Session 1 – CO_2 Capture, Utilization and Storage

C-K1 9:00-9:40am	**Christian Serre** ***CNRS*** Venturing in the Advanced Characterization of Metal Organic Frameworks for CO_2 Capture and other Potential Applications
C-K2 9:40-10:20am	**Thomas Jaramillo** ***Stanford University*** Developing Analytical Techniques to Accelerate Innovative Technologies for the Sustainable Production of Fuels and Chemicals
10:20-10:50am	Coffee break and poster session
C-K3 10:50-11:30am	**Eric Lemaire** ***IFPEN*** From Laboratory to Demonstrator: Deployment and Perspectives of the DMXTM Technology for CO_2 Capture
C-O1 11:30-11:50am	**Fabrizio Croccolo** ***University of Pau and Adour Countries*** Thermal Diffusion Experiments in CO_2-based Mixtures During Parabolic Flight Experiments
C-O2 11:50-12:10am	**Jean-Luc Bridot** ***Teclis*** Influence of CO_2 Content on the Formation, Stability, and Structural Evolution of Liquid Foams
C-O3 12:10-12:30am	**Simona Moldovan** ***University of Rouen*** Microstructural Evolution of Zeolitic Nanocrystals for CO_2 Capture by Environmental in-situ TEM

Venturing in the Advanced Characterization of Metal Organic Frameworks for CO_2 Capture and other Potential Applications

Serre Christian [1]

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At the Institute of Porous Materials from Paris (IMAP), we have devoted a long-term effort to the synthesis, structural characterization, synthesis optimization, scale-up and shaping of new functional, robust, Metal-Organic Frameworks (MOFs) and their related composites while paying a particular attention to translate these highly versatile porous crystalline hybrid solids in practical use [1]. These MOF materials are in general based on non-toxic high valence transition metal or 3p cations constructed from diverse types of commercially available ligands (carboxylates, phosphonates, phenolates) [2]. As representative examples, we have designed micro or meso-porous Fe or Al polycarboxylates MOFs for the separation of small gas molecules or the capture of CO_2 [3-5], eventually assisted by AI [6], as well as other potential applications of strong societal interest (e.g. heat reallocation, capture of pollutants...) [7]. An optimal utilization of these new adsorbophores requires combining a large set of advanced characterizations, sometimes combined with modelling, to understand their behavior at the microscopic scale [2]. This is also crucial when it deals with MOF shaping (beads, coatings, membranes, papers) and the creation of a specific hierarchical porosity, as it impacts strongly the gas diffusivity and thus the performance under real conditions [8, 9]. Recently, in order to fasten the desorption step and rely on renewable electricity, new stimuli responsive strategies have been proposed such as microwave swing absorption which calls for the synthesis of MOF carbon-based composites, raising additional characterization challenges [10].

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Developing Analytical Techniques to Accelerate Innovative Technologies for the Sustainable Production of Fuels and Chemicals

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As atmospheric concentrations of greenhouse gases continue to rise, there is great urgency to develop and scale new technologies that are capable of producing fuels and chemicals in a renewable, sustainable manner. This talk will describe R&D efforts along these lines, with a focus on electrochemical processes, and an emphasis on the development of analytical techniques that can accelerate knowledge and innovation in this space. The primary topic will involve the electrochemical conversion of CO_2 to carbon-based fuels and chemicals, with a focus is on the electrified interface, where the dynamic microenvironment greatly influences reaction pathways, impacting activity, efficiency, selectivity, and durability. This talk will cover the design, development, and implementation of advanced analytical chemistry techniques, ranging from fundamental studies on model catalyst materials to more applied technological systems.

From Laboratory to Demonstrator: Deployment and Perspectives of the DMX™ Technology for CO_2 Capture

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This presentation highlights the development of the innovative DMX™ technology for CO_2 capture, from its origins in the laboratory to the industrial demonstrator, 3D, located in Dunkirk. Particular emphasis will be placed on the analytical methods used to optimize the process, as well as the technical and operational challenges to overcome in integrating this technology into a sustainable industrial value chain.

The DMX™ process is based on an innovative solvent formulation designed to reduce energy consumption while maintaining high capture efficiency. In the laboratory phase, extensive analytical studies were carried out to understand solvent behavior, phase separation phenomena, and reaction mechanisms with CO_2. Advanced spectroscopic, calorimetric, and chromatographic techniques provided detailed insights into thermodynamic and kinetic properties. These tools allowed the identification of degradation pathways, the evaluation of solvent stability, and the optimization of operating windows.

Moving from the lab to pilot scale, IFPEN implemented a wide range of process analysis methods, including online gas monitoring, heat and mass balance closure, and solvent composition tracking under real operating conditions. The combination of fundamental laboratory research with industrial-scale measurements enabled the validation of process models and the fine-tuning of equipment design.

The deployment at the 3D demonstrator in Dunkirk represented a unique opportunity to test the DMX™ process under real flue gas conditions at an industrial site. Here, the focus shifts from proof of concept to long-term operability, reliability, and integration into existing infrastructure. Advanced monitoring systems have been implemented to follow energy performance, emissions, and solvent quality over extended operating periods.

This integrated approach demonstrates IFPEN's capacity to bridge fundamental research and industrial application by combining cutting-edge laboratory capabilities with large-scale experimental platforms. The DMX™ technology has reached a high level of maturity and is commercialized by Axens. Future work will therefore focus not on feasibility, but on further optimization – including long-term solvent management, minimizing potential environmental impacts, and enhancing scalability of process integration with diverse industrial emitters.

Thermal Diffusion Experiments in CO_2-based Mixtures During Parabolic Flight Experiments

Paul Fruton [1], Emma Lisoir [1], Cédric Giraudet [1], Fabrizio Croccolo [1]

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One of the measures to counteract global warming consists in capturing and storing huge quantities of CO_2. The storage can be performed, for example, in deep saline aquifers where the injected CO_2 rises within the porous rock saturated by brine until reaching the cap-rock and forming a layer on top of the brine. Diffusion mixes the two layers generating an intermediate one of CO_2-rich brine that, counterintuitively, is denser than the brine which generates convection. The columns of CO_2-rich brine, in form of fingers, accelerate considerably the dissolution of the CO_2 in the reservoir and understanding this mechanism is crucial in optimizing industrial storage of CO_2.

In this study, we have considered the convection induced in a mixture of CO_2 and 1-hexanol by applying different temperature gradients and also different gravity levels, thanks to a CNES parabolic flight campaign. We have investigated the behaviour of the fluid mixture by means of Shadowgraphy, a non-invasive optical technique able to measure very tiny variations of the fluid density. When the gravity level was reduced to about 0 g, the convective patterns disappeared and from a detailed analysis of the image contrast we could get information about the fluid diffusion coefficient.

Influence of CO Content on the Formation, Stability, and Structural Evolution of Liquid Foams

Jean-Luc Bridot [1], Jurine Victor [1], Cécile Aprili [2], Benjamin Dollet [2], Elise Lorenceau [2]

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The use of foams for carbon dioxide capture or separation is attracting growing interest due to their high surface-to-volume ratio, which enhances mass transfer between phases. This property can be exploited to efficiently separate CO from less permeable gases, or via active mechanisms involving CO-specific molecular carriers transported by the liquid phase.

However, it remains essential to study the behavior of liquid foams when the gas phase consists of mixtures with highly contrasting permeabilities focusing on the coarsening and drainage evolution properties.

This study investigates the impact of gas composition, particularly CO content, on the formation, stability, and structural evolution of liquid foams generated by injecting gas mixtures (N/CO) into a Foamscan™ analyzer. Foamability profiles highlight two distinct phases: a production phase ($t < 90$ s) and a dissipation phase ($t > 90$ s), with the transition marked by the cessation of gas injection.

Results show that increasing the CO molar fraction leads to a decrease in the maximum foam volume and to faster foam degradation. The conversion rate of injected gas into foam, denoted R, reaches 99.5% with pure N but drops to 85.6% with pure CO, suggesting partial CO dissolution in the liquid phase. This dissolution is confirmed by the increase in R when a CO_2 enriched solution is used.

Foam stability is strongly influenced by the nature of the gas: CO rich foams degrade more rapidly than those formed under N. This instability is attributed to the high permeability of CO through the liquid films, its strong solubility, and capillary pressure, which accelerates its diffusion out of the foam.

Structural analysis using ImageJ reveals that bubbles grow and deform over time due to coarsening and drainage. The bubble size distributions broaden with increasing CO content. At high concentrations (> 75%), bubble growth is particularly rapid, affecting the texture and longevity of the foam. Furthermore, the local liquid fraction, confirmed by both imaging and conductivity, shows that foams formed under CO are systematically wetter. These findings highlight the key role of gas composition in controlling the stability, structure, and evolution of foams.

