dynamics, and (iii) the quadrupolar interactions exceed the rf-field. I will present recent techniques we recently introduced to facilitate the observation and analysis of these quadrupolar isotopes.

We have analyzed the performances of the recent cosine low-power MQMAS sequence[1], and showed that for spin-3/2 isotope, this technique is very efficient and requires a low rf-field, whereas for spin-5/2 nuclei, this variant is as efficient as the high-power one but requires rf-fields smaller than 20 kHz and hence, can be employed for low-γ nuclei and large diameter rotors[2].

We have also developed efficient pulse sequences to transfer magnetization from protons to quadrupolar nuclei at slow-moderate or fast MAS (ν_R = 10-25 or > 60 kHz)[3]. For $\nu_R \leq 20$ kHz, the most efficient pulse sequence is *D*-RINEPT with adiabatic pulses. This transfer has been combined with DNP to detect low-γ quadrupolar nuclei with natural abundance near surfaces or sub-surfaces, such as ^{17}O, ^{95}Mo, ^{47,49}Ti, ^{67}Zn[4]. More recently, this transfer has been combined with MQMAS to detect DNP-enhanced high-resolution NMR spectra of quadrupolar nuclei, such as ^{17}O, near surfaces (Fig)[5]. We have analyzed the *T*-HMQC technique[6] for the indirect detection without t_1 noise of spin-1/2 nuclei subject to large CSA (^{195}Pt), as well as spin-1 (^{14}N) and spin-3/2 (^{35}Cl) quadrupolar nuclei. For spin-3/2 nuclei, this method can provide a resolution enhancement of ca. 4[7].

Finally, I will present new developments in the fields of *J*-INADEQUATE of spin-1/2 nuclei and of *D*-HETCOR of two quadrupolar nuclei[8].



2D DNP-enhanced ^{1}H ⟶ ^{17}O *D*-RINEPT-MQMAS spectra of γ-Al_2O_3 with T_{dip} = (a) 40 or (b) 1040 μs.

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Heteronuclear decoupling sequences for fast MAS NMR – from theory to applications

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High-spectral resolution and sensitivity in fast MAS NMR (> 60 kHz) are difficult to obtain using current heteronuclear decoupling sequences. The main drawbacks are the achievement of: (i) robustness for a large chemical-shift range under low-power irradiation, (ii) independence with respect to the radio-frequency (RF) power, and (iii) robustness toward radio-frequency field inhomogeneities.

Recently, we introduced a new heteronuclear decoupling pulse sequence for fast MAS NMR, that overcomes these issues, dubbed Rotor-Synchronized Phase-Alternated Cycles (ROSPAC) [1,2]. Here, we discuss firstly the main aspects that need to be taken into account when a heteronuclear decoupling pulse sequence is designed for fast MAS NMR. Secondly, the benefits of the ROSPAC decoupling sequence compared to that of the established ones are presented. These are illustrated by representative solid-state NMR experiments and theoretical results obtained by using a generalized theoretical framework based on Floquet theory [3]. And finally, further developments to enhance the decoupling sequences' efficiency are exemplified by preliminary experimental results.

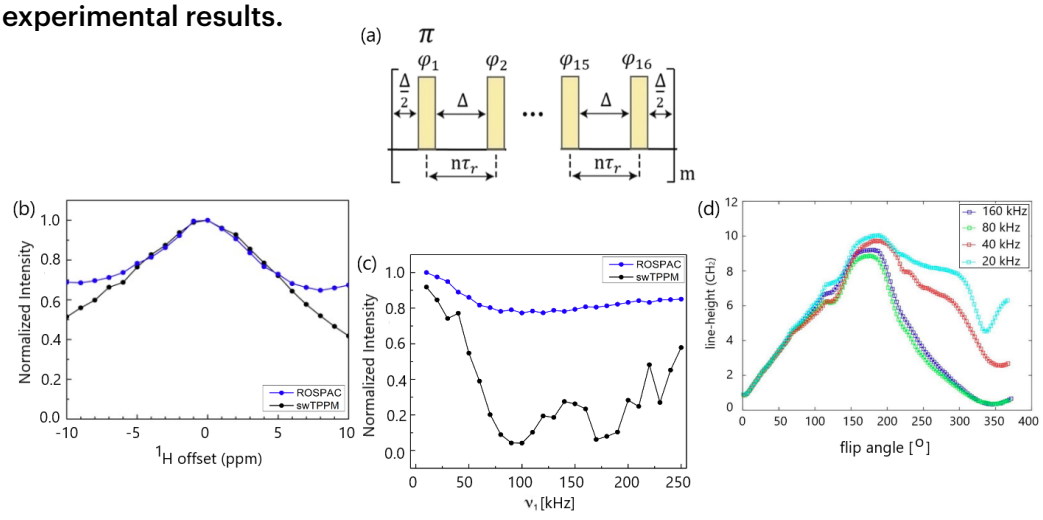

Figure 1. Experimental results on the CH_2 line of Glycine using the ROSPAC heteronuclear decoupling pulse sequence (a), illustrating the robustness toward ^1H offset (b), RF power irradiation (c), and RF field inhomogeneities (d). All experiments have been performed under 100 kHz spinning frequency.

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Proton Ultra-Fast MAS: Promise for Paramagnetic Solids

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Solid-state NMR has developed as a generally applicable characterisation technique, on a wide range of samples in chemistry, materials science and biology[1]. ^{1}H-NMR spectroscopy is the most obvious avenue for rapid routine characterisation due to their large gyromagnetic ratio and high natural abundance. Nevertheless, these same properties lead to a strong dipolar coupling network that prevents the identification of the different ^{1}H sites. In the case of paramagnetic samples, the hyperfine interaction of the high-γ ^{1}H nuclei with the unpaired electrons further exacerbates the problem of acquisition due to paramagnetic-induced shift, shift anisotropy and paramagnetic-induced relaxation[2].

Many of these obstacles were, fortunately, overcome by hardware improvements of ultra-fast Magic-Angle-Spinning probes delivering high radiofrequency power as well as by tailored pulse-sequences. In this tutorial lecture, we will go through important aspects of ^{1}H-detected solid-state NMR of paramagnetics on example of Fe(II)-based catalyst[3] and flexible metal-organic framework (MOF) with coupled pair of Ni(II) ions[4]. We demonstrate how to overcome extensive spectral width (hundreds of ppm), resolve overlapping sideband patters, efficiently acquire homonuclear and heteronuclear correlation, analyse system dynamics, and combine the NMR observables with theoretical calculation.

