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Highest precision radiocarbon measurements for accurate dating and tracer studies

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The Earth's carbon cycle is fundamental for live on our planet. Yet, it is not fully understood, particularly when it comes to its response to global climate change. Radiocarbon (^{14}C) with its half-live of 5700 years is continuously produced by the interaction of cosmic rays with nitrogen in the upper atmosphere. It can not only used for dating organic material over the last 50 000 years, but it also serves as a valuable tracer to determine overturning rates and timescales of processes in the global carbon cycle.

The Laboratory of Ion Beam Physics (LIP) at ETH Zurich is today world-wide leading in the analysis of ^{14}C with accelerator mass spectrometry in various matrixes, such as air, plants, sediments, soils, rivers, or ocean waters thanks to recent instrumental and methodological developments. The latest generation of compact radiocarbon dating systems developed at ETH Zürich allows for highest precision ^{14}C measurements on a routine base. Measurement uncertainties down to 1 to 2‰ are now possible, even with instruments working with tiny 50 kV accelerators. I will explain how new state-of-the-art instruments are build and what is needed to obtain reproducibly high-precision results.

Finally, I will demonstrate the power of using ^{14}C as tracer to study the global carbon cycle. Amongst other applications, measured ^{14}C signatures may give us deep insight into plant physiological processes, spatially resolved emissions patterns of fossil fuel, chronological succession of cause and effect of past climate change or information on past solar activity.

The central role of oxo clusters in zirconium and hafnium-based esterification catalysis.

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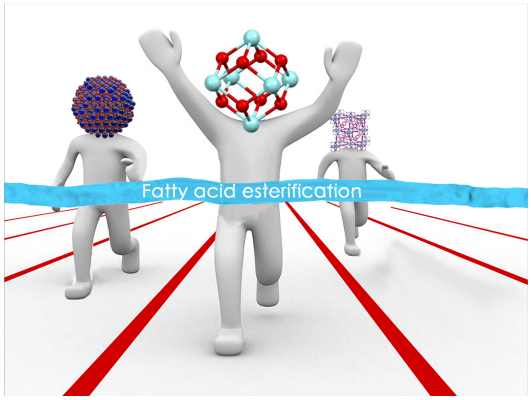
Zirconium and hafnium alkoxides, oxides, and Metal-Organic Frameworks (MOFs) have been extensively explored for esterification catalysis. In this study, we demonstrate that the most active catalytic species among these is the oxo cluster. By comparing the catalytic performance of various zirconium-based materials, including the MOF UiO-66 [1], ZrO2 nanocrystals [2], and $Zr_{12}O_8(OH)_8(OOCR)_{24}$ clusters [3], we establish the superior activity of oxo clusters attributed to their higher surface-to-volume ratio. Our investigations reveal that oxo clusters exhibit significantly higher activity compared to UiO-66, particularly for large substrates such as oleic acid. Even for smaller substrates like acetic acid, while UiO-66 shows appreciable activity, it remains lower than that of homogeneous clusters. Focusing on cluster catalysts for large substrates, we achieve remarkable conversions in solvent-free reactions, even with sterically hindered alcohols (hexanol, 2-ethylhexanol, benzyl alcohol, and neopentyl alcohol). Notably, the homogeneous cluster catalyst demonstrates recoverability without compromising activity. Structural integrity analysis using the Pair Distribution Function confirms the stability of the cluster throughout the catalytic process. Furthermore, our results indicate that the same oxo cluster is retrieved at the conclusion of reactions employing zirconium salts or alkoxides as catalyst precursors.

This study illuminates the active catalytic species in homogeneous, zirconium, and hafnium-catalyzed esterification, highlighting the pivotal role of oxo clusters in achieving enhanced catalytic performance and providing valuable insights for the design and optimization of esterification catalysts for diverse industrial applications [4].



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Retrospective Verification of Exposure of Human Blood Serum to Sesquimustard via Semi-Targeted Proteomic Analysis

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In recent years, the family of sulfur mustards (SM) turned into focus due to their use in the Syrian Civil War, highlighting the ongoing threat originating from these substances[1]. As listed chemicals within the Chemical Weapons Convention (CWC) their retrospective verification of utilization is essential for the Organisation for the Prohibition of Chemical Weapons (OPCW). In biomedical specimens such as human blood serum, the detection of exposure generally relies on defined sample preparation and subsequent targeted analysis of well-established biomarkers specific to a certain chemical warfare agent (CWA)[2]. However, this specificity requires prior information about the CWA potentially used and reduces the information content of the corresponding sample.

The present work addresses these limitations by the establishment of a facilitated and unspecific sample preparation based on single-pot, solid-phase-enhanced sample preparation (SP3)[3] and a rapid-robotic proteomic workflow (R2-P1)[4] for protein isolation and enrichment followed by tryptic digest. The analysis is performed by nLC-tims-qTOF allowing further selection and characterisation of the sample analytes by their collisional cross section (CCS) via parallel accumulation serial fragmentation (PASEF). For proof of concept, Sesquimustard (HQ) was chosen as a representative example of the SM family due to the commercial availability of its precursor as well as the formation of up to three qualifier ions of its adducts by collision induced dissociation (CID) for further verification of findings. The proteomic analysis of human blood serum exposed to different concentrations of HQ resulted in the identification of 26 novel peptide adducts and functionalization sites residing on five different proteins. For the preparation of the corresponding peptide standards, a novel synthesis pathway of SM-functionalized amino acids for further implementation into solid-phase peptide synthesis (SPPS) was developed.

The present approach allows the simultaneous identification of several different biomarkers and, thus, increased confidence in the analysis' outcome. Furthermore, the presented semi-targeted approach allowed the implementation of statistical models into the data analysis workflow improving the level of confidence in verification.

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Oxygen Isotope Analyses of Phosphate and Organo-Phosphorus Compounds by Orbitrap High-Resolution Mass Spectrometry

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Understanding the impact of human activities on the metabolic state of organism from soil and aquatic environments is of paramount importance to implement measures for maintaining ecosystem services. Variations of natural abundance 18O/16O ratios in phosphate have been proposed as proxies for the assessment of variations in metabolic activity given the crucial importance of phosphoryl transfer reactions in biological processes. However, limitations inherent to oxygen isotope analysis by isotope-ratio mass spectrometers have so far restricted a stable isotope-based evaluation of metabolic processes. To that end, we explore novel technological opportunities for oxygen isotope analysis in phosphate and organophosphorus compounds by Orbitrap high-resolution mass spectrometry (HRMS) in three steps. First, we identified and optimized critical instrument parameters for phosphate oxygen isotope analysis from the isotopologues of $H_2PO_4^-$. Subsequently, we established the accuracy of 18O/16O analysis after phosphate fragmentation to PO_3^- to enable oxygen isotope ratio measurements with organophosphates. Finally, we evaluate phosphate (and phosphonate) extraction and sample purification using Zr- and Ce-based metal organic frameworks (MOFs) given the known selectivity of these sorbents for phosphate.
Our results demonstrate that 18O/16O ratios of phosphate can be determined accurately from both $H_2PO_4^-$ and PO_3^- over the range of environmentally observed ratios. Measurements are reproducible over more than one year of repeated analyses on a standard Orbitrap HRMS device at phosphate concentrations of 20-50 μM. Our data furthermore show that analyte extraction and sample purification protocols with MOF sorbents allow for phosphate enrichment from aqueous matrices for isotopic analyses. The procedures developed in our work provides novel and promising avenues for stable isotope analysis of organic and inorganic phosphate species. We foresee applications not only in a metabolic context but also for studying sources and transformation processes of structurally related phosphonate- and phosphate-based contaminants in soil and aquatic environments.

Conformational Analysis with High-Resolution mid-IR Laser Absorption Spectroscopy

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Energy profiling of the different conformations in a molecule is beneficial for material science, drug design or mechanistic studies. Currently, nuclear magnet resonance is the most deployed analytical technique for conformational analysis. Yet, this technique requires expensive instrumentation, has limited sensitivity and typically is restricted to liquid and solid samples. Conformational analysis in the gas phase at low pressures, however, allows for the study of isolated molecules, free from intermolecular interactions. As such, it provides useful information e.g. for astrochemistry, but also for computational methods to restrain their models.