Microstructural Evolution of Zeolitic Nanocrystals for CO_2 Capture by Environmental in-situ TEM

Simona Moldovan[1], Edwin Clathworty [2], Kalthoum Nakouri [1], Svetlana Mintova [2]

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In the current context of demographic evolution resulting in the considerable increase in greenhouse gas emissions, the academic and industrial community allocates more and more resources to the development of new solutions for capturing, storage and recovery of these undesirable products, the main component of which is carbon dioxide (CO_2). Conventional micronsized zeolites such as 13X (FAU) and 4A (LTA) are currently the most widely used and studied zeolites for separation processes, but they have disadvantages such as limited access to all microporosity due to large crystal sizes, long diffusion pathways, and high regeneration costs which negatively impact their efficiency. In this context, functionalized nanosized zeolites (RHO type) with fully accessible active internal and external surfaces and high crystalline yields were synthesized by a one-pot method without organic templates. In this context, functionalized nanosized zeolites (RHO type) with fully accessible active internal and external surfaces and high crystalline yields were synthesized. Considering the ultimate atomic resolutions (In this study, we focus on and the microstructural changes of nanosized RHO zeolites analyzed by the MET in-situ Environmental under a CO_2 flux under high temperatures and pressures.

The RHO nanozeolite was initially heated under Ar at 200°C, and images under these conditions were taken as references. Maintaining the temperature at 200°C, CO_2 was then contacted with the sample followed by heating and imaging at 700°C, 800 °C and 900°C. No significant lattice expansion occurs between 200 and 700°C, when the RHO nanosized zeolite is exposed to CO_2. However, the visible expansion of the crystals at 800°C is consistent with the structural flexibility behavior under air where we observed a substantial increase of the lattice parameter (0.2221 Å) from 700 to 800°C due to the change in symmetry of the crystalline structure from non-centrosymmetric to centrosymmetric. Superposition of the very same nanozeolite crystals recorded at different temperatures revealed distinct differences in the size of the discrete nanocrystallites. Specifically, the images recorded at 800°C (3) and 900°C superimposed with the reference images taken at 200°C under CO_2 show a clear difference in the size of the nanosized crystals, corresponding to an expansion of the particle-matrix by 3 nm and 4.8 nm, or 9% and 15% of the average particle size, respectively. The increase in the volume of RHO crystals was evaluated on the basis of 2D micrographs and corroborated with the exploration of the volume of nanocrystals obtained by electron tomography. The particle expansion between 800°C and 900°C is accompanied by a sharp change of the nanocrystal's microstructure. The crystals morphology remains stable up to 1000°C. This original study highlights for the first time the flexibility and the microstructural stability of RHO nanosized zeolite at high temperatures under CO_2 exposure by in situ HRTEM.

Session 2 – Recycling and End-of-life of Plastics

R-K1 2:00-2:40pm	**Jean-François Gérard** ***University of Lyon*** Analytical Challenges & Plastics Recycling Issues
R-K2 2:40-3:20pm	**Adam Manssouri and Félicie Pachot** ***CITEO*** Closing the Loop: Analytical Challenges in Plastic Packaging Recycling for Sensitive Applications
3:20-3:50pm	Coffee break and poster session
R-O1 3:50-4:10pm	**Jérome Vial** ***ESPCI*** Waste Tires Valorization: Why Advanced Analytical Approaches are Necessary for the Detailed Characterization of Pyrolysis Oils?
R-O2 4:10-4:30pm	**Mariella Moldovan** ***University of Oviedo*** New Analytical Platform for the Sensitive Detection and Quantification of Chlorine and Silicon Compounds in Plastic Pyrolysis Oil
R-O3 4:30-4:50pm	**Gilles Dossche** ***University of Gent*** The Origin of Nitrogenates and Halogens in Polyolefin Waste Pyrolysis Oils by Ultrahigh Resolution FT-ICR MS
R-O4 4:50-5:10pm	**Christopher Rüger** ***University of Rostock*** Advances in Mass Spectrometry Tackling Challenges in Polymer Conversion and Recycling
R-O5 5:10-5:30pm	**Germain Salvato Vallverdu** ***University of Pau and Adour Countries*** Untargeted and Unsupervised High Resolution Mass Spectrometry Data Processing via Mass Differences Analyses

Analytical Challenges & Plastics Recycling Issues

Jean-François Gérard [1]

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Polymer recycling presents significant analytical challenges that must be addressed to ensure effective reuse and support a circular economy. With global plastic production nearing 410 Mt/year, polymers span diverse sectors and applications, often forming complex multi-material products. Despite this, only 9% of plastics are recycled as materials. Polymers are increasingly found in composites, textiles, and elastomers, each requiring distinct recycling approaches, mechanical, chemical, or pyrolytic.

Mechanical recycling involves melting or solubilizing polymers, while chemical recycling includes solvolysis, enzymatic depolymerization, and pyrolysis. Analytical tools are essential across all methods to identify incoming materials, monitor processes, and detect by-products such as NIAS (Non-Intentionally-Added Substances), some of which may pose environmental risks. Chemical recycling, in particular, demands spectroscopic analysis due to its reliance on physico-chemical and reaction mechanisms.

Developing and deploying analytical methods raises fundamental scientific questions. Key challenges include (i) de-formulation techniques to identify waste components, accounting for formulation variability over time and across sources, (ii) integrated chemical and imaging tools for sorting and recognizing mixed or contaminated materials, (iii) leveraging AI (machine learning, big data) to enhance data collection, process monitoring, and predictive analysis, (iiii) ensuring analytical methods support regulatory compliance, especially for recycled plastics intended for food contact, and promoting eco-design, (iiiii) tracking plastic circularity through mass balance assessments, distinguishing recycled from virgin materials, and monitoring recycling cycles using tracers.

This presentation will explore (1) The systemic approach required for plastic recycling within a circular economy; (2) Polymer classes and recycling processes: (i) physical recycling of thermoplastics: decontamination, solvent/supercritical fluid extraction, selective solubilization, and mechanical methods, (ii) chemical recycling: depolymerization via glycolysis, hydrolysis, ammonolysis, enzymatic and thermal method and (iii) pyrolysis.

We will describe the requirements, roles, and challenges associated with analytical tools in these processes, showing that there is a wide variety of analytical techniques in use and potential techniques that need to be combined and associated. Nevertheless, they lead to particular challenges for their integration into recycling, for example for sampling and analysis, particularly automated plastic sorting: molecular spectroscopies (FT-IR, MIR-Hyperspectral Imaging HSI, NIRS and NIR-HSI, Raman, terahertz imaging THz, FT-ICR, NMR, XRPD), atomic spectroscopies (LIBS, XRFS), chromatographies (SEC, GC-MS, GC-2D), etc.

Finally, we will discuss the evolving role of analytical data in large-scale recycling, emphasizing the intersection of AI, regulation, and economic viability.

Closing the Loop: Analytical Challenges in Plastic Packaging Recycling for Sensitive Applications

Félicie Pachot and Adam Manssouri [1]

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This presentation explores the complexities of plastic packaging recycling within the framework of Extended Producer Responsibility (EPR) in France, with a focus on sensitive applications such as food and cosmetics packaging. Citeo, a leading eco-organization, examines the current recycling streams, regulatory constraints, and recycling technologies related to analytical challenges. The session addresses the balance between circularity, safety, and innovation in achieving safe recycled materials. Special attention is given to the contamination, traceability, the role of NIAS (non-intentionally added substances), and the evolving European legislation including EFSA evaluations and PFAS thresholds. The talk also highlights collaborative projects like ReCAPP and Purali, which aim to develop purification technologies and improve the quality of recycled PP/PE for closed-loop recycling.

Waste Tires Valorization: Why Advanced Analytical Approaches are Necessary for the Detailed Characterization of Pyrolysis Oils?

Jérôme Vial [1], Xiangdong Chen [1], Carlos Rincon [2], José Dugay [3], Benoît Gadenne [2], Marc Sutter [4], Fabien Bonnette [2], Michel Sablier [3]

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The human population growth and consequently the increased use of transportation are reflected in higher worldwide tire consumption and tire waste generation. Hence, several methods of tire waste management have been considered in the last few decades, particularly those involving material and energy recovery. Tire pyrolysis has become a well-established waste treatment method enabling to obtain value-added products such as pyrolysis oils which can be reused in the energy and tire manufacturing industry as a source of raw materials and fuel?

Yet, the direct use of resins issue from tire pyrolysis oils led to several problems. It appeared that the presence, even at trace level, of heteroatoms containing compounds in these oils was the cause of these discrepancies. As a consequence, an advanced analytical characterization of these pyrolysis oils is required. To this aim we developed two strategies: A comprehensive bidimensional gas chromatography approach coupled with a medium resolution mass spectrometer (GCxGC-TOFMS) and a one-dimension gas chromatography approach coupled with a high-resolution mass spectrometry. The same samples, i.e., distillation fractions of pyrolysis oils, were submitted to both approaches and optimized conditions of their respective data processing software. GCxGC, thanks to his high-resolution power, demonstrated higher capabilities within the frame on the non-targeted search for heteroatom contaminating compounds. Nevertheless, some complementarity of both approaches has also been evidenced to maximize the number of heteroatoms containing compounds detected.