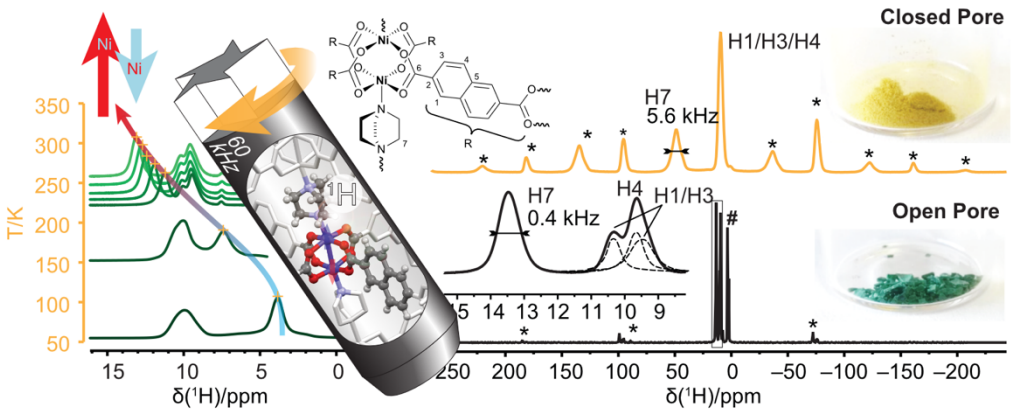

Figure 1: Solid-state ^{1}H MAS NMR spectra acquired at variable temperature (left) indicate an increase of the paramagnetic-induced shift with temperature associated with antiferromagnetic coupling between nickel(II) atoms in the DUT-8-Ni MOF. Similarly, ^{1}H-spectra allow clearly distinguish between the MOF with closed (right top) and open pores (right bottom).

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Charge compensation, hydrogen bonds and packing in polyelectrolyte complexes

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Complexes of oppositely-charged polyelectrolytes are applied for water treatment, paper production or controlled drug release. These complexes exhibit better performance and stability against changes in the surrounding media in particular for applications for the environment or medical applications, therefore an understanding of the inner structure of such complexes is desired.

The repelling force from the charges along the polymer chain, influenced by pH, determine the conformation of polyelectrolytes in solution from which the complexes are formed. Diffusion NMR yields the hydrodynamic size and thus the conformation. Molecules with an electric dipole moment orient in an electric field while those with a net charge move along the electric field. The electrophoretic mobility together with the hydrodynamic friction from diffusion yields the net charge of the molecule. With increasing pH poly(maleic anhydrite-co-ethylene), a weak polyacid, increasingly dissociates generating more charges resulting in a more stretched conformation. Is this retained in the complexes?

Separating ^{1}H solid-state NMR spectra in two-dimensional single-quantum-double-quantum correlation spectra allows to distinguish between acid protons hydrogen bonded to other acid protons thus identifies and quantifies polyanion-rich regions in complexes. At low pH (weak charge) these acid-acid contacts are reduced by a factor of three in the complexes compared to the pure polyanion. At higher pH (high nominal charge) with a more stretched conformation almost no acid-acid contacts are found in the complexes. ^{22}Na (originating from NaOH to adjust pH) spectra distinguish signals from NaCl and sodium maleate compensating a fraction of the charges of the polyanion. Even at the highest pH when all of the polyanion is dissociated and complete intrinsic charge compensation from the polycation is expected, about one quarter of the sodium is detected in maleate in the complexes proving so-called extrinsic charge compensation in polyacid domains.

Structure and dynamics of *Chain-Walking Polymerized* polyethylenes as seen by solid-state NMR spectroscopy

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Polyethylene (PE) chains in solid state occupy mainly *trans* and two kinds of *gauche* conformations, between which there is a little energy difference. Therefore, the polymer adopts different structures under different conditions. Linear PE in solid state has three crystalline phases: orthorhombic, monoclinic and triclinic. There are also non-crystalline and interfacial phases, and their existence strongly affects the physical properties. In polymer chemistry, *chain-walking* (CW) polymerization is a revolutionary concept leading to a dendritic type of branching. This process is characterized by an accurate control of polymer architecture and topology. The polyethylenes used in this work were synthesized with α-diimine palladium and α-diimine nickel catalysts, when the former one exhibits higher propensity to CW, whereas the Ni one undergoes CW in less extent. Polymer chain arrangements and energies of intermolecular interactions stabilizing the structures were investigated by advanced approaches of solid-state NMR spectroscopy. Comprehensive analysis of a wide range of solid-state NMR spectra unveiled extensive structural diversity of CW-polymerized PE chains. The observed structural differences are associated with significant differences in segmental dynamics and polymer chains arrangements. Depending on the catalytic systems the resulting polymer exhibited domain-like morphology with crystalline domains surrounded by partially ordered amorphous, unusual proto-crystalline phase and weakly branched interface up to a hyper-branched gel-like fractions. The combined experimental-computational strategy of solid-state NMR spectroscopy (crystallography) of polymers, which allows to describe the intermolecular interactions stabilizing the anomalous structures in proto-crystalline domains of chain-walking polymerized polyethylenes, is presented.

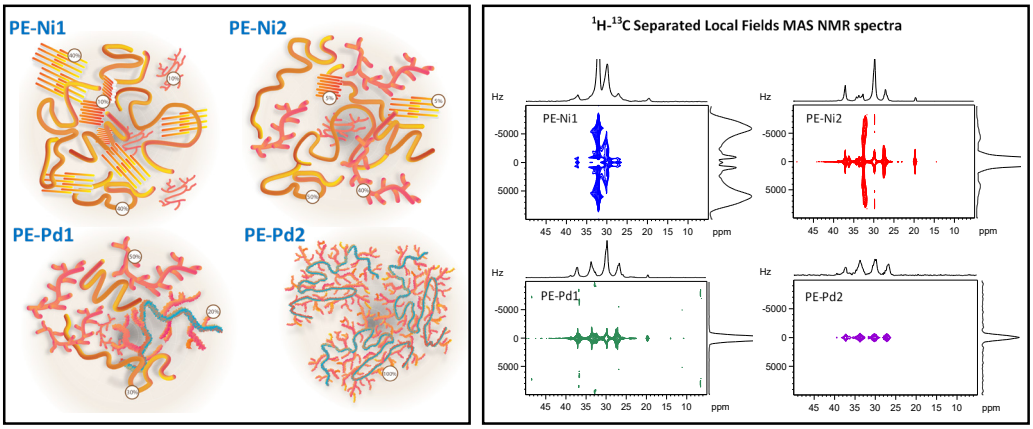

Figure 1. ^{1}H-^{13}C dipolar spectra and idealized structures of various PE systems.