In this work, we demonstrate the capability of mid-IR laser absorption spectroscopy to selectively monitor conformers of *N*-methylformamide (NMF) in the gas phase. The measurements were performed with a custom-developed laser spectrometer [1] at high spectral resolution ($< 10^{-4}$ cm^{-1}). The instrument uses an eXtended Tunable QCL (QC-XT, Alpes Lasers) that is coupled to a multi-pass cell (MPC) with 76 m of optical path. The MPC is kept at 10 mbar to minimise the broadening of the spectral lines.

NMF is the simplest molecular model that contains amide functional group characteristic for proteins and polypeptides. The amide bond is planar with two possible configurations – more stable *trans*-, and higher-energy, *cis*-form (Figure 1a). In case of NMF, the equilibrium is mostly shifted to *trans*-conformer at room temperature. The IR spectrum of its vapor is given in Figure 1b. To enrich the content of the *cis*-form, the substance was heated up close to the boiling point and then the vapor introduced into the MPC (Figure 1c) and let to re-equilibrate. The recorded IR spectra over 20 h clearly indicate the transition from *cis*- to *trans*- conformer (Figure 1d). As the two forms have significantly different ro-vibrational features, it is possible to assign each absorption feature to one of the conformers. Our findings indicate the vast potential to perform conformational studies in the gas phase by means of laser spectroscopic methods.

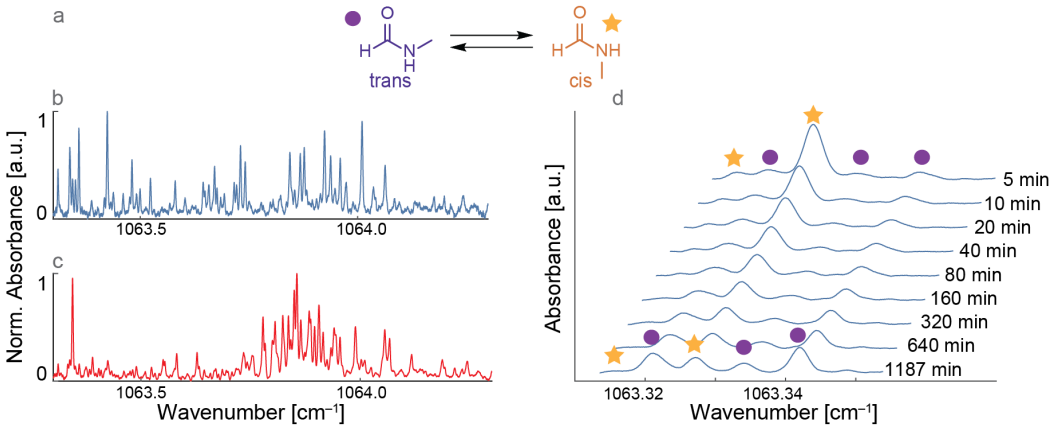

Figure 1: Monitoring of *N*-methylformamide conformational transition with laser spectroscopy.

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OctoChemDB: A Web Service for Efficient Dereplication of Natural Products using High-Resolution Mass Spectra

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Dereplication of natural products is a challenging exercise. One of the most useful resources for this task is mass spectrometry analysis (MS), but commercial MS software tools present multiple constraints such as proprietary data file formats, which limit their use with instruments from different suppliers. Commercial software also require installation and upgrades, making it necessary to undergo regular maintenance. To overcome these limitations, we have previously developed a suite of open-source, web-based MS analysis tools that enable direct processing of high-resolution MS data in the browser These tools have now been enhanced with a new feature called OctoChemDB. The concept behind OctoChemDB was to aggregate data from public databases, merge them, and provide access through a web service, facilitating seamless integration into web applications. The implementation of OctoChemDB has significantly enhanced the dereplication of unknown compounds. This improvement stems from its capability to generate candidate molecular formulas based on a monoisotopic mass and to provide similarity scores through isotopic distribution comparison. Subsequently, these molecular formulas enable the retrieval of matching structures within PubChem, facilitating the correlation of MS/MS experimental spectra with literature counterparts. Further refinement is achievable by filtering structures based on bioactivity, natural origin, and substructure, thereby obtaining candidate structures that meet specific criteria. Additionally, the acquired structures are cross-referenced with literature data, including PubMed articles and patent abstracts, along with information on bioassays conducted on the structure and the taxonomy of the organism from which the structure originated. The power of OctochemDB was demonstrated during an Innosuisse protect (54934.1 IP-LS) for the search of new compound with antibiotic activity against multi-drug resistant pathogens. OctochemDB accelerated the identification of previously unreported bioactive compounds from marine fungal extracts. OctochemDB is a robust solution for the efficient processing and characterization of unknown compounds via mass spectrometry. Notably, its web-based architecture, free access and open-source nature will ensure universal accessibility to the scientific community.

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Mitigating Bottlenecks in NIR Model Development

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style="font-weight: 400;">If you have a working analytical application with NIR-Spectroscopy, you are a winner: Virtually no sample preparation, no chemicals, fast, easy to use, this leads to low cost in routine application with a multitude of side benefits.

Famous applications are: Water content measurements or quantifying active ingredients in natural products, such as THC and CBD in Cannabis or caffein in coffee beans, sugar content in sugar cane, fat in meat, protein in flour etc. Another famous example is Diesel: cetane index (ASTM D613), flash point (ASTM D56), cold filter plug point (CFPP) (ASTM D6371), D95 (ISO 3405), and even physical parameters, such as viscosity at 40 °C (ISO 3104) are key quality parameters that can be quantified or identified with NIR.

For a working application you need a model to properly interpret the NIR Spectrum. NIRS is a secondary method, and therefore needs samples with reference values from a primary technique to train the model, primary (absolute) methods, such as titration, gravimetry etc.. Chromatography methods also can be used although they are not strictly primary methods.

Training the system and creating a chemometric model is typically challenging. In the past it required a deep understanding of the mathematics, proper pretreatment of the spectra, and the selection of relevant wavenumbers for the desired parameter.

Modern systems can combine primary and secondary methods to first get a set of reference spectra to train the model.

Recently developed algorithms (OMD) allow the automatic creation of models. Experienced NIR-specialists tried to beat the algorithm and failed. It really works surprisingly well.

Last but not least, the improved spectrometer hardware is more robust and compact than previous models. Long lasting light source and improved optics allow for shorter heat up time**s** and faster measurements. All this secures your investment and results in even faster payback time.

Facet: creating and maintaining NIR models has become much easier through connected platform reference determination, model creation through an intelligent automatic developer and easier operations in routine application.

Label free identification of full-length proteins and protein modifications using a nanopore

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Proteins have critical importance in all cellular processes and are thus implicated in numerous diseases. Methods for proteoform identification are therefore of high interest but often require complicated analysis protocols with low efficiency, and struggle with assignment of post-translational modifications (PTMs). Here, we demonstrate the abilities of an engineered aerolysin nanopore to directly identify full-length proteins without the need for chemical linkage, or enzymatic sample-processing. Our data show that under low pH conditions, a robust net flux is induced, enabling the capture and threading of chemically unfolded proteins through the nanopore. Employing machine learning classifiers, we are able to identify various full-length proteins, including PTMs in Alpha-synuclein and Cytochrome C. Furthermore, by comparing signals from seven related proteins of the Turandot family of Drosophila Melanogaster, we investigate the influence of sequence identity on the nanopore readout and their identification. This in-depth analysis not only deepens our understanding but also accelerates the path towards fast and simple nanopore based protein identification.