As an illustration, GCXGC-TOFMS has been used to monitor the degree of abatement of an experimental treatment process as a function of the compounds. Quite different behaviors have been observed depending on the physicochemical properties of the compounds considered.

New Analytical Platform for the Sensitive Detection and Quantification of Chlorine and Silicon Compounds in Plastic Pyrolysis Oil

Mariella Moldovan [1], Montserrat Redondo Velasco [1], Francisco Calderon Celis [1], Charlotte Mase [2], Pierre Giusti [2], Jorge Ruiz Encinar [1]

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Plastic pyrolysis oil can serve as valuable feedstock for chemical industry and as alternative fuel source. However, plastic pyrolysis oil could be contaminated by unwanted elements, such as, chlorine and silicon. Such impurities, even at trace levels, can degrade the quality of the pyrolysis oils and derivatives produced. Thus, it is critical to obtain information about the content and identity of the chlorine- and silicon-containing compounds present in order to facilitate their removal from plastic pyrolysis oil. First, a GC-ICP-MS/MS based method for the analysis of chlorine in real (post-industrial or post-consumer origin) pyrolysis plastics oil samples is presented. The speciation and total quantification analysis of real samples was accomplished using generic Cl-containing standards after development and optimization of a compound-independent quantification methodology. Quantitative speciation analysis was carried out using a regular chromatographic column and an internal standard spiked in the samples. In the case of total chloride content, the analysis was performed after changing the column by an inert transfer line and resorting to external calibration with a chlorine-containing generic standard. Detection limit as low as 1 ng/g was obtained under optimal conditions.

Then, we describe a new analytical platform based on the use of ICP-MS/MS able to provide complete and sensitive quantitative characterization of Si in plastic pyrolysis oil, again without the need for specific Si-containing standards. The use of GC-ICP-MS/MS employing a transfer line provided fast total Si content while the use of a low-bleed column provided speciation of the present volatilizable Si with a LOD of 0.3 ng/g. Such highly specific Si profile was key to achieve for the first time generic quantification and identification by GC-MS of up to six siloxanes (D3- D8). Complementary XRF analysis proved that a very significant part of the Si present was not amenable of GC analysis, being sample dependent. This finding differs with the Cl-containing compounds results, since all Cl content was found in the volatilizable fraction (amenable to GC analysis) of the sample. Therefore, a capillary FIA-ICP-MS/MS approach was developed for the sensitive (LOD 2.4 ng/g), fast (< 5 min), and accurate quantification of total Si directly in the liquid phase. Further insight into Si speciation in the liquid sample was performed with GPCICP-MS/MS (LOD 7 ng/g). GPC profiles allowed discrimination of the different oils according to their plastic waste feedstock and their subsequent refining process, being in agreement with the results obtained with the rest of the platform.

In summary, the analytical platform presented here is the appropriate tool to delve into Si and Cl migration from plastic waste and/or the formation of new Si- and Cl-species during the different pyrolysis processes.

The Origin of Nitrogenates and Halogens in Polyolefin Waste Pyrolysis Oils by Ultrahigh Resolution FT-ICR MS

Gilles Dossche [1], Yannick Ureel [1], Martha L. Aguilera [2,3], Marvin Kusenberg [1], Ryan P. Rodgers [2,3,4], Maarten K. Sabbe [1], Kevin M. Van Geem [1]

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The ever-increasing plastic waste stream urges the development of large-scale recycling technologies. Among emerging technologies, thermal pyrolysis is highly promising for complex plastic waste streams, like mixed polyolefins. However, the use of pyrolysis oils as petrochemical feedstocks is hampered by contaminants, particularly nitrogen-, oxygen-, and halogen-containing species, which are problematic downstream. Detailed knowledge of those contaminants is essential to design efficient purification techniques. In this study, we employed ultrahigh-resolution 21 T Fourier transform cyclotron resonance mass spectrometry (FT-ICR MS) to determine the molecular composition of nitrogenates, nitrogen oxides, and halogens in different plastic pyrolysis oils.

Four polyolefinic plastic pyrolysis oils were analyzed: one produced from virgin low-density polyethylene (LDPE) and three postconsumer plastic waste pyrolysis oils, made from polyethylene (PE), polypropylene (PP), and mixed polyolefins (MPO). Analyses were performed with a 21 T FT-ICR MS, using positive and negative electrospray ionization ((+)ESI and (–)ESI). The oils were dissolved in a 1:1 (volumetric) toluene:methanol solution at a concentration of 50 µg mL^{-1}. The samples were infused at 0.55 µL min^{-1} and ionized with a needle voltage of 3.6 kV and -3.2 kV, respectively. An external multipole ion trap accumulated 2×106 charges over 1-5 ms. After transfer to the ICR cell, ions were excited to an *m/z*-dependent radius. The dynamically harmonized ICR cell operated at a trapping potential of 6 V. For all samples, 100 time-domain transients of 3.2 s each were acquired and averaged.

Nitrogen and halogens are among the most problematic contaminants in plastic waste pyrolysis oils. Basic nitrogen-containing species, like amines, pyridines, and quinolines, are efficiently ionized by (+)ESI. The (+)ESI FT-ICR MS results are depicted in Figure 1. Only N_1 compounds were detected in the virgin LDPE pyrolysis oil. In contrast, postconsumer plastic waste pyrolysis oils also contained N_2 and N_3 nitrogenates. For all pyrolysis oils, there was a high abundance of N_1 nitrogenates with a double bond equivalent (DBE) of zero, i.e., saturated aliphatic amines. One of the most abundant species was $C_{38}H_{79}N$, most likely originating from distearyl dimethyl ammonium chloride ($C_{38}H_{80}ClN$), which is used as a fabric softener and detergent. In addition, nitrogenates with a DBE above four were abundant and are most likely aromatic amines, anilines, pyridines and quinolines. These aromatic compounds have a higher stability and hence act as important "nitrogen scavengers".

Similar trends were found for N_2 and N_3 nitrogenates. In the case of halogens, chlorine had the highest abundance, with only traces of fluorine and no bromine. Many specific species could be identified and traced back to particular additives, organic residues or trace polymers.

Advances in Mass Spectrometry Tackling Challenges in Polymer Conversion and Recycling

Christopher Rüger [1], Lukas Friederici [1], Simon Backens [2], Timon Doose [1], Steffen Rittner [3], Thorsten Streibel [1], Ralf Zimmermann [1]

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High-performance materials are indispensable for modern society. Fiber-reinforced composites, in particular, offer outstanding properties such as corrosion resistance and high durability, which have made them essential in fields ranging from aerospace to renewable energy. Their role in wind turbine rotor blades exemplifies this success but also illustrates a growing challenge: limited service life forces the industry to develop effective dismantling and recycling strategies. Pyrolysis and solvolysis are increasingly envisioned for material recovery, yet their optimization requires a detailed molecular understanding of the complex transformations that occur during composite conversion. Mass spectrometry has proven to be a pivotal tool in this context, enabling real-time monitoring, structural elucidation, and toxicological assessment of complex degradation mixtures.

Recent work has combined laboratory-scale and pilot-scale studies supported by advanced mass spectrometry workflows. Subcritical hydrolysis of anhydride-cured epoxy resins was established as a model system for studying composite matrix decomposition. By systematically varying temperature, water volume, and treatment time in a design-of-experiments framework, it was shown that temperature is the dominant factor controlling degradation kinetics. Gravimetric and calorimetric analyses confirmed incomplete and heterogeneous degradation, while glass transition temperature measurements indicated a core-shrinking mechanism with preferential surface breakdown. Gas chromatography mass spectrometry (GC–MS) of the aqueous fractions revealed a broad distribution of degradation products, including anhydrides, alcohols, and oxidized oligomers, many of which represent molecular markers of recyclability and potential environmental concern.

At the pilot scale, fiber-reinforced composites subjected to thermal recycling were studied with online mass spectrometry coupled to downstream offline analyses. The online monitoring provided continuous chemical fingerprints of volatile and semi-volatile products, revealing dynamic emission patterns that included light hydrocarbons, oxygenated aromatics, and nitrogen-containing compounds. Offline GC–MS analysis enabled further structural identification, while toxicological assays demonstrated cytotoxic responses for selected compound classes. These results underline that mass spectrometry does not merely support efficiency assessments of recycling processes but also provides indispensable information on possible health and environmental risks associated with emission profiles.