Establishing hydrogen atom position in molecular crystals with solid-state NMR

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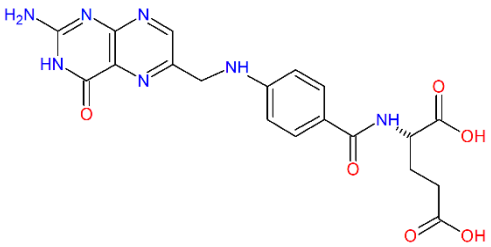
The location of the hydrogen atom position(s) in molecular crystals is a significant challenge for crystal structure determination techniques. This is mainly because single-crystal X-Ray diffraction, a method of choice in establishing crystal structures is less sensitive to hydrogen atoms, due to their low electron density. In particular, this is the case of the hydrogen atoms located between two electronegative atoms, such as nitrogen and/or oxygen, leading to still lower electron density on hydrogens. On the other hand, finding a correct protonation state can be crucial for the understanding of the formation, chemistry and energetics of a given crystal form, as well as from the regulatory perspective, in particular in pharmaceutical industry. In this contribution we showcase the many ways in which solid-state NMR can be used to determine hydrogen atom position(s) in binary crystals/salts and in crystals built by different tautomeric forms [1-2], featuring in particular the case of folic acid dihydrate and a new mesylate salt of folic acid (FA). FA (vitamin B9, Figure 1) can exist in several tautomeric forms (pteridine ring) in addition to zwitterionic forms (glutamyl moiety). This abundance results in the difficulty in establishing hydrogen atom positions of solid forms of FA, especially when molecular salts are formed. Our NMR studies resulted in the evaluation of the published structure of FA dihydrate, in addition to establishing the protonation state of a new mesylate salt.



Molecular structure of folic acid (FA)

The NMR studies has been supported by PANACEA which received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No 101008500.

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NMR/DNP crystallography, MAS MRI and theory for inorganic materials and biomaterials

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Hydrated calcium oxalates are among the most represented mineral structures among human pathological calcifications. Although their presence in kidney stones is crucial, their formation remains largely mysterious. This is primarily due to a confined precipitation environment where the rules of microfluidics fully apply. In addition, organic compounds such as proteins also participate in the crystal growth process. This results in original structures that are not well understood at the moment.

In the first part of this presentation, we will show that despite very simple chemical formulas, the detailed study of synthetic and natural calcium oxalates requires the combined approach of advanced NMR and DNP experiments, DFT calculations of structural models and the GIPAW method [1].

We will show that these structures are extremely dependent on temperature variations leading to phase transitions (reversible and irreversible) which can be monitored inside an NMR rotor rotating at the magic angle. In fact, there is a very large variety of structures that differ only in their ^{13}C CP MAS NMR spectra, on the scale of a few hundredths of ppm. Local dynamics are essential to consider when interpreting the spectra in detail. The study of synthetic compounds has led to a much better understanding of the structure of natural kidney stones and provides a better understanding of their temporal evolution.

The very first MAS MRI (^{1}H, ^{31}P CSI) images of KS will be presented as well.

In the second part of the presentation, a new derivation of spin dynamics for quadrupolar nuclei will be presented (here, ^{43}Ca, I = 7/2 in the case of calcium oxalates and ^{17}O, I = 5/2 in the case of MOFs [2]).

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Optimal control methods for multidimensional solid-state NMR of proteins

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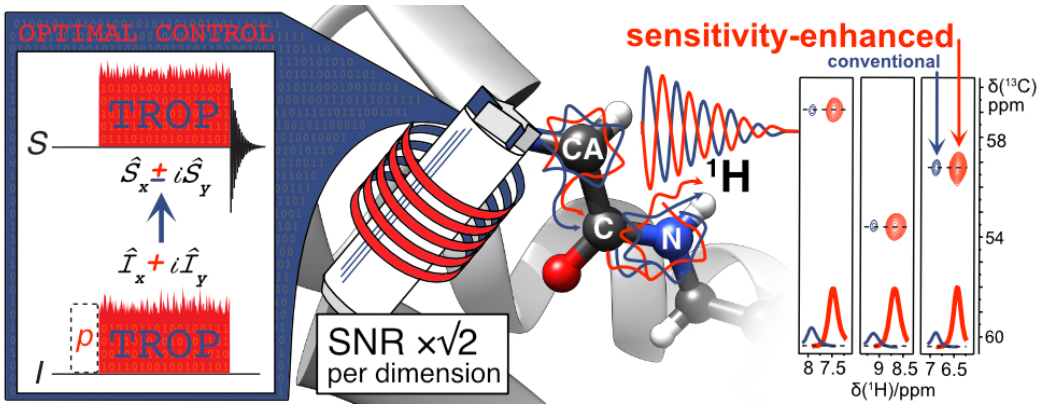

Solid-state NMR investigations of protein samples is a rapidly developing area that benefits from recent technological advances in probe design that allow for fast and ultra-fast magic angle spinning, reaching rotation frequencies of 200 kHz. Similar to solution-state NMR, proton-detected multidimensional methods are used to resolve spectral overlap challenges and to yield connectivity between atoms. However, sensitivity remains the major obstacle to broader applicability due to the integrated loss of sensitivity through multiple magnetization transfer in high-dimensional pulse schemes.

Here, we present heteronuclear[1] and homonuclear[2] dipolar recoupling elements using TRansverse mixing based on Optimal-control Pulses (TROP). This concept explores the preservation of equivalent pathways principle in multidimensional experiments known from solution-state NMR. Transferring both x- and y- magnetization components after indirect chemical shift evolution leads to a 1.41-fold increase in sensitivity per indirect dimension. This provides an order of magnitude time savings in just emerging 4-5D proton-detected experiments.

[1] J. Blahut, M. J. Brandl, T. Pradhan, B. Reif, Z. Tošner, *J Am Chem Soc* **2022**, 144, 17336–17340.
[2] J. Blahut, M. J. Brandl, R. Sarkar, B. Reif, Z. Tošner, *J Magn Reson Open* **2023**, 16–17, 100122.

How ultra-high field NMR spectroscopy can contribute to the design of advanced functional

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The rational design of functional materials with applications in the field of energy, health, optoelectronics or catalysis, is often limited by the lack of information on their atomic-level structure, notably near defects and interfaces. As a local characterisation technique, solid-state NMR spectroscopy can provide unique insights into the atomic-level disorder. Nevertheless, the use of this technique is limited by its lack of resolution and sensitivity, notably for the observation of defects, interfaces and thin-films but also for the detection of isotopes with low gyromagnetic ratio, low natural abundance or subject to large quadrupolar interaction, such as ^{33}S, ^{35}Cl, ^{63,65}Cu and ^{67}Zn.