Quantification of laser generated aerosols via microdroplet calibration using a downwards pointing ICP-TOFMS

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Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is a powerful technique employed in a wide variety of different research areas and has been studied for almost 40 years.[1] It offers fast and reliable data acquisition for bulk or spatially resolved information with little sample preparation.[2]

A major challenge of LA-ICP-MS is the matrix dependent laser-sample interaction, resulting in issues for accurate quantification. However, in contrast to direct laser material interaction-based techniques, LA-ICP-MS allows to sequentially sample the material and then ionize it at constant plasma conditions. For non-matrix matched calibration, two requirements must be fulfilled a) 100 % transport of the ablated material into the ICP and b) complete vaporization and ionization within the ICP, thus enabling quantification of major, minor and trace elements in solids. Various strategies have been developed, one being the quantification of laser aerosols using liquid standards.[3-5] Reported methods, such as mixing the liquid and solid aerosols using a Y-piece[3], merging the flows before the plasma[4] or employing dried solution-based aerosols[5] showed the applicability of liquid standards for the quantification of different Standard Reference Materials (SRMs).

In this work, a single droplet approach for the quantification of laser aerosols using microdroplets employing a downwards pointing ICP-TOFMS (Time Of Flight) is presented. As the plasma faces downwards, droplets are introduced by gravitational force using low gas flows of He to focus and dry the droplet. For sample flow merging, a T-piece or a gas mixing bulb was used to introduce the laser aerosol into the ICP. Therefore, both sample introduction systems were operated under optimum conditions. Dry and wet plasma conditions were investigated for the quantification of different SRMs. Preliminary results indicate that this approach allows non-matrix matched quantification of laser aerosols for a selection of samples. Various optimization procedures and the respective figures of merit will be presented.

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The potential of ultra-trace lanthanide impurities in nuclear forensic evidence

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Sample attribution and comparison are essential skills in a nuclear forensics investigation. Over the past two decades, the analysis of trace element impurities by sector-field inductively coupled plasma mass spectrometry (sf-ICP-MS) has become a valuable source of information for sample attribution [1].

One such impurity are lanthanide (Ln) elements, which represent 14 valuable analytes for nuclear forensics. Natural uranium (U) materials (e.g., yellow cake) feature specific lanthanide patterns at comparably high concentrations. Their progressing depletion in processed U materials has been justified by the low volatility of trivalent Ln fluorides and the thermodynamic instability of their tetravalent analogs. This has led to the assumption that the conversion process toward U hexafluoride (UF_6) and the subsequent enrichment process removes all Ln impurities [2]. However, Moody et al. [3] described the neodymium (Nd) isotopic ratio in plutonium as being affected by a combination of fission products as well as Nd of natural origin, introduced from solvent extraction during reprocessing. This supports the hypothesis that Ln elements are indeed present in reprocessed U material.

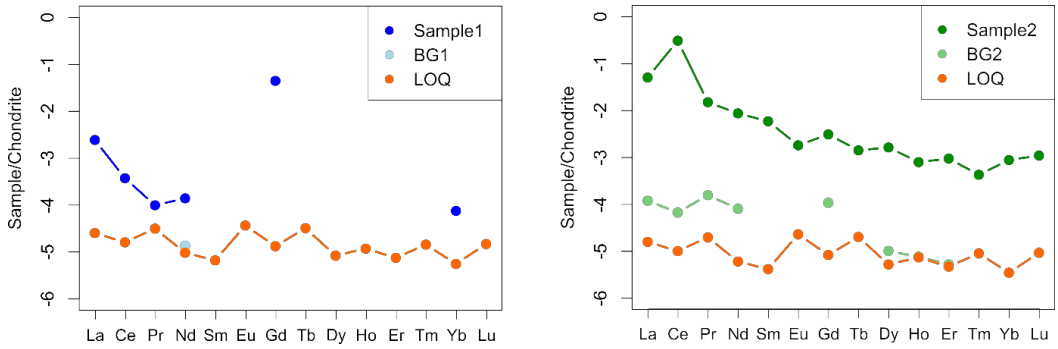

Figure 1: Pattern comparison between two depleted and reprocessed uranium materials UO_2 (left) and $UO_2(NO_3)_2$ (right) with the associated background (BG) and limit of quantification (LOQ).

In this work, a method was developed to quantify Ln elements in U materials of high chemical purity. With the new method, a limit of quantification in the lower ppt-range was achieved. Simultaneously, several polyatomic interferences (e.g., $^{238}U\,^{40}Ar^{++}$) were found, which proved to be important for subsequent interference correction. This allows us to apply this important analytical tool to most materials present in the U fuel cycle and to draw conclusions on the origin and purpose of a U material under investigation.

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Detection of nanoplastics using SERS tags at environmentally relevant concentrations

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Nanoplastic detection (defined here as plastic particles smaller than 100 nm) has become critically important due to its widespread presence, persistence in various ecosystems, and potential harm to wildlife and humans. Despite this concern, the analytical techniques available for detecting and quantifying nanoplastics, especially at environmentally relevant concentrations (µg/L – ng/L) and for the smallest sizes, remain significantly limited. Surface-enhanced Raman spectroscopy (SERS) has shown promising potential for achieving the necessary sensitivity to detect nanoplastics below the conventional Raman resolution limit (~500 nm), even at concentrations as low as ng/L. However, many existing SERS approaches, which rely on aggregated plasmonic particles, suffer from limitations that can hinder their reproducibility and applicability in biological and environmental contexts. To address these limitations, we adopted a strategy that employs SERS tags to detect nanoplastics. This method enhances our ability to detect nanoplastics at more realistic concentrations in natural freshwater and marine environments, providing a more reliable and effective approach for analyzing nanoplastics in complex environmental matrices.

Capacitive displays as direct signal transducers for potentiometric measurements

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Fully self-powered chemical sensors are very attractive because they should be environmentally friendly and have the potential for miniaturization. Among all self-powered sensors, chemical sensors based on electrical-optical conversion seem attractive because of their precision and compatibility with wearable devices.

Our group reported on electronic paper (e-paper) as transducer to convert the voltage signal from an ion-selective electrode (ISE) to a readable color change for the first time. [1] E-paper displays may precisely tune their absorbance to the applied voltage with an uncertainty on the order of 0.5 mV.[1,2] Unlike traditional electrochromic materials that slowly change their colour through chemical processes on a time scale of minutes, such display elements respond to the applied voltage electrophoretically by the migration of charged pigments in an electrical field. This allows one to observe a much faster signal transaction with a few seconds and in a wide voltage range of about 1 V.

To further promote the performance of this sensor, we multiplied the signal with a passive amplifier circuit. This circuit charges three parallel connected capacitors with the voltage generated by an ISE. The parallel connection is then shifted to a serial connection by a slider and the enhanced signal was used to drive the display. This sensor demonstrated an approximately tripled sensitivity compared to the one without amplifier.[3]

This contribution will demonstrate three self-powered sensors using capacitive displays to convert the potential signal directly to an optical readout and further multiply the sensors' sensitivity by an electronic design.

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Mechanistic understanding of electric field enhancement in gap-mode tip-enhanced Raman spectroscopy