Supporting investigations further broaden the picture. In studies of respirable particulate matter released during the cutting of carbon-fiber-reinforced concrete, MS and SEM analyses confirmed the absence of WHO-classified fibers, yet detected bisphenol A, polycyclic aromatic hydrocarbons, and BPA derivatives adsorbed to PM2.5 and PM10 fractions. These findings demonstrate that even in the absence of fibrous hazards, polymer-associated dusts may pose chemical risks, reinforcing the need for MS-based particle characterization in occupational safety evaluations. Additional studies on carbon-fiber precursors derived from asphaltene-rich feedstocks revealed that molecular composition of inputs strongly influences downstream fiber quality. Here, MS analysis was crucial in linking feedstock heterogeneity to the efficiency of conversion, paralleling challenges observed in recycling workflows where diverse polymer waste streams enter pyrolysis or solvolysis processes. Complementary pyrolysis-MS studies further demonstrated how laboratory coupling thermal analysis with MS provides detailed fingerprints of gaseous and condensed products, enabling process optimization for both energy recovery and material revalorization. Altogether, these results demonstrate that mass spectrometry serves as a unifying axis in the analytical toolkit for polymer conversion and recycling. From identifying oligomeric degradation products in laboratory hydrolysis to tracking transient species in pilot-scale pyrolysis, MS provides the molecular-level clarity necessary for both mechanistic understanding and practical process monitoring. Importantly, it also enables safety assessments by uncovering toxicologically relevant emissions in particulate matter and thermal off-gases. The case of wind turbine rotor blades exemplifies how these insights can guide the development of dismantling and recycling strategies for complex composite materials.

Untargeted and Unsupervised High Resolution Mass Spectrometry Data Processing via Mass Differences Analyses

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Recent advances in high-resolution mass spectrometry instrumentation have increased mass spectral performance metrics and expanded complex mixture applications. However, complex mixture data processing methods have lagged the advanced pace of analytical capabilities, which has created a bottleneck in the overall workflow. To reach the highest confidence in the data assignment and handle large time-dependent or imaging data sets, we need new unsupervised and automatic methodologies that rely on the data itself to reduce possible bias. Herein, a fully automated data processing workflow applicable to a variety of complex matrices is described (dissolved organic matter, biofuels, Li-ion batteries, and emerging contaminants). The method relies on extremely accurate mass differences to create a new spectrum: the mass difference spectrum used to shed light on the sample.

Our data processing is implemented in an academic, open-access, Python-based software platform, PyC2MC processing.

One common characteristic of the analyzed samples is that they contain repeating mass differences, linked to their structures, chemical composition, or chosen synthetic pathways for chemical production/degradation patterns. Statistical analyses of these mass differences provide, prior to any spectrum assignment, an overview of the representative chemical patterns and elemental composition of the sample. This analysis relies on the identification of pairs of peaks belonging to the same mass difference and the connections between all peaks. This can be used to identify with high confidence the most relevant Kendrick series in a sample in order to feed a calibration list, using an internal calibrant. The most abundant match (or a collection of matches) is then used to recalibrate the entire spectrum using the selected equation and theoretical mass differences values, which enables accurate recalibration of the mass spectrum (< 100 ppb rms error) without internal calibrants. The capability of the method is demonstrated here in the context of bio-oil and plastic applications and reveals how mass difference analyses can provide an accurate overview of the current stage of feedstock processing.

Session 3 – Photovoltaic Solar Energy

P-K1 9:00-9:40	**Daniel Lincot** ***SOYPV and CNRS*** Panorama of Photovoltaic Development with a Focus on Device Evolutions with More Thin Films, Interfaces and Analytics for Better Performances and Lower Costs
P-K2 9:40-10:20	**Frédéric Sauvage** ***University of Picardie*** Decoding Degradation in Hybrid Halide Perovskite Solar Cells Through Advanced *in situ* Characterization Techniques
10:20-10:50	Coffee break and poster session
P-O1 10:50-11:10	**Bertrand Paviet-Salomon** ***CSEM*** Multi-isotopic Analysis for Robust Traceability of Crystalline Silicon Wafers
P-O2 11:10-11:30	**Lars Korte** ***Helmotz Berlin*** Insights into High-efficiency Perovskite Photovoltaics from Photoelectron Spectroscopy and Related Methods
P-O3 11:30-11h50	**Christine Lartigau-Dagron** ***University of Pau and Adour countries*** Challenges of Eco-friendly Organic Photovoltaics: Development of Semiconducting Water Dispersions
P-O4 11:50-12:10	**Brice Hoff** ***ThermoFisher*** Femtosecond Laser Ablation (fs-LA) XPS Depth Profiling of Lead Halide Perovskite Thin Film Solar Cells
P-O5 12:10-12:30	**Mathieu Fregnaux** ***UVSQ*** *In situ* Coupling of Photoemission and Photoluminescence Spectroscopies: a New Analytical Tool for the Characterization of Photovoltaic Devices

Panorama of Photovoltaic Development with a Focus on Device Evolutions with More Thin Films, Interfaces and Analytics for Better Performances and Lower Costs

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Photovoltaics is reaching today a major role in the supply of electrical energy worldwide. With 600 GW installed in 2024 and a cumulative power of 2,2 TW at the end of 2024 it is now supplying about 5,5% of the electricity production worldwide. China accounts for 60% with 357 GW installed in 2024 and more than 1 TW cumulated (8,3% of electricity). Europe is the second market with 63 GW installed (9%), with 16.7 GW in Germany (15%) and 5.9 GW (4.2%) in France. USA is the third market with 47 GW in 2024 (5.6%). This growth is based on both technological and economic achievements. PV technology is almost entirely based on silicon wafer technology (98%), the rest relying on thin film technology (CdTe and CIGS). Technological fiability withTremendous cost reductions makes PV about the cheepest source of electricity (from 20 to 40 euros/MWh) paving the way of its economic competitiveness.

Instead of being a smooth evolving technology based on conservative production processes and device architectures, the dominant silicon technology is in permanent evolution, with increasingly complex production steps and materials, together with high level quality controls. This is illustrated by different generations of cells, PERL, PERC, HJT, TOPCON, IBC allowing to increase the efficiency limit closer and closer to the theoretical one of silicon (about 29%), with a record value of 27,8% for cell and 26 for module. We will present these evolutions with the different steps of production highlighting the growing importance of hybridation with thin film technologies and laterally controlled properties.

This evolution is even reinforced by the endeavour of perovskite thin film technology, besides CdTe and CIGS. This open a new avenue for photovoltaics towards higher efficiencies, based on the concept of multijunctions, with a theoretical value of about 43% for silicon-perovskite tandems. Present record efficiency already breaks the 30% symbolic level with 34,9%. This opens new challenges with more complex stuctures and materials, more interfaces and the need for more analytics. Besides silicon-perovskite tandems, full thin films tandems are in progress with combining CIGS and perovskite. This is the aim of the start up SOYPV, created in Orsay by Daniel Lincot and Jean-Michel Lourtioz and the tandem project France 2030 , supported by ADEME, with IPVF-CNRS. To conclude, a special mention will be given to the importance of analytical chemistry and electrochemisty in the development of the CIGS technology.

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Decoding Degradation in Hybrid Halide Perovskite Solar Cells Through Advanced *in situ* Characterization Techniques

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Hybrid halide perovskites have rapidly established themselves as a leading thin-film photovoltaic technology. In barely a decade, the hybrid organic-inorganic halide perovskite solar cell achieved to compete with all mature crystalline technologies, by reaching a certified 27.0 % power conversion efficiency (PCE) on cells and 20.6 % PCE on small modules.[1] Perovskite's strength stem from their remarkable opto-electronic properties. However, the technology still requires significant attentions regarding stability, in particular rapid structural and electronic degradation can be engendered when exposed to various external stressors (temperature[2-3], humidity[4-6], light[7-8], electrical bias[9]).

To cope with the long-term stability issue, it is a paramount to precisely understand the multiple degradation pathways of the perovskite upon and during the external stressing. To this end, in situ or operando characterization techniques are central tools. In this communication, we will be discussing the degradation of different perovskite composition on the basis of humidity or temperature-controlled in situ x-ray diffraction and corroborated with in situ electron spin resonance spectroscopy and in situ transmission electron microscopy. For example, one key finding which we will discuss is that α-FAPbI3 degradation is substantially accelerated when temperature is combined to illumination and when it is interfaced with the extraction layers, and, second the existence of a temperature gap region which takes place only under illumination involving an intermediate stage between the thermal-induced perovskite degradation and the formation of PbI2 by-product.[10]

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Multi-isotopic Analysis for Robust Traceability of Crystalline Silicon Wafers

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The global photovoltaic industry, which heavily relies on monocrystalline silicon wafers, faces increasing pressure to ensure the traceability and transparency of its supply chain. With over 95% of the photovoltaic production based on such crystalline silicon wafers – primarily manufactured using the Czochralski method – there is a growing need for robust, scientific methods to verify the origin of these materials. Current traceability systems are largely declarative and lack analytical rigor.

Inspired by geosciences and food traceability applications, the use of non-traditional stable isotopes, particularly silicon isotopes (29Si and 30Si), has emerged as a promising approach. These isotopic signatures can potentially reveal both the geographical origin and the manufacturing processes of silicon wafers. The goal of this research is to assess whether isotopic analysis, particularly using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), can serve as a reliable tool for authenticating the origin of crystalline silicon wafers and understanding the processes that influence their isotopic composition.