We show how the advent of NMR spectroscopy at ultra-high magnetic fields with B_0 > 23.5 T, *i.e.*, ^{1}H Larmor frequency $\nu_0(^1H)$ > 1 GHz, opens new avenues to probe the atomic-level structure of functional materials by enhancing both resolution and sensitivity. These ultra-high field magnetic fields were first produced by DC powered hybrid magnets combining LTS and resistive wires with B_0 = 35.2 T and $\nu_0(^1H)$ = 1.5 GHz and more recently, persistent hybrid superconducting magnets built from high- and low-temperature superconductors (LTS) with a static magnetic field (B_0) of 28.2 T and $\nu_0(^1H)$ = 1.2 GHz. The resolution and sensitivity gains at ultra-high magnetic fields have been leveraged to probe the local environments of ^{33}S, ^{67}Zn, ^{35}Cl and ^{63}Cu quadrupolar isotopes in solids. The NMR observation of these isotopes provided new insights into the presence of defects in ZnS quantum dots and the mechanism of mechanosynthesis of copper complexes with N-heterocyclic carbene (NHC) ligands.

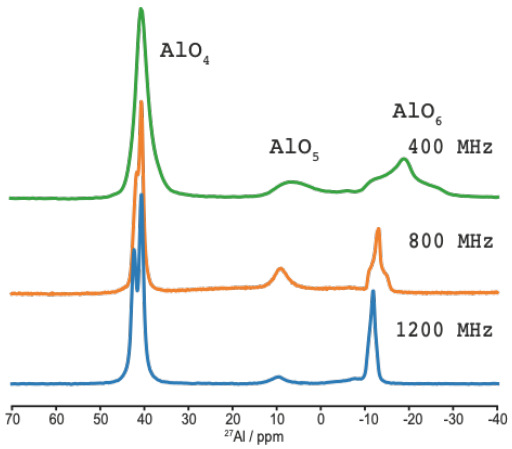

Figure. 1D ^{27}Al NMR spectra of a sample of the crystalline microporous aluminophosphate VPI-5 recorded on 400, 800 and 1200 MHz NMR spectrometers.

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ABSTRACTS
POSTERS

NMR Study of ^{15}N-6-Aminosugars

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p01

Carbohydrates play an important role in specific recognition processes, including e.g. immune response and pathogen virulence. Since the recognition is driven by specific 3D structure of sugar, the development of analytical tools for their conformational analysis is required. This work focuses on the NMR conformational study of 15N labelled 6-amino- and 6-anilinosugars. The labelling provides additional experimental NMR parameters, such as J-couplings, which can be combined with computational methods to predict conformational behavior of the amino group and its pH-dependence.

This work has been supported by the Czech Science Foundation – project 22-17586S.

^{31}P NMR Parameters for Structural Analysis

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p02

P-chirogenic compounds, which are a key element in modern organic synthesis, have a stereogenic centre on the phosphorus atom. Combination with another stereogenic centre in the molecule leads to the formation of diastereoisomers which are often difficult to separate and crystallise to determine their relative configuration. Therefore, an NMR method able to assign the stereochemistry would be a solution. In this work, we examine 31P NMR parameters for the structural study of model phosphorus-containing compounds, which may exist in several conformations. We present a profound analysis using classical and new NMR and computational methods in combination with quantum-chemical calculations.

NMR Crystallography of Amino Acids

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p03

Solid-state NMR (SS-NMR) spectroscopy, in the combination with DFT calculations, is a powerful technique for crystal structure determination. In this work, ^{1}H and ^{13}C SS NMR spectra of 20 canonical amino acids were measured. Signals of crystalline amino acids were assigned with the use of 2D SS-NMR spectroscopy, and the experimental data were compared with a series of DFT calculations for structures obtained from the Cambridge Structural Database.

Diketo-Ketoenol Tautomers in Curcuminoids

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p04

Curcumin represents a class of drugs possessing wide range of pharmacological properties. Curcumin and its derivatives exist in an equilibrium between diketo and ketoenol tautomers. Each of the tautomeric states exhibits dissimilar potency to bind biomacromolecules which affects their pharmacological activities. Here, we described equilibrium properties of curcumin and its 12 derivatives including FDA-approved drug ASC-JM17 in different solvents. Moreover, we separated two tautomers of ASC-JM17 on column chromatography and studied their equilibration in solution. Solid-state NMR and X-ray diffraction studies revealed two new polymorphs of ketoenol tautomer of ASC-JM17.

P-chirogenic compounds analyzed by ^{31}P NMR parameters

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p05

P-chirogenic molecules with an additional chiral center form pair of diastereomers which are often challenging to separate and distinguish by commonly-used NMR methods. In this work, we examined a series of diastereomers to explore novel approaches utilizing ^{31}P NMR parameters, complemented by quantum-chemical calculations. We investigated the feasibility of employing ^{31}P-^{13}C *J*-couplings and RDCs to verify the representation of individual conformers, unequivocally assign the relative configuration, and uncover the characteristics of our compounds.

The Hydrogen Bond Continuum in Quinoline and Chloronitrobenzoic Acid Based Systems

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p06

In our work, we implement solid state NMR spectroscopy in combination with quantum chemical calculations including nuclear quantum effects in order to get realistic results concerning hydrogen bond behavior in molecular solids containing short hydrogen bonds. We studied a total of 5 systems containing different regioisomers of chloronitrobenzoic acid and quinoline. Our experimental suite includes experiments such as variable temperature ^{1}H, ^{13}C, ^{15}N and also ^{14}N experiments like RESPDOR which allow us to measure interatomic distances. These methods enable full understanding of hydrogen bonding in the studied systems at different temperatures.

NMR-Challenge.com: Boosting NMR Interpretation Skills with Interactive Tasks

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p07

NMR spectra interpretation, a core skill for organic chemists, can be difficult for many students to master due to its complexity and necessity for extensive practice. Our interactive website, nmr-challenge.com, aids students in mastering this skill, featuring over 180 categorized tasks with real recorded 1D and 2D NMR spectra. The site provides immediate feedback and accommodates learners at all stages, from novices to experienced chemists. The tool offers a realistic, practice-based approach to learning and sharpening NMR skills.

Coupling constants of vinyl protons in porphyrins

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p08

The coupling constants of vinyl protons in protoporphyrin IX are well described[1]. The ^{1}H NMR (360 MHz, $CDCl_3$, δ (ppm)) of vinyl protons in pheophorbide a follows: 6.17 (dd, J_1=11.4 Hz, J_2=2.1 Hz, HA), 6.28 (dd, J_1=18.2 Hz, J_2=2.5 Hz, HB), 8.00 (dd, J_1=17.7 Hz, J_2=11.3 Hz, HX). In methyl pheophorbide a follows: 6.20 (dd, J_1=11.8 Hz, J_2=1.9 Hz, HA), 6.30 (dd, J_1=18.7 Hz, J_2=2.2 Hz, HB), 8.00 (dd, J_1=18.1 Hz, J_2=11.8 Hz, HX).