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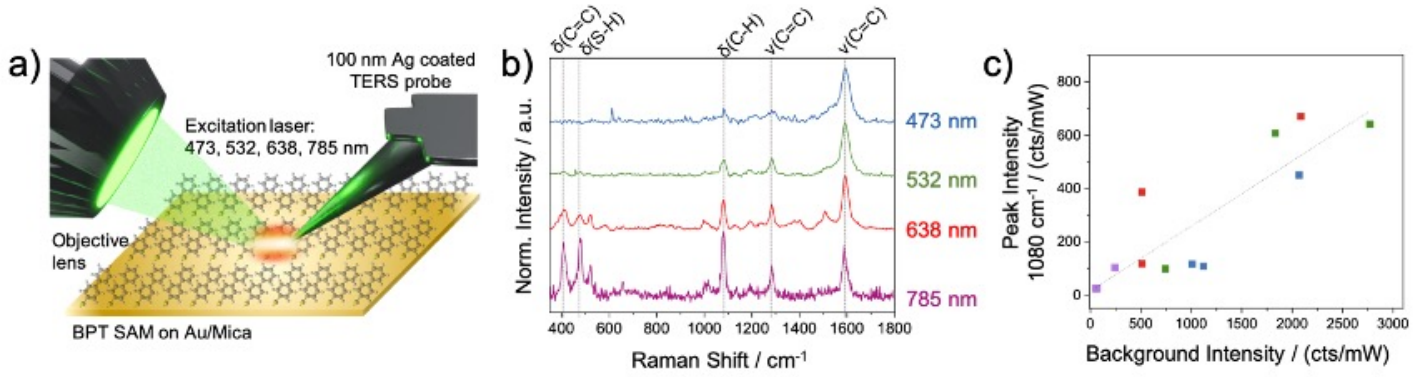
Tip-enhanced Raman spectroscopy (TERS) is a powerful analytical tool for nanoscale molecular characterization for a wide range of materials including two-dimensional (2D) materials, polymeric materials, biomaterials and catalytic materials [1]. The combination of Raman spectroscopy with scanning probe microscopy (SPM) enables nanoscale spatial resolution as well as high chemical sensitivity and specificity. However, mechanistic understanding of the local electric field (also called near-field) enhancement at the apex of metallic TERS remains unclear [2]. In literature, two different effects are postulated to contribute to the generation of TERS near-field, including the wavelength-depended localized surface plasmon resonance (LSPR) effect and the wavelength-independent lightning rod effect (LRE) [3]. In this study, we investigated the relative contribution of LSPR and LRE effects in gap-mode atomic force microscopy (AFM)-based TERS by evaluating the wavelength dependence of the TERS signal. TERS measurements were conducted on a self-assembled monolayer (SAM) of biphenyl thiol (BPT) on Au(111) surface using Ag coated probes. TERS signal of BPT SAM was measured using 473, 532, 638 and 785 nm laser excitation. The experimental and supporting computational results of this study establish that the LSPR is the dominant effect in gap□mode TERS and the contribution of LRE is negligible. Furthermore, we demonstrate that the spectral background in TERS provide a direct measure of the LSPR and the plasmonic enhancement of Raman signals. Finally, the study reveals probe-to-probe variations in plasmonic sensitivity, which is relevant for the TERS-based quantitative nanoanalysis. The novel insights gained from this fundamental study enable a more comprehensive interpretation of TERS results and a more rational design of TERS experiments.



a) Schematic diagram of the AFM-TERS setup used in this study. b) Average TERS spectra showing the wavelength dependence of the Raman signals. Each spectrum is an average of 100 individual TERS spectra, normalized to the Raman peak at 1580 cm^{-1}. c) Correlation between the peak intensity at 1080 cm^{-1} and the intensity of background at the same spectral position.

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A Physical-Chemical Approach Towards the Assessment of the Degradability of Plastics

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The majority of plastics are derived from non-renewable petrochemical resources, which often end up as plastic waste polluting terrestrial and aquatic ecosystems. Moreover, they can spread toxins that affect wildlife and human health. To date, the environmental risks of conventional and newly developed bioplastics are not fully characterized. In the environment plastics degrade through chemical, mechanical and biological processes and generate micro- and nanoplastics as a result of the fragmentation process. Of particular interest is the migration, accumulation of these particles and how they enter into the food chain. However, all these processes are far from being fully understood at a molecular level. This research aims to investigate under controlled experimental conditions physical and chemical weathering processes on the structure and surface functional changes of plastic particles and the influence of these changes on the interaction with environmental factors, such as microorganisms or chemical pollutants.

Overall, this research aims to deepen the understanding of plastic pollution and to provide molecular insights into processes that potentially increase the toxicity of plastic micro and nanoparticles. The study will employ physicochemical as well as microbial degradation approaches to deliver quantitative data that can for instance help to predict degradation processes of specific plastic materials in different climate zones. Outcomes of this study might also provide valuable insights for the development of new plastic polymers with less negative effects on the climate and the environment.

Main outcome: as one of the hydrolysable polymers, the -OH functional groups of PET particles are the dominant species changing upon aging when exposed to O_3, simulated solar radiation and microbial colonization.

Based on obtained data: the KFR seems to be by far the more sensitive technique when analyzing the interface of a material in comparison with ATR FTIR under short-term aging conditions.

Gas-phase fluorescence spectroscopy and ion mobility-mass spectrometry for investigating time-resolved unfolding mechanisms of cytochrome c after desolvation

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Native mass spectrometry (nMS) has emerged as a pivotal technique for elucidating stoichiometry, binding kinetics,homogeneity, and topology of mass-selected proteins and their complexes with high sensitivity. To correlate gas-phase data of biomolecules to data obtained in the native environment, conditions for nMS are chosen to conserve properties and native structural features after ionization and desolvation. However, the assumption that structures and function of gas-phase biomolecular ions produced by soft ionization techniques such as electrospray ionization (ESI) mirror those in the condensed phase remains a subject of debate, largely due to insufficient structural insights afforded by solitary MS-based investigations. Especially, globular proteins are believed to follow a temporal evolution of intermediate conformational ensembles, which ultimately result in complete unfolding following an ‘inside-out’ geometry where the hydrophobic protein core is exposed to the vacuum.

In this work, we combine ion mobility-mass spectrometry (IM-MS) and gas-phase fluorescence spectroscopy, i.e. Förster resonance energy transfer (FRET), to interrogate the time-resolved unfolding mechanisms of cytochrome c. A customized quadrupole ion trap is utilized, which allows for irradiation of the ion cloud by a pulsed laser. Combining global shape (IM-MS) and intramolecular distances (tmFRET) allow a fairly high-fidelity deduction of gas-phase structures. Previous studies utilizing IMS have shown that for a rather short time window, the protein unfolds in the gas phase. However, the structural information obtained by IM-MS alone is limited, because IM-MS affords only a global shape parameter. Also, the time period reported focused on the early stages of conformational rearrangement, up to 250 ms. The present work sheds light on a longer time frame of up to 10 seconds.

We designed a workflow to label the protein at the N-terminus with a fluorescent dye, which is compatible with the absorption range of the heme group inside cytochrome C, utilizing the iron ion as the quench partner. This novel approach reduces the necessary modification of the molecule and maintains a close-to-native state of the structure. Since cytochrome C has 16 lysine residues in its sequence, we employ different labeling sites to obtain structural insights from multiple secondary structures.In combination with computational modeling and IM-MS data, we are able to propose a detailed unfolding mechanism for the protein in the gas phase. This workflow provides in-depth insight into the unfolding mechanism.

Our findings demonstrate the potential of integrating MS, FRET, and IMS to study biomolecular structures and their dynamics. The methodologies developed in this study can be applied to a wide range of proteins, providing a valuable tool for structural biology and analytical chemistry. This research not only advances our understanding of protein dynamics but also showcases the potential of combining mass spectrometry with fluorescence-based techniques to study biomolecules. The significance of this work lies in its ability to extend our understanding of protein behavior in the gas phase over extended time frames, offering new perspectives on their structural properties and unfolding mechanisms.

Combining NIR spectroscopy and chemomemtrics for the online determination of process temperature and spectra prediction

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Near-infrared (NIR) spectroscopy is a widely utilized analytical method for online monitoring of chemical processes. Combination with chemometrics methods is necessary to capture and highlight changes in spectra occurring during physico-chemical processes that are otherwise imperceptible by visual inspection (Næs, 2004; Siesler et al., 2001). Batho- and hypsochromic shifts, as well as peak broadening, may occur due to variations in process temperature and pressure. Therefore, it is possible to analyze these spectral changes and correlate them with process parameters such as temperature (Renati et al., 2019). In this study, we focused on the spectral behavior of water between ambient conditions (25°C, 1 bar) to elevated temperature and pressure (185°C, 14 bar) in a closed reactor. Spectra were continuously acquired every 30 s with an immersion transmission probe connected to the NIR spectrometer through fiber optics. Different chemometrics methods were applied to analyze the data. Principal Component Analysis (PCA) is well suited for data exploration and pattern recognition. The score plot of PC1 versus PC2 (explaining 90.7% of the total variance in the spectral data) enabled us to obtain a qualitative model of temperature, suggesting that temperature is encoded in PC1. PC2, on the other hand, seems to represent blue-shifts of the different peaks. A quantitative model, i.e. a temperature sensor, was developed utilizing Partial Least Squares (PLS) regression. Several pre-processing methods were evaluated (Figure 1a). The PLS model was compared with different machine learning modeling approaches such as kNN, SVM, and XGBoost to assess potential improvement in temperature prediction accuracy. Finally, we made use of a machine learning approach to predict the near infrared spectra at given temperature. Figure 1b show predicted spectra and their residuals for water at 25°C and 100°C.