The study employed two complementary analytical techniques, namely: (i) High-resolution MC-ICP-MS, in which samples were subjected to alkali fusion followed by ion exchange chromatography, before proceeding to the measurement of the 29Si/28Si and the 30Si/28Si isotopic ratios. The external precision achieved was better than ±0.10‰ for δ29Si and ±0.15‰ for δ30Si. (ii) Femtosecond laser ablation coupled with MC-ICP-MS, which enables the direct solid sampling without chemical preparation, hence significantly reducing the analysis time (from 3 weeks to 1 day for 30 samples) while providing comparable precision to the liquid method and additionally enabling the spatial resolution for intra-sample variability.

A total of 82 samples were analyzed, including Czochralski wafers from six suppliers (from Europe and Asia), float-zone and epitaxial wafers (1 supplier each), and polysilicon chunks from two suppliers. Each sample was measured in replicates (n=10), and results were compared to reference quartz rocks from known geological sources (e.g., Spruce Pine, Altay, Norway).

Regarding isotopic variability, a wide range of δ30Si values was observed within the samples under investigation (−1.27‰ to +1.43‰), exceeding the natural planetary reservoir range (~1‰). This variation suggests that isotopic fractionation occurs during wafer manufacturing, not just from geological origin.

However, no unique isotopic signature was found for any single supplier, and significant differences were observed between different wafer lots from the same supplier (e.g., up to 1.4‰ in δ30Si among 3 lots from supplier B). This indicates that the manufacturing conditions of the crystalline silicon wafers (e.g., temperature, purification method) may induce mass-dependent fractionation. All samples were found to follow mass-dependent fractionation trends in three-isotope space. However, the analytical precision was insufficient to distinguish between equilibrium and kinetic fractionation mechanisms.

The investigated polysilicon samples showed isotopic compositions beyond the natural range, overlapping with multiple wafer suppliers. This suggests that recycled or mixed-source materials may be used in polysilicon production.

Comparing our results to geological references, most wafer samples fell within or above the isotopic range of bulk silicate earth, rhyolites, and high-temperature quartz, whereas some other samples (e.g., B2, E) had very negative δ30Si values, possibly indicating low-temperature hydrothermal quartz sources or unique processing steps.

The study demonstrates that silicon isotopic analysis using MC-ICP-MS – both via liquid introduction and laser ablation – offers a promising pathway for tracing the origin and processing history of crystalline silicon wafers. While no supplier-specific isotopic fingerprint was identified yet, lot-specific signatures suggest that isotopic fractionation during manufacturing could be exploited for traceability. Future work will focus on expanding the sample base, refining analytical precision, and further investigating the mechanisms behind isotopic fractionation along the silicon value chain.

Insights into High-efficiency Perovskite Photovoltaics from Photoelectron Spectroscopy and Related Methods

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The performance of metal halide perovskite (MHP)-based solar cells, both single junction and in tandems with Silicon, CIGS or another MHP cell, has been advancing at a pace that is unprecedented in the history of photovoltaics. Many of these advancements have been driven by similarly fast progress in understanding the electronic properties of the materials in the device stack, with a focus on the perovskite bulk and its interfaces to the charge-extracting contacts.

In this contribution, we will discuss how advanced variants of photoemission spectroscopy and related methods can provide insights into these electronic properties.

Focusing first on electronic losses at electron-selective contacts, we employ constant final state yield spectroscopy (CFSYS) with tuneable UV excitation (3–7 eV) to probe the valence band and band gap of thin films, with enhanced signal-to-noise ratio and information depth as compared to conventional He-I UPS. CFSYS can therefore be used to both quantify in-gap defect states, and to resolve the valence band maximum (VBM) of MHPs beneath ultrathin C60 layers. Comparative studies of LiF and piperazinium-based interlayers reveal distinct passivation mechanisms: While LiF induces field-effect passivation by modulating carrier concentrations, piperazinium-salt based treatments with different anions allow to adjust the interfacial band bending and interface dipole, eliminating conduction band offsets and achieving record *V*oc values in solar cells [1,2,3]. These findings are correlated with photoluminescence and surface photovoltage data, establishing CFSYS as a critical tool for interface-specific electronic structure analysis.

Shifting to scalable tandem device fabrication, we address challenges in co-evaporated perovskite growth on silicon. Vacuum co-evaporation of MHPs is an especially attractive route to upscaling on rough surfaces such as industry standard random pyramid textures on silicon. However, co-evaporated MHPs show lower efficiency and reproducibility than solution-processed films. Using X-ray photoemission spectroscopy (XPS), we correlate variations in MHP stoichiometry to these reproducibility issues, and we demonstrate that introducing a CsCl seed layer enables conformal FA+-rich perovskite growth, suppressing PbI2 formation and enlarging MHP apparent grains. Furthermore, using X-ray photoemission electron microscopy (XPEEM), a variant of XPS with nm-scale spatial resolution, we gain insights into how the CsCl seed layer mitigates lateral variations in the hole contact layer coverage or thickness, thereby improving MHP film growth and homogeneity.

By linking atomic-scale interface analytics (CFSYS, XPS, XPEEM) with process-oriented innovations (CsCl seeding), this contribution thus demonstrates how advanced characterization guides both fundamental understanding and industrialization of MHP-based solar cells.

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Challenges of Eco-friendly Organic Photovoltaics: Development of Semiconducting Water Dispersions

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The potential of the sun to assess the energy transition is no longer to demonstrate. One way to largely exploit it concerns photovoltaics, that could be implemented in various purposes, individual buildings, solar plants, farms, on rooftops, on grounds, on water, etc. The most developed technology remains panels based on silicon or with other inorganic materials, all presenting pro and cons. Organic photovoltaics (OPV) exhibits relevant features to diversify the implementation, such as light weight, aesthetic, coloured, flexibility, conformability, semi-transparency, not dependent on the tilt angle nor on the quality of light. The state of the art at the labscale is reaching 19.2%. However, efforts should be put in more sustainable processes to lower costs and more specifically the environmental impact. Indeed, the processing of the active layer of OPV, mainly done with organic solvents, is one of the current limitations, slowing down the industrial up-scaling since they are toxic to human beings and the environment.

In recent years, a new way to think about OPV arose, in which the active donor/acceptor materials required in the active layer are no longer solubilized in organic solvents but dispersed as nanoparticles (NPs) in an eco-friendly solvent, the best being water.1,2

Herein, results related to OPV devices fabricated from water-based inks will be presented, mainly using the nanoprecipitation technique, considering different parameters as surfactant, concentrations, temperature, etc. Indeed, these parameters may control the NPs size and more importantly the morphology obtained between the two materials. All these parameters were optimised on the cheap reference system for OPV: P3HT/PCBM. Then, a more efficient system PTQ10/Y6 was considered due to its compromise between cost and high power conversion efficiency (PCE). After preparation of NP dispersions and study of their properties, solar cells were prepared, leading to PCE greater than 10%, very close than that of cells made from organic solvents (11%).1 This was a world record when considering that no additive was put in the ink in plus of the surfactant. A study of the material structuration in the dispersed state and in thin film, allowed to identify the key parameters. The control of the morphology and crystallinity of materials within NPs is essential to optimise the process of devices. Depending on the considered couple, an unexpected morphology was observed for the first time with semiconducting materials, the Janus one (from the roman God with two faces).3 This was demonstrated by microscopic analyses, in particular cryo-TEM. Unfortunately, this technique is insufficient to give clear insights on the morphology, when changing the fullerene acceptor by a non-fullerene one. So, complementary analyses were required, mostly based on advanced characterisations such as transient absorption spectroscopy (TAS), steady-state fluorescence, and in some cases, scanning transmission electron microscopy by energy dispersive X-ray (STEM-EDX).

These experiments allowed us to also emphasise the effect of the water dispersion technique used, nanoprecipitation and mini-emulsion, yielding to ‘soft' and ‘hard' NPs, attributed to a low and high content of crystalline domains, respectively. A relevant result on OPV devices, is that the ‘soft' NPs, prepared by nanoprecipitation, exhibited the double advantage of requiring a lower annealing temperature (130°C versus 200°C) while leading to higher performance (10.14% versus 7.70%) than ‘hard' NPs prepared by miniemulsion.

Femtosecond Laser Ablation (fs-LA) XPS Depth Profiling of Lead Halide Perovskite Thin Film Solar Cells

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Perovskites are an exciting field of photovoltaic devices which can be used as solar cell materials for a range of applications. These devices have shown significant improvements over the last decade in both efficiency and stability. The stability of these devices within the deployed environment is a key area of interest, as their performance can be affected by degradation due to the conditions they are exposed to. X-ray photoelectron spectroscopy (XPS) is a technique which can be used to investigate changes to the chemistry of these materials. As XPS is a very surface sensitive technique, the experiment method used involves depth profiling the material by interleaving analysis with removal steps, commonly using ion beams. However, ion beam methods can induce changes in the material chemistry, affecting the validity of the results. XPS depth profiling of different spin-coated formamidinium lead Iodide ($CH_5N_2PbI_3$) based perovskite thin film solar cells, both pristine and following environmental testing, have been performed. Depth profiling has been carried out using traditional monatomic and gas cluster ion beam (GCIB) bombardment and compared to profiles recorded using a new femtosecond laser ablation (fs-LA) method. A femtosecond laser with a 1030 nm peak wavelength and a pulse duration of 160 fs was employed. The monatomic and cluster ion sputtering depth profiles exhibited chemical damage due to preferential sputtering of C, N and I. Pb0 was also observed in the Pb 4f spectrum as a preferential sputtering artefact. fs-LA XPS depth profiles fully retained the true chemical composition of the 500 nm thick perovskite layer [1]. Following different exposures to proton irradiation, fs-LA XPS depth profiling enabled changes in the perovskite chemical composition as a function of depth to be identified and correlated with solar cell performance. An additional propane-1,3-diammonium iodide ($PDAI_2$) surface treatment following perovskite deposition was shown to reduce the extent of ion beam damage due to self-healing.