[1] Smith KM, Fujinari EM, Langry KC, Parish DW, Tabba HD, Manipulation of vinyl groups in protoporphyrin IX: Introduction of deuterium and carbon-13 labels for spectroscopic studies, *J. Am. Chem. Soc.* 105: 6638-6646, **1983**.

Using NMR analysis to identify unconventional adducts of indole-2,3-dione

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p09

Organic synthesis is fairly predictable, but sometimes there are surprises when instead of the expected products other compounds with unusual structures are obtained. This report will present the adduct of indole-2,3-dione, methyl acrylate, and aminolutidine.

Acknowledgements: The research was partially supported by NAIR of the Republic of Moldova under projects No.23.00208.5007.04/PDI, № 20.80009.5007.11, and № 20.80009.5007.17.

Utilizing NMR analysis to detect atypical outcomes in reactions of 5-bromo-indole-2,3-dione with acrylonitrile

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p10

Generally, organic synthesis is renowned for its predictability in determining results. Nevertheless, there are situations where instead of the expected products, unexpected compounds with unique structures may arise. This report's main focus will be the presentation of one such remarkable cyclic compound with four chiral centres prepared in situ by diastereoselective addition of acrylonitrile to 5-bromo-indole-2,3-dione.

Acknowledgements: The research was partially supported by NAIR of the Republic of Moldova under projects No.23.00208.5007.04/PDI.

Applying NMR for the detection of unusual reaction products of steroids

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p11

Typically, organic synthesis is known for its reliability in predicting outcomes. However, there are instances where unexpected compounds with unusual structures may emerge instead of the anticipated products. This report will be focused on the presentation of such surprising products resulting from the skeletal rearrangement of steroidal derivatives in the presence of cupper(I) ions.

Acknowledgements: The research was partially supported by NAIR of the Republic of Moldova under projects 23.00208.5007.04/PDI, 22.80013.8007.1BL and 20.80009.5007.17.

Applying NMR for ascertaining the product's structure of unexpected dehydropregnenolone moiety skeletal rearrangement

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p12

Organic synthesis is generally reliable in its predictability, but occasional surprises may arise when unexpected compounds with unusual structures are obtained instead of the anticipated products. This report will present a compound that emerges as a product of the skeletal rearrangement of.

Acknowledgements: The research was partially supported by NAIR of the Republic of Moldova under projects 23.00208.5007.04/PDI, 22.80013.8007.1BL and 20.80009.5007.17.

NMR characteristics of molecular complexes for a series of Zn(II) and Cd(II) coordination polymers based on 2-thiophenecarboxylic acid and azine ligands

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p13

Solution state NMR spectroscopy is widely used for efficacious characterization of the polymer dynamics in solution, whilst recent data about solution studies on biodegradable polymeric coatings open mesmerizing perspectives for their involvement as medical devices in drug delivery. Current report present the full 1H, 13C and 15N NMR characterization of the molecular complexes including solvates for some Zn(II) and Cd(II) coordination polymers decorated by 2-thiophenecarboxylate. The results of NMR studies clearly attest the chelation of the investigated molecular complexes in DMSO-d6 solutions, the signals of nitrogen and carbon nuclei that are the mandatory participants of coordination giving the most informative evidence for it.

Acknowledgements: The research was partially supported by NAIR of the Republic of Moldova under project 20.80009.5007.27.

NMR characterization of (±)-monastrol, an inhibitor of the mitotic kinesin Eg5

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p14

Vivid interest in the synthesis of 3,4-dihydropyrimidin-2-(1H)-ones- Biginelli compounds- and their derivatives is powered by their therapeutic and pharmacological properties, e.g. antiviral and antitumor. Although monastrol (M) is a well-studied molecule, there are no available data in the literature attesting the full assignment of ^{1}H, ^{13}C and ^{15}N nuclei in its structure. We report herein on the ecologically friendly synthesis of (±)-M and its complete NMR characterization on the basis of 1D and 2D HETCOR ^{1}H-^{13}C and ^{1}H-^{15}N NMR experiments, the data for nitrogen nuclei of N,N'-disubstituted thiourea fragment being presented for the first time.

Acknowledgements: The research was partially supported by NAIR of the Republic of Moldova under project 20.80009.5007.17.

Atropisomerism in *S*-alkylated 4,5-diaryl-4*H*-1,2,4-triazole-3-thiols observed by NMR spectroscopy

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p15

Atropisomerism is a type of conformational chirality, in which rotation around a single bond is hindered due to steric strain or other factors. The rotation energy barrier is high enough, so two distinct atropisomers can be formed by slow interconversion. The two stereoisomers can be identified by various spectroscopical methods, including NMR. In case of biological active compounds, it is important to resolve the atropisomers due to their different activity. In our work, we demonstrated the presence of two atropisomers in the class of novel *S*-alkylated 4,5-diaryl-4*H*-1,2,4-triazole-3-thiols by NMR spectroscopy.

Light-induced SMR by Pd Complexes of Polyaromatic NHC Ligands

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p16

In this study we report light-induced Suzuki-Miyaura reaction catalyzed by palladium-polyaromatic NHC complexes, as studied in situ by LED-NMR spectroscopy. Two LED light sources at UV (365 nm) and blue light (460 nm) was applied for excitation. The kinetic profiles of light-activated reactions are examined. Light-irradiated reactions unambiguously demonstrate accelerated rates and increased conversions in comparison to dark experiments at the same temperature.

A source apportionment of rural atmospheric aerosol using NMR aerosolomics

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p17

NMR aerosolomics represents an approach that allows assignment of dozens of individual compounds in each ^{1}H NMR spectrum of complex aerosol mixtures, which is inspired by compound profiling used in NMR metabolomics. The method was used in the analysis of PM2.5 aerosol samples collected at three different rural background sites in Central Europe during summer and winter campaigns and resulted in identification of around 60 compounds throughout the samples. A specific source apportionment method was employed in order to identify the main sources of aerosol particles and provided a four-factor solution.

NMR spectral data as a robust evidence in studies of the antioxidant's interplay: report on some grape metabolites

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p18

An analytical approach based on the use of 13C NMR for getting an insight into antioxidant's interactions will be herewith reported. Test with 1,1-diphenyl-2-picrylhydrazyl radical (DPPH) has been employed for studying the radical scavenging abilities of the mixtures of some natural antioxidants found in grape. The proofs offered by 13C NMR experiments regarding synergistic/antagonistic effects were confronted with the UV-Vis spectroscopic data. For the trans-resveratrol (tRes):L-ascorbic acid mixtures strong synergy has been demonstrated in the cases when the DPPH assisted tRes oxidation occurred, producing viniferins.

Acknowledgements: The research was partially supported by NAIR of the Republic of Moldova under project 20.80009.5007.27.