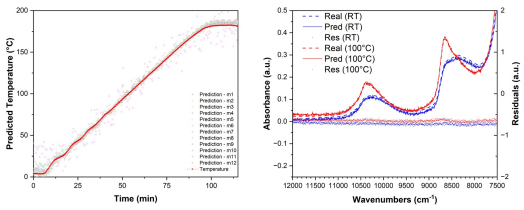

Figure 1: a) Results of temperature prediction applying different pre-processing methods before PLS computation; b) prediction of spectra from temperature values using a neural network architecture; in blue the spectra at room temperature; in red the spectra at 100°C. Solid lines refer to the predictions, the dashed lines refer to the real spectra, dotted are the residuals. Overall, our study underscores the power of combining NIR spectroscopy and chemometrics in the analysis of complex physico-chemical processes and highlights the effectiveness of various modeling techniques in predicting critical process parameters. In addition, it also shows the potential of machine learning for prediction of near infrared spectra.

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Automated Prediction of Ground State Spin for Transition Metal Complexes and Benchmarking Physics-based Representations

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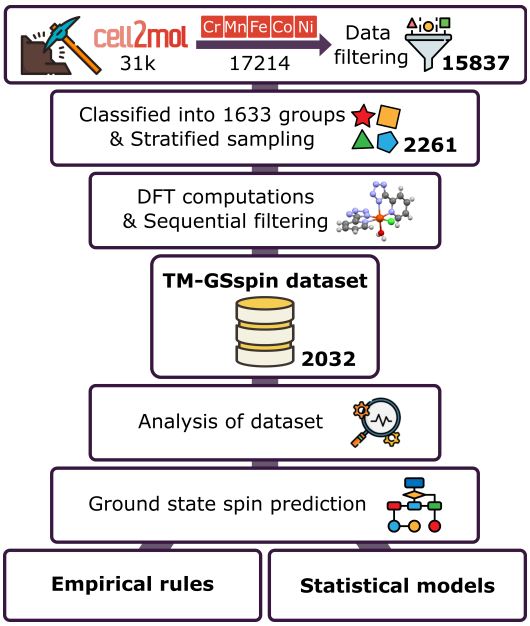
Exploiting crystallographic data repositories for large-scale quantum chemical computations requires rapid and accurate retrieval of all the necessary information (molecular structure, charge, and spin state) directly from crystal structures. Here, we develop a general approach to predict the ground state spin of transition metal complexes, complementing our prior work on determining metal oxidation states and bond order within the *cell2mol* software. Starting from a previously curated database extracted with cell2mol [1], we construct the TM-GSspin dataset, which contains 2,032 mononuclear first row transition metal complexes and their computed ground state spins. TM-GSspin dataset is analyzed to identify correlations between the structural and electronic features of the complexes and their ground state spins. Leveraging this knowledge, we build a rule-based empirical model as well as interpretative statistical models that assign the ground state spin of transition metal complexes, with a high accuracy of 97%. Our approach provides a practical way to determine the ground state spin of transition metal complexes directly from the crystal structure without additional computations, thus enabling the automated use of crystallographic data for large-scale computations. Moreover, we utilize our diverse dataset to benchmark the performance of various physics-based representations [2] in predicting the molecular properties of transition metal complexes.



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A flow-electrolysis approach for the separation and analysis of plutonium

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The identification and quantification of plutonium isotopes is critical in the context of maintenance or decommissioning of nuclear facilities, radioactive waste management, and environmental contamination monitoring. The analysis of the two prevalent isotopes ^{239,240}Pu can be carried out with α-spectrometry. However, this method is sensitive to interferences of other α-emitters, and a chemical separation from the other actinide elements is necessary to reliably identify and quantify these two radioisotopes. Radiochemical separation methods based on ion-exchange[1] and extraction chromatography[2] are typically used for such preanalytical purifications. However, the resins used with these methods tend to introduce organic impurities which complicates the electrodeposition of thin α-sources for the subsequent analysis by α-spectrometry. An alternative approach based on the selective electrolysis of Pu at anodized glassy carbon electrode surfaces has been successfully used and proved to reliable for the removal of the sample matrix without the introduction of chemical impurities[3]. Therefore, flow-electrolysis separation of Pu from other actinide elements prior to α-spectrometry was investigated in this work. A flow-through electrolyzer with a high surface area carbon fiber working electrode was used for controlled-potential electrolysis in a 3-electrode configuration. After anodization of the carbon fiber electrode, the setup could be used for (1) the selective adsorption of Pu at a positive potential of 1.2 V vs. Ag/AgCl in 1M HNO_3 and (2) its recovery at a negative potential of -0.2 V vs. Ag/AgCl. The separation and recovery yields were evaluated by electroplating the present actinide elements in each fraction on stainless steel disks and subsequent α-spectrometry measurements[4]. The first experiments with simple tracer solutions show successful separation of ^{242}Pu from, e.g., ^{243}Am and ^{244}Cm, which are not retained on the carbon fibers at the potentials studied here. The anodization procedure as well as the flowrate of the solution were shown to have an important influence on the recovery yields of Pu. With optimized conditions recoveries of 88.0% ± 5.8% (n = 4) could be obtained for Pu with excellent separations from typically interfering trivalent actinide elements (< 0.2% Am and Cm retained). In addition, the use of flow electrolysis enabled the recovery of Pu in a media directly suitable for the preparation of higher quality α-sources. The results obtained in these proof-of-concept experiments pave the way toward routine separations of Pu from other actinides in more complex matrices using flow-through electrolysis.

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Examining the volatile organic compound profile of wild-type and gnotobiotic honey bees by high-resolution mass spectrometry

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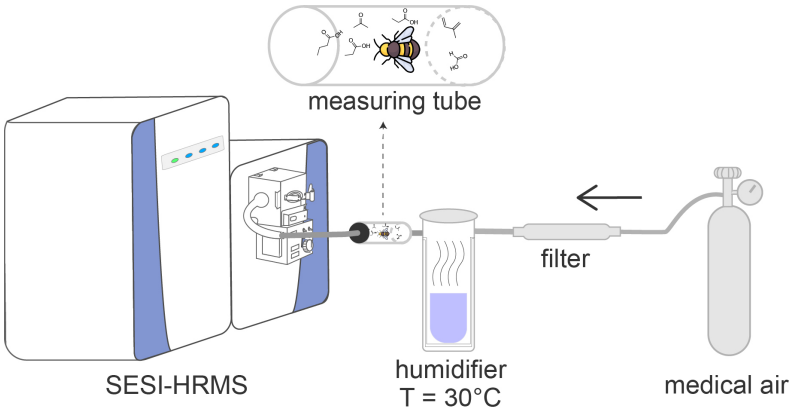
Studying the relationships between gut microbiota and their host is often challenging due to the complex nature of their interactions, cross-feeding products and the need for invasive sampling techniques. Honey bees are a simple and accessible model organism for studying gut microbiota because of their simple genome, social structure that facilitates bacterial transmission, and well-defined roles within the colony. As a result, honey bees are ideal subjects for investigating how gut microbiota affects various aspects of metabolism, including immune function, stress response, and overall colony productivity.[1] We developed a non-invasive method to analyze volatile metabolites in honey bee headspace, eliminating the need for invasive sampling techniques. Our approach involves introducing a controlled flow of synthetic air into a measuring tube containing bees, allowing us to collect and direct the released volatile compounds to the high-resolution mass spectrometer. We combined high-resolution mass spectrometry (HRMS) with secondary electrospray ionization (SESI), a soft ambient ionization technique that enables the analysis of gaseous analytes without sample preparation or preconcentration requirements.[2]



In our analysis, we compared gnotobiotic bees depleted of any microbiota to ones colonized with a synthetic community, and also to wild-type bees from the region of Zurich. We found over 3000 mass-to-charge features in the corresponding volatilome profiles of the different honey bees, with some corresponding to gut microbiota activity, namely short-chain fatty acids (SCFAs) We observed significant differences in SCFA abundance in bees depleted of microbiota and the differently colonized bees.