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In situ Coupling of Photoemission and Photoluminescence Spectroscopies: a New Analytical Tool for the Characterization of Photovoltaic Devices

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Photovoltaic energy is a key driver of the energy transition. Designing increasingly efficient photovoltaic devices requires a detailed understanding and precise control of the physical and chemical phenomena occurring during solar cell operation. The fundamental mechanisms include photon absorption, the generation of electron–hole pairs, their separation and transport - which are closely linked to the crystalline quality and optoelectronic properties of the absorber material - as well as charge collection, which depends on the physiochemistry of the interfaces with the transport layers, particularly through favorable band alignment and the suppression of recombination processes.

In this context, X-ray photoelectron spectroscopy (XPS) enables quantitative analysis of the surface chemical composition of materials and devices. It provides essential information on the nature of the elements detected on the surface and their respective chemical environments. When combined with ion sputtering, XPS becomes a powerful technique for studying buried interfaces, allowing the evaluation, for instance, of diffusion phenomena or the effectiveness of passivation layers. The quality of the interfaces with the absorber material - an essential bottleneck - plays a critical role in solar cell performance, determining both charge collection efficiency and recombination-related losses.

Photoluminescence (PL) offers complementary insights into the optoelectronic properties of materials and interfaces. It probes material quality more deeply than XPS by revealing defects or recombination sites. A strong and homogeneous PL signal is generally associated with low non-radiative recombination, indicating high performance potential for the photovoltaic cell. Conversely, weak PL emission reflects enhanced non-radiative recombination, typically caused by defects in the crystal structure or at interfaces. PL therefore serves as an ideal complement to XPS for assessing photovoltaic material quality.

ILV-CEFS2 has pursued experimental development to combine XPS and PL on the same ultra-high-vacuum platform, ensuring perfect co-localization. The proof of concept for XPS/PL coupling was carried out on a modified Escalab 250xi XPS spectrometer. InP substrates (n- and p-type) - a III-V binary compound well-known for its extremely low surface recombination velocity (SRV < 10^{-4} cm·s^{-1}) - were selected as “test materials” for joint PL and XPS measurements. The low SRV of InP makes it highly sensitive to even minor surface perturbations. For this study, the semiconductor was exposed to various monatomic ion (Ar^+) bombardment, a process traditionally used for compositional profiling or accessing buried interface regions.

On InP, ion sputtering is known to alter the surface chemical composition through preferential sputtering. The evolution of the In/P ratio within the crater was monitored and quantified by XPS.

Analysis of this same bombarded area revealed that PL intensity gradually decreased with increasing ion beam exposure time. The progressive extinction of the PL signal can be partly attributed to a higher surface recombination rate induced by disorder (amorphization). For longer exposure times, morphological transformations were observed by scanning electron microscopy. This was accompanied by enrichment of the heavier group III element (indium). The accumulation of metallic indium on the surface was clearly visible in the XPS valence band spectrum.

The joint and fully correlated evolution of XPS and PL signals will be central to the discussion, as it opens new avenues for studying critical interfaces in photovoltaic devices.

Session 4 – Decarbonized Hydrogen

H-K1 2:00-2:40	**Hubert Girault** ***EPFL*** Green Hydrogen: Bridging the Gap Between Promise and Practice
H-K2 2:40-3:20	**Marian Chatenet** ***INP Grenoble*** The Analytical Challenges of Low Temperature Fuel Cells and Water Electrolyzers – from Materials Discovery to Operation Mechanisms in Membrane Electrode Assemblies
3:20-3:50	Coffee break and poster session
H-K3 3:50-4:30	**Julien Durst** ***Symbio*** From Lab-scale to Industrial Scale, the Analytical Challenges of Low Temperature Fuel Cells and the Complex Interplay between Product and Process
H-O1 4:30-4:50	**Nathalie Delaunay** ***ESPCI*** Development of Different Methods for Analyzing Leachates from Polymers Used in Fuel Cells
H-O2 4:50-5:10	**Nikolai Utsch** ***Jülich Research Center*** Stress-Testing and Advanced Characterization of Low-Iridium Loaded Electrodes for PEMWE
H-O3 5:10-5:30	**Alexandr Oshchepkov** ***ESPCI*** The Hidden Power of Electrochemical Techniques in Revealing the Role of Ni/NiOx Interfaces in Alkaline H_2 Evolution

Green Hydrogen: Bridging the Gap Between Promise and Practice

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After several years of hopeful planning around a hydrogen-based economy, enthusiasm has waned in many countries. This talk begins by revisiting the motivations behind the development of green hydrogen production processes and why they remain crucial in the transition to a sustainable energy future.

We will then examine the limitations of water electrolysis—often considered a mature and well-established technology—and explore why it has struggled to meet the challenges posed by intermittent renewable energy sources.

Finally, we will delve into fundamental aspects of ionic transport within electrochemical cells and highlight the analytical challenges that must be addressed to design and operate efficient electrolysis plants.

The Analytical Challenges of Low Temperature Fuel Cells and Water Electrolyzers – from Materials Discovery to Operation Mechanisms in Membrane Electrode Assemblies

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Hydrogen technologies are now seen as part of the future energy transition [1]. Indeed, electrochemical production of green hydrogen by water splitting is one manner to valorize renewable electricity during production peaks, while this electricity surplus would be lost overwise [2, 3]. Then, this green H_2 can be used as a chemical or fuel in the industry, or back-transformed into electricity using fuel cells, notably in (heavy-duty) transportation or stationary systems. In this effort, low-temperature systems have the lead and start being implemented. For example, the French 2030 strategy [4] aims at installing 6.5 GW of water electrolyzers (most of them from the alkaline, or proton-exchange membrane technologies), while European, Japanese and US companies target the deployment of proton exchange membrane fuel cells for heavy transportation (trucks, buses, trains, ships and planes). This requires optimizing the materials used in these systems, but also the way they are implemented and operated.

As a matter of fact, these electrochemical hydrogen technologies (fuel cells and water electrolyzers) are so complex that their electrochemical characterizations alone cannot unveil the different phenomena at stake on the materials, interfaces and in the systems. Advanced physicochemical characterizations, ex situ, in situ and operando, are absolutely mandatory to reach sufficient understanding and solve the problems we face to deploy them industrially. This presentation will provide several examples of present analytical techniques that need to be used to fulfill these goals, but also stress what needs to be done next to make these systems an industrial reality.

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From Lab-scale to Industrial Scale, the Analytical Challenges of Low Temperature Fuel Cells and the Complex Interplay between Product and Process

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Since the early 2020s, the European Union has significantly accelerated its support for hydrogen technologies through the IPCEI (Important Projects of Common European Interest) framework. These initiatives aim to strengthen European industrial competitiveness by funding strategic projects across the hydrogen value chain—from production to end-use—with a strong emphasis on scaling. Among the four IPCEIs dedicated to hydrogen, Hy2Tech plays a pioneering role, involving 41 projects from 35 companies. Its focus lies in advancing innovative technologies for renewable and low-carbon hydrogen production, primarily via electrolysis, as well as its use in fuel cells for both mobile and stationary applications.

SYMBIO, founded in 2010, exemplifies this rapid industrial transition. With support from France and the EU, Symbio inaugurated in 2023 Europe's largest gigafactory for Proton Exchange Membrane (PEM) fuel cells. This shift from lab-scale to industrial-scale production within a short time frame has revealed technical challenges similar to those encountered in lithium battery gigafactories:

- Scaling manufacturing processes while maintaining consistent quality and tight control over critical parameters (e.g., temperature, humidity, material purity),
- Securing and managing critical materials, including sustainable sourcing, traceability, and recycling,
- Ensuring safety throughout the manufacturing process.

Addressing these challenges requires considerable progress in physicochemical characterization techniques—ex situ, in situ—to master the complex interplay between product and process. This presentation will highlight current analytical methods used to tackle these issues and outline the technological gaps that must be bridged to enable full industrial deployment of hydrogen technologies.