From fruit to jam: NMR investigation on sweeteners

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p19

Strawberry jam, a longstanding culinary delight with historical roots, has a comprehensive chemical composition that remains relatively unexplored. This study employed NMR profiling to analyze jams produced with 26 different sweeteners commonly used in their production. Liquid-state ^{1}H NMR and semi-solid HR-MAS NMR techniques were used to investigate the complex chemical composition of jams, syrups and raw strawberry fruits. Chemometric techniques were applied to identify subtle compositional differences between syrups and final jams. This analytical approach, which is guided by statistical methodologies, reveals the dynamic transformations that occur during the jam-making process.

Revisiting saturation-recovery experiment for T_1 relaxation measurements

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p20

An improved saturation-recovery experiment as an alternative to the conventional inversion-recovery experiment is proposed. Some general improvements in the saturation block are discussed, leading to excellent suppression in ^{1}H and ^{13}C detected experiments, while circumventing the tedious experimental setup of the original pulse sequence. In the case of ^{13}C measurements, the use of a new acquisition scheme was also investigated in order to speed up the analysis.

NMR metabolomics at work in host plant resistance

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p21

NMR spectroscopy excels in providing a comprehensive view of plant chemistry and dynamic metabolic processes in host plant resistance. Gerbera leaves aqueous-methanolic extracts of 4 resistant and 4 susceptible varieties to powdery mildew were analyzed on a 500MHz NMR (Bruker pulse sequence "noesypr1d", t_1 4µs, t_{mix} 0.1s, t_{aq} 4s, SW 16ppm, t_2 5s). With the aid of statistical methods, a resistance detection model based on resistance-driving metabolites gerberin, parasorboside, gerberinside and 5-hydroxyhexanoic acid 3-O-*β*-D-glucoside was developed and validated with 25 resistant and 27 susceptible varieties for Dutch breeders/growers. This enables them to screen for resistant varieties reducing the use of fungicides.

European Pilsner beers – comparison via NMR metabolomics

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p22

Pilsner is one of the most widespread lager beers. Originating in Plzen, Czech Republic, it soon became popular in other European countries with slight variations in the amount of hops used in brewing. ^{1}H NMR spectroscopy allows studying the chemical profile of this alcoholic beverage, along with statistical methods to distinguish its origin.

NMR investigation of a high-affinity ruthenium-based galectin-1 inhibitor

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This work focuses on the QM-assisted NMR investigation of a novel *N*-acetyllactosamine-based "piano stool" ruthenium complex, which showed promising selectivity to human galectin-1 over galectin-3. To decipher the structural basis of molecular recognition, we studied this process by established NMR methods such as ^{1}H-^{1}H transferred NOESY, ^{1}H-^{1}H saturation transfer difference, or ^{1}H-^{15}N chemical shift perturbation. The investigation provided a reasonable explanation for the selectivity with implications for galectin-focused medicinal chemistry.

Calculation of NMR Chemical Shift: The Importance of Conformational Averaging

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Prediction of NMR chemical shifts by computational methods has become an integral part in the analysis and interpretation of experimental NMR spectra. In this approach commonly the 0 Kelvin energy minimum structure is considered in the calculation. However, at room temperature many dynamic processes are active too. Here we investigate to what extend high energy conformers populated by dynamics need to be considered, in order to accurately predict chemical shifts of room temperature ^{1}H and ^{13}C NMR experiments.

Hyperpolarised ^{129}Xe NMR Spectroscopy Characterisation of weathering induced Porosity of Polystyrene

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p25

Nowadays abundant in nature, microplastic particles (MP) endanger human health and ecosystems. Their Interaction and, consequently, the degradation, toxicity and transport strongly depend on the surface characteristics. HP ^{129}Xe NMR spectroscopy is highly sensitive to probe changes in the MPs' surface morphology. With our home built ^{129}Xe polariser, we investigated weathered polystyrene MPs and observed an increase in mesopores agreeing with the fracturing model proposed by Meides et al.

Prediction of Pathologic Change Development in the Pancreas Associated with Diabetes Mellitus Assessed by NMR Metabolomics

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NMR metabolomics was used to identify metabolic changes in pancreatic cancer (PC) blood plasma samples and to construct predictive models to identify individuals at risk of developing PC among patients with recently diagnosed diabetes mellitus. Such an approach could improve the current state of PC diagnosis and subsequent outcomes.

Structure alterations of cement hydrates under the effect of chemical attack

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^{29}Si, ^{27}Al and ^{23}Na solid-state nuclear magnetic resonance spectroscopy was used to study the structural changes in cement pastes exposed to sulfate-chloride attack. Material's deterioration was marked by the polymerization of Si-Al chains of the main binding phase (calcium (aluminate) silicate hydrate), the transformation of calcium aluminate hydrates into $Al(OH)_3$, and the association of detectable amounts of Na in the Si-Al chains. Limestone in cement triggered these alterations. Chlorides mitigated their extent, while sulfates reduced chloride binding by calcium aluminate hydrates.

NMR studies of synthetic polymer aerogels

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The term aerogel is used to describe a family of open porous solids that can be fabricated from a wide variety of base materials, e.g. inorganic oxides, carbon, biopolymers, synthetic polymers. Besides reinforced silicas, the most promising aerogels close to reach the technology readiness level needed for commercialization are synthetic polymer aerogels, mainly polyurea, polyimide and polyamide. Nuclear magnetic resonance (NMR) methods have been proven to be powerful tools for exploring the physical interactions of water molecules with the nanostructured backbones of mesoporous materials.

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THE CENTRAL EUROPEAN NMR
SYMPOSIUM & BRUKER USERS MEETING
/ SOLID-STATE NMR WORKSHOP

OTHER
INFO

PRAGUE THROUGH THE OPTICS OF CONTACT LENSES

History of Contact Lenses in National Technical Museum

The permanent exhibition presents the evolving history of contact lenses and introduces the achievements of Otto Wichterle – the Czech chemist and inventor of material suitable for the soft contact lenses production and the inventor of manufacturing methodology of soft contacts. Otto Wichterle is well-known not only for his achievements in the field of chemistry but also for the story behind. He constructed the first prototypes of "contact lenses maker machines" at home using a Merkur building kit for kids, dynamo from bicycle and a bell transformer. Now, you have the opportunity to see one of the first contact lenses maker machine from 1961, a vial containing part of the first million pairs of casted contacts lenses, a casting plate for preparing prefabricated lenses for contacts production by turning them on lathes and many other machines and kinds of contact lenses from different periods. Exhibition includes a working model of lenses maker machine made from pieces of a Merkur building kit.

Prices and opening hours

Single admission: approx. 12 EUR (adult) or 6 EUR (students up to 26 y.o.). Ticket includes admission to all exhibitions apart from the coal and ore mine.