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Defining factors that influence chemical transformation rates in gut microbiota cultures grown ex vivo

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The gut microbiota performs essential chemical reactions with direct impact on human health. Sequencing of microbiota communities is insufficient to accurately decipher the chemical reactions occurring within the gut environment. Thus, we use anaerobic fermentations of fecal microbiota, time-series sampling, and a merged targeted/untargeted LC-MS/MS analysis to quantify chemical transformation rates of known food, drug, and endogenous host metabolites. Metabolic profiles encompassing deglycation, nitroreduction, sulfoxide reduction, deglucuronidation, bile acid metabolism, benzisoxazole ring reduction, and unique food chemical transformations were generated for 5 human donors. Chemical reaction rates varied dramatically by chemical structure and across donors. Conditions of fermentation were tested including multiple growth media, fresh and frozen samples, and fecal slurry dilutions. Dilution of the inoculated microbiota decreased chemical reaction rates dependent on microbial metabolism but did not decrease the rate of spontaneous chemical reactions. Nutrient rich media increased reaction rates compared to nutrient scarce media for most monitored reactions, while glucuronidation, and bile acid metabolism rates remained unchanged. Fresh or frozen microbiota storage did not influence chemical reaction rates for chemicals targeted in this study. Untargeted metabolomics analysis resulted in annotation of 350 metabolites. One human subject had a higher abundance of cholesterol-3-sulfate, 2-hydroxypalmitic acid, and urobilin in frozen samples compared to fresh samples. Media type and dilution factor strongly influenced the metabolome, and time-specific chemical profiles were apparent in nutrient rich media but not observed in nutrient scarce media. In summary, ex vivo fermentations monitored by LC-MS/MS provide quantitative metabolic profiles and global metabolome measurements applicable for individualized assessment of microbiota function that are not possible to glean from other -omics technologies.

Comprehensive Characterization of PLGA and Liposomal β-Carotene Nanocarriers in Simulated Gastrointestinal Fluids

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Among the carotenoids found in nature, β-carotene (βC) is the most significant and effective precursor of vitamin A, known for its antioxidant properties. However, its functional use is limited by its poor water solubility, chemical instability, and low bioavailability. Encapsulation in nanocarriers has been shown to enhance the bioaccessibility of βC by improving its stability and solubility. Despite this, there are limited studies characterising the colloidal stability of these nanocarriers under simulated gastrointestinal conditions to confirm the benefits of nanoencapsulation for oral delivery. We have developed and thoroughly characterised poly(lactic-co-glycolic acid) (PLGA) nanoparticles and liposomes loaded with βC, exposing them to simulated gastrointestinal fluids using advanced nano techniques. To fully characterise the nanocarriers in the gastrointestinal fluids, we employed dynamic light scattering (DLS), Taylor dispersion analysis (TDA), nanoparticle tracking analysis (NTA), and transmission electron microscopy. Our results showed that TDA provided better size resolution in the fluids than DLS or NTA. HPLC results demonstrated that PLGA nanoparticles incorporate and preserve βC more effectively over long-term storage compared to liposomes. However, the release of βC from liposomes was quicker (85% after 36 hours) than from PLGA nanoparticles (25% over 168 hours). These findings highlight suitable techniques for characterising oral nanocarriers, which is essential for assessing the bioavailability of encapsulated bioactives.

Could mineralised textiles be considered as time capsules?

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Radiocarbon dating (^{14}C) has become an essential tool for establishing the chronology of past events, particularly in the field of archaeology [1-2]. However, the method reaches its limits when little remains of the original layout of archaeological sites and little organic material is found. Today, state-of-the-art instrumentation allows the analysis of samples in the range of tens of micrograms of carbon and has encouraged the development of innovative strategies that cover a wider range of materials that can be used for dating in the field of cultural heritage. In particular, it has been shown that lead white, a basic lead carbonate pigment, retains the ^{14}C signature of atmospheric CO_2 during its production and can therefore be used as a dating proxy [3-4]. In this context, we have undertaken to date mineralised textiles, where the organic material has almost entirely disappeared to be replaced by metal corrosion products. In burial contexts, these textiles are preserved by their close association with corroded copper-based metal artefacts. They are ideal for dating archaeological sites, as weaving is one of the earliest craft technologies developed by humans in time. We coupled dating methods with imaging techniques, in particular synchrotron submicroscopic tomography, and demonstrate that the formed carbonate minerals (malachite and azurite) bear unexplored sources of information. Here, we present the first ^{14}C ages obtained from mineralised textiles and highlight their potential as time capsules. The nucleation and authigenic growth of these carbonates must be further investigated to support the interpretation of the ^{14}C ages obtained.

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Towards Streamlined Environmental Persistence Assays for Trace Organic Contaminants: Findings from High-Throughput Method Optimization and Biodegradation Testing

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The 2022 European Commission framework entitled "Safe and Sustainable by Design chemicals and materials" emphasizes the need for early assessment of the hazardous properties of chemicals during their design. However, evaluating the environmental persistence of the large number of candidate molecules generated through the design process requires innovative methods that are high-throughput, automatable, and time-efficient. This poster presents an optimized reverse phase liquid chromatography (LC) tandem high-resolution mass spectrometry (HRMS) method for the high-throughput detection of micropollutants in wastewater, which was developed using a mix of 200 test compounds, primarily pharmaceuticals and agrochemicals. In addition, the presented results contain findings on the adaptation of standard large-volume biodegradation tests into a small-volume 24-well plate format suitable for automation, which were obtained with the high-throughput LCMS method. We carried out comparative biodegradation tests in activated sludge at multiple scales using a subset of 40 chemicals, selected due to their reproducible degradation behaviour in activated sludge experiments.

We discuss the considerations for LC-HRMS method development in the context of high-throughput experimentation as well as the comparison of biodegradation rates between large-volume and 24-well plate formats.

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Cost-Effective Method for Trace Elements Analysis in Solids by LA-N_2-MICAP-MS

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The introduction of the Microwave Inductively Coupled Atmospheric-Pressure Plasma (MICAP), a nitrogen-sustained high-power plasma source, proved its competitiveness for elemental analysis of liquid samples when coupled to a mass spectrometer, demonstrating similar analytical figures of merit in comparison to conventional argon-based ICP-MS.[1] The similarity in the analytical performance was later extended to the direct analysis of solid samples using a Laser Ablation (LA) setup coupled to the MICAP plasma source to the field of LA-ICP-MS.[2] In the initial studies, helium was used as aerosol carrier gas because it resulted in superior sensitivity when used with argon-based ICP-MS.[3]

The higher gas tolerance towards molecular gases of the N2-MICAP, however, allows for using a much wider range of ablation environment. The use of nitrogen as carrier gas is of major interest as it allows simplification by using a single gas supply to sustain the plasma while using the same gas as aerosol carrier for laser ablation. Particle deposition was apparently more pronounced during ablation in nitrogen than in helium, suggesting similar losses as with argon. The figures of merit obtained in nitrogen were nonetheless very similar to those obtained using helium as carrier gas. A detailed characterization of different effects observed in nitrogen was thus carried out including particle size distribution measurements, scanning transmission electron microscopy images of the laser generated aerosol and measurements of the crater geometry using laser scanning microscopy. These data can be related to the quantification results for various glass standard reference materials and allow for better understanding of the fundamental aspects of laser ablation in nitrogen. These can open the door for new applications by reducing the measurement costs and simplifying the hardware requirements.

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Quantification of substances in exhaled breath using secondary electrospray ionization beyond MS^1measurements.