Development of Different Methods for Analyzing Leachates from Polymers Used in Fuel Cells

Nathalie Delaunay [1], Louis Genain [1,2], Christophe Chendo [1], Audrey Combès [1], José Dugay [1], Pierre Furtwengler [2], Valérie Pichon [1,3], Jérome Vial [1], Laurent Gervat [2]

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The European Green Deal aims to reduce greenhouse gas emissions by 2030 and achieve carbon neutrality by 2050. In order to meet these targets, the automotive sector is turning to greener energy sources such as electricity to power its vehicles. Companies such as the Renault Group are therefore developing vehicles that incorporate fuel cells. A fuel cell provides electrical energy through an electrochemical reaction between hydrogen and oxygen, which produces water. It consists of a stack of electrochemical cells and auxiliary components, including an air and hydrogen supply system. This assembly consists of various elastomeric, thermoplastic and metal parts. A humidifier regulates the water content in a fuel cell to ensure optimal operation. However, the passage of water in gaseous and liquid form through the polymer auxiliary components can cause the leaching of elements and molecules from the polymer to the water. These elements and molecules can significantly reduce the efficiency of the fuel cell. It is therefore necessary to characterize the leachates of the auxiliaries to ensure that the choice of materials used is appropriate and has no impact on the efficiency of the fuel cell.

The leaching of materials in aqueous matrices has already been studied, particularly in the pharmaceutical and agri-food industries [1,2]. A study was also conducted in the United States by the National Renewable Energy Laboratory (NREL) on various materials used in the structure and assembly of fuel cells [3]. This laboratory analyzed leachates using inductively coupled plasma optical emission spectroscopy, gas and liquid chromatography coupled with mass spectrometry, and ion exchange liquid chromatography. They identified organic molecules and inorganic ions in the leachates. The latter can contaminate or damage the electrodes and membranes of the fuel cell, thereby reducing its efficiency and durability [4].

Our study is therefore based on various mixed-mode liquid chromatography analysis techniques coupled with high-resolution mass spectrometry, ion exchange chromatography coupled with conductometric detection, and inductively coupled plasma mass spectrometry (ICP-MS). Various analytical methods have been developed and implemented to assess their relevance for leachate analysis and to prescribe the polymers to be used in the design of fuel cell auxiliary systems.

However, to date, there is no standard procedure for analyzing leachates obtained in this context. Our study is therefore based on various analytical techniques such as mixed-mode liquid chromatography coupled with high-resolution mass spectrometry, ion exchange chromatography coupled with conductometric detection, and inductively coupled plasma mass spectrometry (ICP-MS).

Various analytical methods have thus been developed and implemented to assess their relevance for leachate analysis and to prescribe the polymers to be used in the design of fuel cell auxiliary systems.

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Stress-Testing and Advanced Characterization of Low-Iridium Loaded Electrodes for PEMWE

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Gigawatt-scale deployment of PEM electrolyzer plants will require reducing the iridium-specific power to below 0.10 mgIr W-1. Lack of harmonized testing generates protocol-dependent scatter that confounds performance/durability benchmarks and blurs the roadmap for required technological improvements.[1] Progress therefore hinges on harmonized testing protocols[2–4], such as used in this work and on analytics that can explain how materials evolve under stress at the device level.

Here, we combine extensive device-level testing with a multimethod diagnostic toolbox to map the coupling between iridium loading, structural evolution, and durability testing. Our testing campaign totals ~20,000h. Performance screening was conducted for four commercially available iridium catalysts (Alfa Aesar, 2xHeraeus, and Umicore) with iridium loadings from 0.10 to 0.80 mgIr cm^{-2}. High-frequency resistance (HFR)-corrected polarization data showed, catalyst-dependent sensitivity as loading decreases, which directly impacts iridium-specific power. Durability protocols emphasized 0.40-0.10 mgIr cm^{-2} and consisted of two galvanostatic phases with dynamic cycling between. The most promising materials underwent extended 1,000h tests by extending the stress test from 31.5k to 81.0k cycles. The high-frequency resistance and charge-transfer resistance was monitored periodically to deconvolute ohmic and kinetic contributions. Python-based analysis quantified phase-specific degradation rates under galvanostatic versus dynamic operation. The diagnostic toolbox included XRD, SEM/EDX, XPS on pristine powders and post-mortem specimens, sheet-resistance measurements via a recently published approach[5] and a refined image analysis to extract catalyst-layer thickness distributions pre- and post-test. XPS-derived descriptors, such as the Ir4+/Ir3+ ratio, and μ_1-O/μ_2-O ratio were used to rank catalysts related to their more rutile or amorphous structure which was compared to the post-mortem analysis for varying loadings after durability testing. Cross-sectional analysis highlights that higher loadings and longer exposure times correlate with a stronger increase in thickness variation. Overall, the obtained dataset underscores that understanding degradation, not chasing performance, is decisive for scaling PEMWE with low iridium loading. Early-time changes are most pronounced but tend toward quasi-steady regime with extended operation. By coupling device-level protocols with advanced analytics, this work assesses the low iridium loading durability and highlights diagnostics for future usage.

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The Hidden Power of Electrochemical Techniques in Revealing the Role of Ni/NiOx Interfaces in Alkaline H_2 Evolution

Julie Guehl [1], Amandine Brige [1], Antoine Bonnefont [2], Jean-Jacques Gallet [3], Eric Sibert [2], Tristan Asset [1], Elena Savinova [1], Alexandr Oshchepkov [4]

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Anion exchange membrane (AEM) water electrolysis is a promising technology for the large-scale production of green hydrogen. The use of alkaline media enables the replacement of noble metal electrocatalysts (Pt, IrO_2), currently employed in the most advanced proton exchange membrane water electrolyzers (PEMWEs), with less expensive and more abundant transition metals, such as nickel. NiFe mixed hydroxides are highly efficient electrocatalysts for the anodic oxygen evolution reaction [1]. However, the development of high-performing and stable precious metal-free electrocatalysts for the cathodic hydrogen evolution reaction (HER) remains a significant challenge [1]. One of the most promising strategies involves the use of Ni/NiOx heterostructured materials [2, 3], which exhibit specific activity in alkaline hydrogen evolution and oxidation reactions comparable to that of Pd [4], with the Ni/NiO*x* interface playing a key role even in bimetallic NiM electrocatalysts [5, 6]. Despite this importance, direct measurement of the Ni electrode surface composition remains highly challenging and is often overlooked in many studies in the field.

In this presentation, we will discuss the origin of the enhanced reactivity at the Ni/NiOx interface, as compared to metallic Ni and fully oxidized NiOx model surfaces [7, 8], along with the techniques used to probe the interfacial electrode composition. In particular, the dynamic evolution of Ni electrode surface, comprising metallic (Ni) and (hydr)oxide (NiOx) sites, will be assessed by cyclic voltammetry (CV) and further examined through *in situ* dip & pull X-ray photoelectron spectroscopy (DP-XPS) measurements. The characteristic features of the CV profile will be analyzed using microkinetic modeling, which enables identification of surface adsorbates as a function of the applied potential.

We will further demonstrate how these key findings can be translated to nanoparticulated Ni/C electrodes with high specific surface area, prepared by electrodeposition – a conventional technique that enables exploration of various Ni surface states, starting from a fully metallic one. The impact of the morphology and surface state of Ni nanoparticles will be discussed based on a combination of electrochemical measurements during synthesis (via electrodeposition), HER characterization (using both potentiodynamic and potentiostatic techniques), and dissolution behavior (via linear sweep voltammetry). The effectiveness of this straightforward electrochemical approach will be demonstrated through comparison with the results of transmission electron microscopy (TEM) and inductively coupled plasma optical emission spectroscopy (ICP-OES).

Importantly, this integrated methodology can be readily extended to a wide range of transition metal-based electrocatalysts, offering powerful insights into how morphology and surface composition govern their activity and stability across diverse electrocatalytic reactions.

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Session 5 – Bioresources

Bi-K1 9:00-9:40	**Sylvain Verdier** ***Haldor Topsoe*** Renewable and Recycled Carbon Fuels – From Policy to Analytical Chemistry
Bi-K2 9:40-10:20	**David C. Dayton** ***RTI international*** Advanced Biofuels Technology Development to Decarbonize Transportation
10:20-10:50	Coffee break and poster session
Bi-O1 10:50-11:10	**Carlos Afonso** ***University of Rouen*** Advanced Characterization of Lignocellulosic Biomass Biooils by Ultra-high Resolution Mass Spectrometry Hyphenated with Liquid Chromatography and Ion Mobility Spectrometry
Bi-O2 11:10-11:30	**Marco Beccaria** ***University of Ferrara*** Lipid extraction, Fatty Acids Derivatization, and Minor Lipid Components Investigation in Rich Lipidic Samples. From Food Analysis to Biomass Applications
Bi-O3 11:30-11h50	**Patrick Le Clercq** ***DLR*** Comprehensive and Quantitative GCxGC Combined with Property Modeling to Support the Development of Sustainable Aviation Fuels
Bi-O4 11:50-12:10	**Jorge Ruiz Encinar** ***University of Oviedo*** Combustion-MS to Enhance GC-MS Features with Selective Detection of all Major Elements and Quantification without Specific Standards
Bi-O5 12:10-12:30	**Enderle Benedict** ***DLR*** Enabling Online Monitoring of Sustainable Aviation Fuels through Data-Driven and Sensor Integration

Renewable and Recycled Carbon Fuels – From Policy to Analytical Chemistry

Sylvain Verdier [1]

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The global drive toward decarbonization is fundamentally reshaping the fuels landscape. Ambitious policies and regulations, ranging from blending mandates to sector-specific emission reduction targets, are accelerating the deployment of renewable and recycled carbon fuels across transportation and industry. These evolving policy frameworks not only dictate which fuels are prioritized but also introduce a range of new analytical chemistry challenges.