Opening hours: Tues–Sun 9–18 h, Mon closed

How to get there

Address: Kostelní 42, Praha 7, 50°5'51"N, 14°25'29.4"E

How to get there: from Conference Centre take **tram no. 8** from **Lotyšská** to **Letenské náměstí** (20 min)

Exhibition Chemistry around us

Once you have entered National Technical Museum, do not miss the exhibition called Chemistry around us. It presents noteworthy pioneers in the field of chemistry, like the work of noted Czech chemist Jaroslav Heyrovský, who received the 1959 Nobel prize for his discovery of polarography. In addition, you can take a glimpse into the past – part of the exhibit is an alchemist's workshop and an old chemist's laboratory.

ALCHEMISTIC METROPOLE IN A HEART OF EUROPE

Jánský vršek and surroundings

Historical Prague is famous for its magical atmosphere. Not surprisingly, it was an epicenter of alchemists in medieval and renaissance, mainly during the reign of Rudolf II (1576–1612). Rudolf II patronized natural philosophers such as botanist Charles de l'Ecluse and astronomers Tycho Brahe and Johannes Kepler. He was also interested in occult sciences and aimed to find a philosopher's stone. He invited to his court famous alchemists John Dee and Edward Kelley.

You can start your walk on the Malostranské náměstí (Lesser Town Square) and follow the street Nerudova. On your left side, take the stairs down to the street Jánský vršek. In house number 8 called "U Osla v kolébce" ("at the Donkey in the Cradle"), Edward Kelley lived the last three years of his life. Nowadays, you can visit a Museum of Alchemists and Magicians of Old Prague with an innovative and informative exhibition including guided tour on the house's attic where Kelley made his experiments. For a refreshment, you can spend a nice and enjoyable time in Kellyxir – an alchemical Lab Pub. They offer both of alcohol and soft drinks arranged in flasks and fuming from dry-ice. You can also take a small dish therein.

Following Jánský vršek street you end up in the street Vlašská. Here alchemists meet chemist – in number 9 the Nobelist Jaroslav Heyrovský worked in years 1954–1967.

Prices and opening hours

Single admission to Museum: approx. 9 EUR (adult) or 7 EUR (students).

Opening hours:
Mon–Sun 10–20 h (Museum)
Sun–Thur 11–22 h, Fri–Sat 11–23 h (Kellyxir)

How to get there

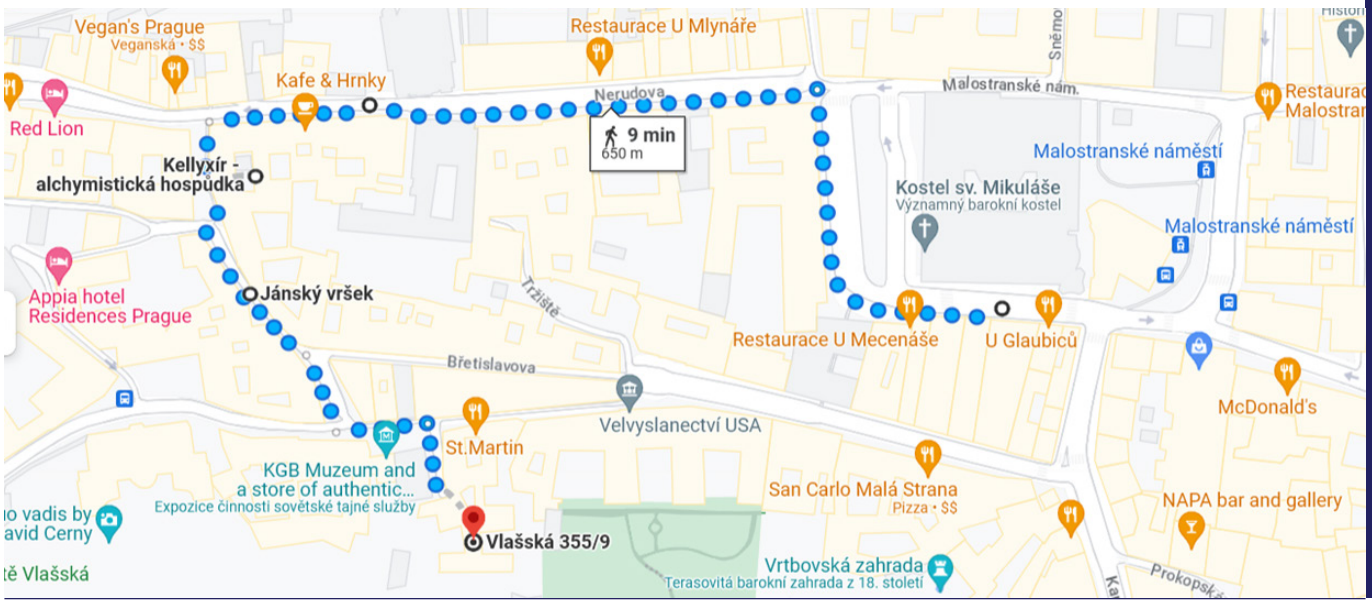
Address: Jánský vršek 8, Praha 1, 50°5'17.01"N, 14°23'55.19"E

How to get there: from Conference Centre take **tram 20 or 12** from **Dejvická** to **Malostranské náměstí** (10 min)

Accessibility

Museum of Alchemists and Magicians: 60 stairs on the way to attic during tour

Jánský vršek: To avoid stairs from Nerudova street, you can start your tour on Malostranské náměstí, follow Karmelitská and turn right to the Tržiště street.



MERCURY IN PRAGUE: FROM PHILOSOPHER'S STONE TO POLAROGRAPHY

Speculum Alchemiae Prague: a UNESCO treasure

t had been believed that mercury is a key ingredient in the Eternal Youth Elixir and that it is possible to change liquid mercury into gold. One of the oldest alchemical laboratories has been discovered in the building number 1 on the street Haštalská. This building is listed by UNESCO and – as a miracle – it survived a demolition of Jewish quarter at the end of 19th century. Nowadays, you have an opportunity to visit Museum of Alchemy Speculum Alchemiae Prague on this address and taste some of their alchemical elixirs. Elixirs are alcohol-containing and cost about 41 EUR (55 mL) or 88 EUR (250 mL).