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Until today, most studies using secondary electrospray ionization (SESI) to analyze breath have primarily relied on MS^1 measurements, utilizing accurate mass measurements but lacking additional confirmation. Several studies have employed auxiliary measurements using exhaled breath condensate or exhaled breath particles to identify substances. However, even after confirmation, the studies rely on MS^1 features to monitor changes between measurements and individuals. In this case, the potential for overlapping features of isomeric compounds cannot be ruled out. The gold standard for quantitative analysis using LC-MS is selected reaction monitoring (SRM) or multiple reaction monitoring (MRM). These techniques separate specific MS^1 ions of interest and apply optimized fragmentation energy to generate MS^2 ions. Distinct MS^1 to MS^2 transitions are selected for each substance, and their intensity serves for quantification. Adopting this approach in breath analysis would help mitigate the risk of interferences from isomeric compounds. However, in direct injection mass spectrometry using a Q-Orbitrap, substances that are isobaric and cannot be separated by the quadrupole will occupy the C-trap and elevate the detection limit. This raises the question of whether MS^2 measurements can provide increased sensitivity compared to MS^1 measurements for breath analysis. To explore this, we mixed different gas standards to quantify various compounds in human exhaled breath and compared the sensitivity and selectivity of MS^1 and MS^2 measurements. Our preliminary results indicate that both MS^1 and MS^2 methods can be employed for quantification. MS^2measurements reduce the number of compounds that can be analyzed within one exhalation, but facilitate the separation of isomeric compounds and their quantification with SESI. However, careful selection of specific transitions is essential to maintain selectivity.

Tracking Coordination Environment and Reaction Intermediates in Homo- and Heterogenous Epoxidation Catalysts via Ti $L_{2,3}$-edge NEXAFS

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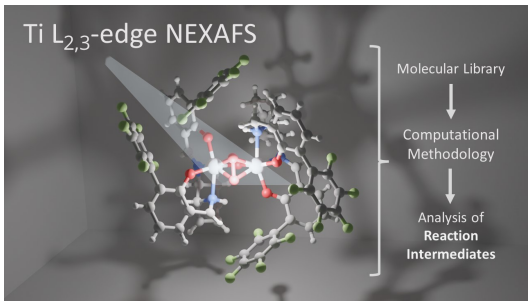

Ti-based molecules and materials are ubiquitous, and play a major role in both homogeneous and heterogeneous catalytic processes.[1,2] In heterogenous catalysis, X-ray Absorption Spectroscopy (XAS) is often used for the characterization of active sites as it offers a unique combination of element selectivity and sensitivity to local symmetry. Commonly, for early transition metals such as Ti, K-edge XAS is applied for in situ characterization and subsequent structural analysis with high sensitivity towards tetrahedral species.[3] Ti $L_{2,3}$-edge spectroscopy is in principle complementary and offers specific opportunities to interrogate the electronic structure of five-and six-coordinated species. It is, however, much more rarely implemented, because the use of soft X-rays implies ultra-high vacuum conditions. Furthermore, the interpretation of the data can be challenging.[4]

Here, we describe the development of a relationship between Ti $L_{2,3}$-edge spectroscopic signatures and electronic structures on the molecular level. Towards this goal, we first establish a spectral library of molecular Ti reference compounds, comprising various coordination environments with mono- and dimeric Ti species having O, N and Cl-ligands. We next implement a computational methodology based on multiplet ligand field theory and maximally localized Wannier orbitals[5] benchmarked on our library to understand Ti $L_{2,3}$-edge spectroscopic signatures. We finally use this approach to track and predict spectra of catalytically relevant intermediates, focusing on Ti-based olefin epoxidation catalysts.[6]

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Development of a Total *N*-Nitrosamines Analyzer and Its Optimization for Real Water Applications

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N-nitrosamines, known as potential carcinogens, have been detected in industrial wastewater effluents and in water and wastewater after disinfection processes using chloramine and ozone[1-4]. In this study, we developed and optimized an automated *N*-nitrosamine (TONO) analyzer for environmental sample analysis. Total N-nitrosamines were measured using a chemiluminescence detector coupled with an automated flow controller and autosampler. Both components were custom-designed and built in-house using 3D-printed parts, a modified 3D printer, and commercially available fluidic devices. The system operation and data processing are managed by a customized Python package.

The limit of quantification for N-nitrosodimethylamine (NDMA) and a mixture of 9 N-nitrosamines from the EPA 8270 method was 41 μg/L and 52 μg/L, respectively. A relative standard deviation of 5.6% across 50 injections of 1 μM NDMA demonstrated the stable performance of the developed TONO system. Factors that could interfere with the analysis were examined. Nitrite showed 53% sensitivity to the EPA 8270 mix within the concentration range of 0.1-10 μM. To remove nitrite and eliminate this interference, 10 mM sulfamic acid was added to the samples before the analysis of environmental samples. Higher pH increased signal intensity, reaching a plateau at pH 11 with a 125% signal increase compared to pH 7. In testing real water applications with a wastewater sample containing 9.2 mg_C/L DOC spiked with the EPA 8270 mixture, the slope of the calibration curve was 62% compared to ultra-purified water, likely due to the suppression of nitric oxide by reactions with dissolved organic matter (DOM) in the wastewater. Signal suppression by DOM was also observed in water containing 5 mg_C/L of Suwannee River fulvic acid, with the slope of the calibration curve at 56% compared to ultra-purified water. The TONO analysis will be further optimized for pre-concentrated samples and a wider variety of N-nitrosamines to expand its applicability to real water samples in industrial and municipal wastewater effluents.

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A quantitative targeted GC-MS approach to characterize lactose malabsorption

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Approximately 68% of the world population has a reduced ability to digest lactose in adulthood. The genetic and hydrogen breath tests currently in use for assessing symptoms of lactose malabsorption (LM) exhibit limited sensitivity and specificity. In a randomized controlled intervention study (Lactobreath) involving 120 participants undergoing a lactose challenge followed by on-line breath analysis, intestinal gas monitoring via the Atmo® Gas Capsule, and the assessment of gastrointestinal (GI) symptoms, we aim to identify distinct metabolic breath profiles indicative of LM symptoms. To validate these breath profiles, we will also quantify lactose and lactose-derived metabolites in urine. Excreted levels of lactose, galactose, galactitol, and galactonate provide insights into the digestive pathways stimulated by lactose consumption.

A quantitative targeted approach was developed. Calibration curves were obtained from fasting urine spiked with pure standards of lactose, galactose, galactitol and galactonate. Samples underwent a two-step derivatization procedure before injection in triplicate into a GC-MS 8890/5975 (Agilent Technologies). Helium carrier gas was used at 0.9ml/min, and electron ionization at 70 eV. The temperature program began at 60?C for 2 minutes, increased to 160?C at 5?C/min and finally to 300?C at 10?C/min for 36 minutes. The mass range covered was from 28.6 to 600 m/z. Quadrupole analyzer and source temperatures were set to 230?C and 150?C, respectively.

Absolute quantities were then determined in urine samples collected from two healthy adults before and up to six hours after a 25g-lactose challenge.

Calibration curves were built within the ranges of 0 to 4 µg/100µL for lactose and galactonate, within a range of 0 to 3 µg/100µL for galactose and a range of 0 to 0.4 µg/100µL for galactitol. The signals for these four compounds increased linearly within these ranges (lactose: R^2 =0.976 [±0.223]; galactose: R^2 =0.999 [±0.0278], galactitol: R^2 =0.969 [±0.0245]; and galactonate: R^2 =0.998 [±0.0635]). The relative coefficient of variation of triplicate measurements ranged from 0.02% to 9% and was below 5% for the majority (75%) of triplicate measurements. Using this method, we were able to successfully quantify lactose and lactose-derived metabolites in baseline and postprandial samples after a lactose challenge. These results confirmed the efficacy and repeatability of the approach, which could potentially enhance our comprehension of the variability in digestive pathways in individuals with LM.

First insights in untangling bulk ^{14}C dates in painted artwork through Compound Specific Radiocarbon Analysis

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Radiocarbon (^{14}C) dating of paintings has traditionally been limited to the analysis of the support material due to sample size limitations. Thanks to state-of-the-art instrumentation, samples as small as tens of micrograms of carbon can now be accurately dated. As a result, the analysis of the pictorial layer is now accessible. While the selective dating of the natural organic binder was successfully demonstrated on inorganic pigmented paint, its daily application is troublesome[1]. Most artworks are likely to present complex stratified surfaces, carrying multiple paint layers, as well as historical and modern restauration and conservation products. Despite recognizing the potential impact of exogenous carbon sources on data interpretation, there is no systematic research addressing this question or the development of a separation strategy to purify samples[2].

This research project focuses on developing a Compound Specific Radiocarbon Analysis (CSRA) methodology to overcome the limits of the traditional approach. A sample-specific extraction followed by a chromatographic separation step are to be implemented with the aim to isolate all the major paint components of interest prior to individual dating. This approach revolutionizes the experimental paradigm, where pigments and conservation products are no longer considered as contaminants anymore, but as components worthy of attention. This work presents preliminary results of extraction and isolation experiments performed on madder lake and linseed oil paint samples.

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Bee bread collected by honey bees (Apis mellifera)as a terrestrial pesticide biomarker to complement water studies

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The global focus on pesticide use has driven the development of new pesticide monitoring approaches. In Switzerland, water quality has been monitored for over 20 years by the National Groundwater Monitoring Programme (NAQUA) and the National Surface Water Quality Monitoring Programme (NAWA)[1,2]. However, studies on terrestrial environments, particularly involving pollinators, are still scarce. So far, only a few studies have focused on soil contamination in Switzerland[3-5], which may be due to spatial heterogeneity and the complex composition of soils, such as organic content, pH, and microbial activity. Honey bees may be exposed to environmental contaminants through foraging activities[6]. Consequently, their products, such as pollen or bee bread (stored pollen in the bee hive), can contain various pesticides[7]. Therefore, this study provides the temporal occurrence of pesticides in bee bread from a typical Swiss agricultural setting on the Central Swiss Plateau on two apiaries located in Witzwil and Bellechasse near the Bibere Canal in the Seeland region, sampled over the agricultural season in 2022. The results show the presence of 31 (62%) pesticides in bee bread. The results were further compared with water monitoring studies performed at the Bibere Canal to examine the temporal distribution patterns of pesticides in these two matrices (bee bread and water). Our study shows that some pesticides, such as the fungicide azoxystrobin, have similar temporal distribution patterns in bee bread and water. However, other pesticides, like the fungicide cyprodinil, exhibit different temporal occurrences. Physical-chemical properties, parameters like sorption (e.g., carbon-water partition coefficient (K_{oc}) or Freundlich distribution coefficient (K_{foc})), soil degradation (DT_{50}), and groundwater ubiquity score (GUS) were investigated to understand their behavior.[8,9] Our results show that certain substances measured in water do not adequately represent the exposure risk for terrestrial organisms. Consequently, bee bread is a valuable matrix for better assessing the acute exposure risk to honey bees in terrestrial environments. With over 182’000 honey bee colonies in Switzerland[10], there is substantial potential to include honey bees in environmental monitoring efforts in the future.

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High resolution Imaging of Dawsonite using LA-ICP-TOFMS

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Over the past decades Carbon Capture Storage (CCS) has been widely investigated as a possibility for the safe storage of anthropogenically emitted CO_2.[1] A mineral, which shows promising characteristics for CCS, is Dawsonite, $NaAl(CO_3)(OH)_2$, which is formed in saline aquifers through a process known as mineral trapping, wherein CO_2 becomes immobilized.[2] Initially discovered in Quebec, Canada, in 1874, Dawsonite has since been found in numerous locations worldwide, like the Green River Formation (USA)[3] and the Hailaer Basin (China)[4]. Variations in the composition of the host-rock minerals have been identified as significant factors influencing the quantity of storable CO_2 and the formation of Dawsonite in general.[5,6] However, a comprehensive examination of the precise composition, including trace elements, of both Dawsonite itself and the host-rock mineral remains incomplete.

Elemental imaging offers a promising approach to determine a geological material's composition. By using the method proposed by Neff et al. in 2020[7], employing LA-ICPTOF-MS (Laser Ablation-Inductively Coupled Plasma-Time of Flight-Mass Spectrometry), a 2D quantitative elemental distribution over the sample's surface with a remarkable resolution as fine as 5 µm can be achieved. Notably, major, minor and trace elements can be detected due to the high sensitivity of ICP-MS. In this study, we carry out the analytical characterization of a dawsonite sample occurring within rocks of the geothermal system of Mt. Amiata (Italy) to constrain the conditions at which this mineral formed in its geological environment.

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Discovering breath metabolic profiles associated with lactose metabolism using secondary electrospray ionization mass spectrometry

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Lactose malabsorption (LM), a reduced ability to digest lactose, is present in ca. 68% of the adult world population[1]. Currently available tests suffer from limited sensitivity and specificity for assessing symptoms of LM[2]. Moreover, not every person who is a malabsorber develops symptoms and, therefore, lactose intolerance (LI). Secondary electrospray ionization (SESI) coupled to high-resolution mass spectrometry (HRMS) is a powerful tool for the detection of volatile biomarkers in exhaled breath[3]. Performing postprandial on-line breath analysis after consumption of lactose can generate characteristic breath metabolomic profiles, providing a holistic approach to understanding and diagnosing LM and LI. Since the metabolic response can be highly individual, inter- and intra-individual variations need to be assessed.

After a standardized dinner and overnight fasting, 3 adults underwent a lactose challenge (consumption of 25 g or 12.5 g of lactose dissolved in 150 ml water) on 3 different days. On-line postprandial breath analysis was carried out for 6h with a SESI source (*Fossil Ion Tech*, Spain) coupled to a Q-Exactive Plus Orbitrap mass spectrometer (*Thermo Fischer Scientific*, Germany). Additionally, breath was condensed at -80°C and analyzed using an Acquity UPLC system (*Waters Corporation*, USA) coupled to the same mass spectrometer under reverse phase and hydrophilic interaction conditions. Furthermore, the hydrogen concentration in breath was determined using a QuinTron BreathTracker SC (*Quintron Instrument Company*, USA) and symptoms were assessed using the adult carbohydrate perception questionnaire.

Using SESI-HRMS on-line breath analysis, features that increased in intensity after the consumption of lactose were detected in both positive and negative ion mode. Differences in the metabolic response between individuals, but also within the same individual on separate intervention days were found. Tentative chemical formula annotation was performed using the m/z values obtained and heuristic algorithms. Compound identification was facilitated by UPLC-MS analysis of collected breath condensate and employing spectral libraries. The rise of hydrogen concentration in breath was found to be dependent on the dosage of lactose. We found that a minimum amount of lactose needs to be consumed before detecting an increase in hydrogen concentration and also the onset of symptoms. At a fixed dose, the response of the same individual still shows great variation. These preliminary results will aid a larger clinical intervention study with 120 participants with a targeted feature analysis within the detected breath metabolic profiles.

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Tracking cyanobacterial toxins and their biotransformation in Swiss surface waters

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Cyanobacterial blooms are increasing globally and posing threats to aquatic ecosystems and human health especially by releasing toxic metabolites. Besides widely studied microcystins, a legion of other secondary metabolites has been identified over the past decades. However, we lack data on their co-occurrence and fate process in surface waters. Here, we investigated the temporal trends and biotransformation potential of co-produced metabolites across a five-year lake study. We performed a comprehensive screening by high resolution mass spectrometry using CyanoMetDB, a database of 2425 known metabolites from cyanobacteria curated by our team. In lake Greifensee, 35 metabolites were co-occurring throughout the 5 year-study, confirmed by annotation of MS^2 spectra supported by in-silico fragment predictions. Not only microcystins, but particularly less-studied anabaenopeptins and microginins showed highest abundance and frequency. By deconvoluting the toxin fingerprints of three isolated cyanobacteria from the lake, we demonstrate that the succession of different toxic blooms throughout the years. We further studied the biotransformation potential of these toxins by in-situ grown biofilm communities and observe a wide range of transformation kinetics. We are currently exploring structure-activity relationships, transformation products and effects of toxin load and degrader density. Together, our work aids to define the exposure side of the risk equation by assessing toxin fingerprints of cyanobacteria in surface waters.