Prices and opening hours

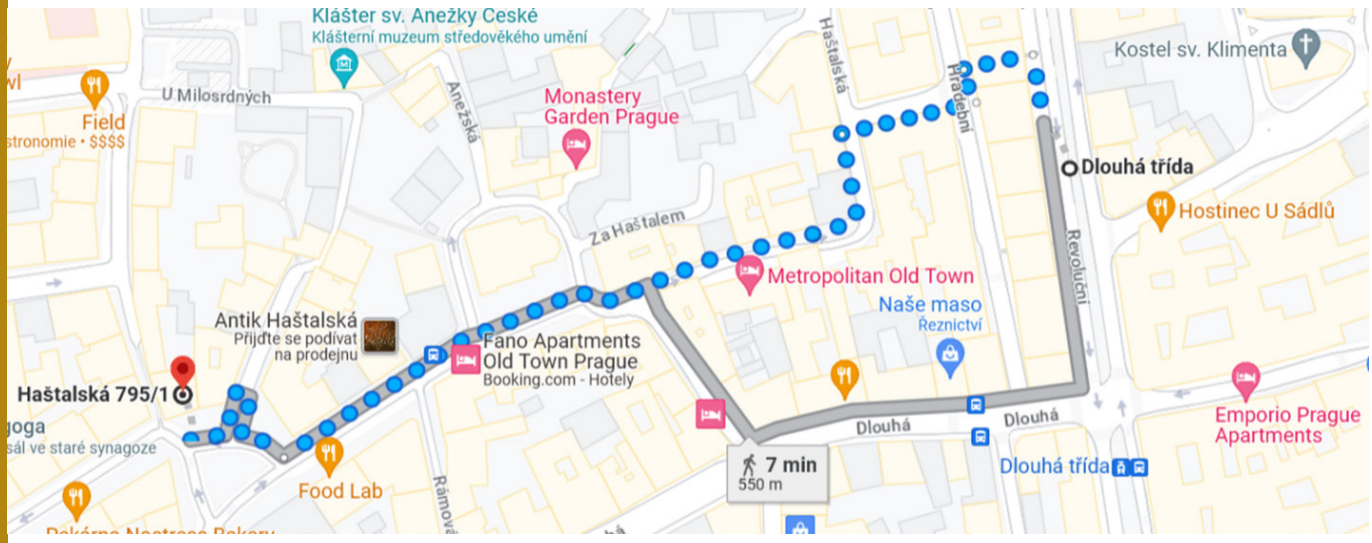
Single admission to Tour: approx. 8 EUR (adult) or 6 EUR (students).
Tour are led every 30 min.

Opening hours:
Mon–Sun 10–18 h (Museum)

How to get there

Address: Haštalská 1, Praha 1, 50°5'26.687"N, 14°25'21.063"E

How to get there: from Conference Centre take **tram 8** from **Zelená/Lotyšská** to **Dlouhá Třída** (15 min)



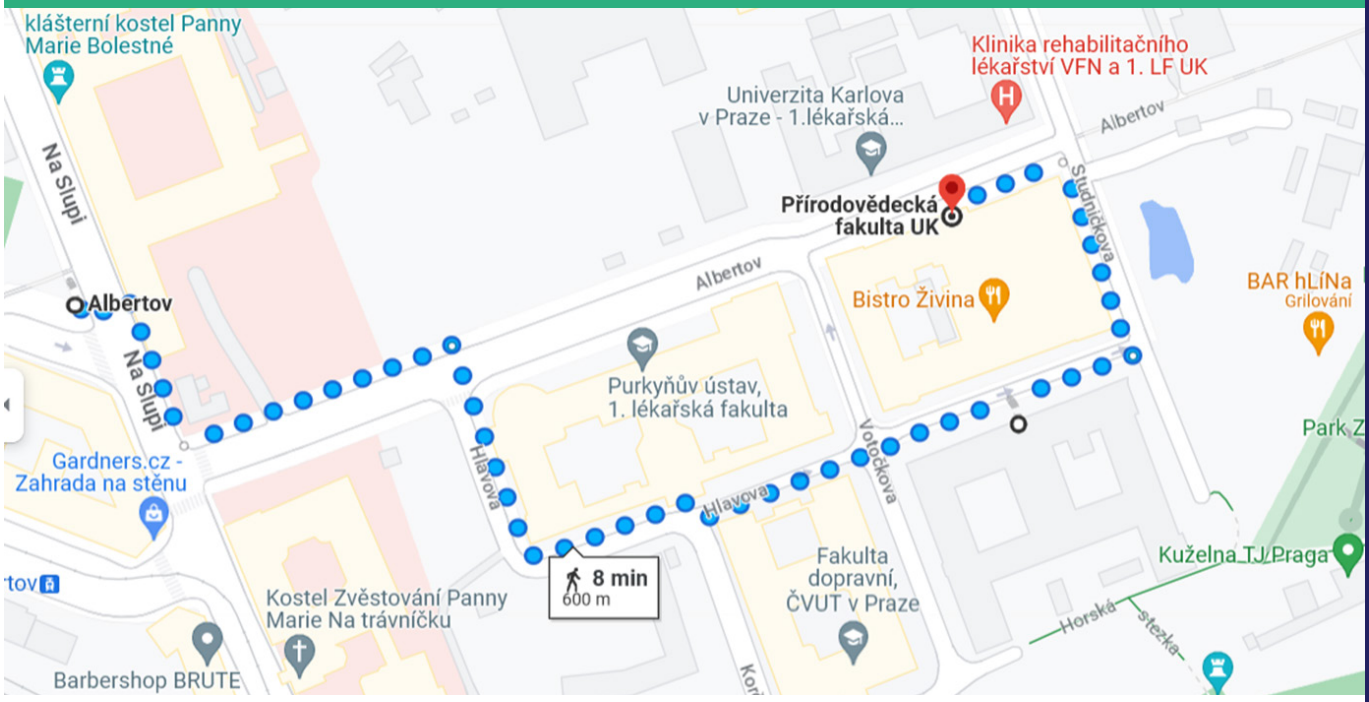
Polarography

Apart from ancient alchemical elixirs, mercury plays a crucial role in a modern analytical method – polarography – developed by Czech chemist Jaroslav Heyrovsky. Heyrovsky was awarded by Nobel Prize for his finding in 1959. Polarography is a type of voltammetry using a dropping mercury electrode. The main advantages of this electrode are a large voltage window, very reproducible electrode surface and a very easy cleaning of electrode surface by making a new drop of mercury from a large pool connected by glass capillary. Not surprisingly, the biggest disadvantage is mercury toxicity. Polarography has been widely used to the 1990s as a major tool in analytical chemistry and electrochemistry.

Professor Heyrovsky worked in his laboratory at the Faculty of Science of Charles University, where you can find his very first polarograph. While visiting the campus do not miss a memorial of Albert Einstein in the building on street Albertov number 6.

How to get there

Address: Hlavova 8, Praha 2 (Chemistry building), Albertov 6, Praha 2 (main building)
50°4'8.002"N, 14°25'28.168"E
How to get there: from Conference Centre take **tram 18** from **Zelená/Lotyšská** to **Albertov** (40 min)



CONFERENCE DINER – VILLA PELLÉ

Location: 50°5'56.385"N, 14°24'27.488"E

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