This presentation will explore the critical link between policy decisions and the analytical requirements for emerging fuels. As the feedstock base expands from conventional fossil sources to a diverse array of renewable oils, waste materials, plastics, and biogenic residues, the complexity of chemical analysis increases dramatically. Each new feedstock brings unique contaminants, molecular structures, and process considerations, demanding innovative analytical approaches to ensure product quality, regulatory compliance, and process efficiency.

Drawing on real-world examples from road, aviation, and maritime sectors, this presentation will highlight:

- How policy shapes the types of renewable fuels entering the marke
- The resulting analytical challenges associated with new and unconventional feedstocks
- The importance of developing robust, adaptable analytical methods to support the energy transition

Advanced Biofuels Technology Development to Decarbonize Transportation

David C. Dayton [1]

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Advanced biofuels derived from lignocellulosic biomass are expected to be drop-in replacements that meet the same specifications developed for petroleum derived fuels. However, robust technology development is hindered by challenges that require ever-increasing understanding of the physical and chemical properties of feedstocks, intermediates, and finished fuels. Input feedstock composition has an impact on the carbon efficiency of the conversion process while introducing potential impurities that can adversely affect downstream processing. Understanding the physical and chemical properties of complex liquid intermediates from direct biomass liquefaction processes can be critical for selecting catalysts and understanding catalyst deactivation to optimize the upgrading step. While standardized analysis and characterization methods ensure that the finished biofuels meet commercial fuel specifications.

Judicious application of molecular-level analytical techniques can be invaluable for understanding and overcoming technical challenges encountered in advanced biofuels technology development. Molecular-level analytical techniques—such as high-resolution mass spectrometry, nuclear magnetic resonance spectroscopy, gas and liquid chromatography, and spectroscopic imaging—provide the resolution and sensitivity needed to comprehensively characterize advanced biofuels process streams. These methods allow researchers to identify and quantify diverse chemical constituents to ultimately track the transformation of biogenic carbon in biomass to biofuel.

At RTI International we have been developing an advanced biofuels technology that integrates a catalytic biomass pyrolysis step and a hydroprocessing step to produce infrastructure compatible biofuels and bioproducts. Carbon efficiency and hydrogen utilization are two of the primary challenges to the economic competitiveness of this integrated technology. During the primary direct liquefaction step, catalysts are applied, and process conditions are optimized to maximize the yield and adjust the chemical composition of the liquid biocrude intermediate. Biocrude quality is typically described by the amount of oxygen contained in the organic liquid, however, biocrude oxygen content is inversely proportional to yield.

Biocrude is a complex mixture of hundreds of compounds with a wide boiling range and molecular weight distribution that presents considerable challenge for upgrading using conventional hydroprocessing technology. Oxygen content is directly proportional to upgrading hydrogen demand, but the type of oxygenated compounds is proving important to understanding reactor fouling and hydrotreating catalyst performance during upgrading. This is prompting new strategies for upgrading biocrude that look beyond bulk oxygen content that require advanced analytical techniques.

Separating biocrude into different fractions with narrower boiling ranges and molecular weight distributions could segregate undesirable components and provide flexibility to utilize different catalysts and process conditions for upgrading each fraction separately to maximize carbon efficiency, minimize hydrogen consumption, and potentially recover higher value bioproducts. Co-processing biocrude with petroleum refinery intermediates or other non-conventional feedstocks also benefits from detailed molecular characterization to reduce the risk to existing unit operations for fuel production.

Downstream processing options and fuel quality assessment relieve heavily on robust analytical methodologies. Biocrude purification, fractionation, and upgrading demands accurate quantification of energy content, stability, viscosity, and the presence of impurities or oxygenates. Techniques such as GC-MS/FID, FTIR, and ASTM-standardized fuel testing protocols are utilized to ensure that final products meet regulatory and engine compatibility standards. Moving forward, there needs to be a balance between what can be measured and what should be measured with an emphasis on applying appropriate techniques to interrogate specific process streams. Fortunately, comprehensive molecular-level details of the complex advanced biofuels process streams are starting to provide the needed insights to overcome key technical barriers for developing economically viable, scalable, and environmentally sustainable advanced biofuel technologies.

Advanced Characterization of Lignocellulosic Biomass Biooils by Ultra-high Resolution Mass Spectrometry Hyphenated with Liquid Chromatography and Ion Mobility Spectrometry

Theo Imhoff[1, 2, 3], Julien Maillard[2, 3], Maxime Sueur [2,3], Caroline Barrère-Mangotte[2, 3], Marie Hubert-Roux[1, 3], Mélanie Mignot[1, 3], Christopher A Wootton[4], Pierre Giusti[2, 3], Carlos Afonso[1, 3]

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Bio-oils produced from the pyrolysis of lignocellulosic biomass are highly oxygenated mixtures, causing problems such as corrosion, storage issues, and catalyst poisoning, hence requiring advanced upgrading, *e.g.* hydrotreatment. Direct introduction Fourier-transform mass spectrometry is typically used to evaluate upgrading efficiency at the molecular level. To obtain information on the isomeric content of these samples, the addition of a separation method is required such as chromatography and ion mobility spectrometry. Here we evaluate the use of reverse phase liquid chromatography (RPLC) and a new gated trapped ion mobility spectrometry (gTIMS) coupled to an 18 T Fourier-transform ion cyclotron resonance (FTICR) instrument for the characterization of different upgraded bio-oils [1].

The samples were loblolly pine bio-oils from a reactive catalytic fast pyrolysis (RCFP), supplied by RTI International, North Carolina. The bio-oils were hydrotreated for 144 hours using a sulfide hydrotreating catalyst. Six effluents were then collected at different times before completion, to conclude on hydrotreating efficiency and catalyst evolution. Samples were analyzed by direct infusion using a new 18 T FTICR MS equipped with gated trapped ion mobility (gTIMS) (Bruker tims MRMS). Details on the instrument can be found elsewhere [1].

Direct infusion FTICR MS allowed to accurately identify thousands of molecules for each effluent. Initial FTICR results showed a rapid decrease in the number of oxygen atoms per formula and overall aromaticity. The ultra-high mass resolution and accuracy of the 18 T FTICR MS allowed precise annotation of molecular classes, revealing detailed compositional trends throughout the hydrotreating process.

The integration of Trapped Ion Mobility Spectrometry (TIMS) with time-controlled gating prior to FTICR-MS analysis represents a major advance in the fine characterization of bio-oils. This combination allowed separation of isomers while improving dynamic range and detection of low abundance species. The gTIMS-FTICR MS approach applied to bio-oils revealed a complex distribution of chemical species according to their mass/charge ratio and mobility, revealing a high degree of isomeric diversity for each previously identified molecular formula. The trends observed in the molecular classes resolved by gTIMS provide a deeper understanding of hydrotreatment pathways, including deoxygenation, hydrogenation, cracking and aromatic stabilization.

In particular, the ability to resolve recalcitrant compounds-highly condensed aromatic species with low H/C and high stability-allows for a more comprehensive evaluation of catalyst performance and reaction efficiency over time. These results highlight the potential of this technique for better understanding and optimizing upgrading processes and the great interest of gTIMS-FTICR for complex mixture characterization.

LC-FTICR MS method was developed for bio-oil analysis. A resolution of 1.3 M at *m/z* 200 was obtained, enabling the unambiguous assignment of thousands of molecular formulae. Compromises had to be made, however, to maintain a high resolution while ensuring the correct number of scans for the entire chromatogram.

In comparison to direct introduction RPLC-FTICR, the ionization competition was reduced, enabling the observation of 1 610 additional molecular formulae. These compounds, detected only with LC-MS coupling, are mainly those with low O/C ratios corresponding to less polar compounds expected to be more affected by ionization competition.

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Lipid Extraction, Fatty Acids Derivatization, and Minor Lipid Components Investigation in Rich Lipidic Samples. From Food Analysis to Biomass Applications

Marco Beccaria [1], Carlo Bellinghieri [1], Giulia Giacoppo [1], Donatella Ferrara [2], Flavio Antonio Franchina [1], Jean-François Focant [3], Pierre-Hugues Stefanuto [3], Giorgia Purcaro [2]

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Lipids comprise a wide range of structures, characterized by predominantly non-polar and hydrophobic molecular skeletons. However, some exhibit a slight polar or hydrophilic character, giving them amphiphilic properties. Lipids can provide useful information in different fields of chemistry such as the origin of and overall quality of a food product (food chemistry) as well as the quality of biodiesel (petrol chemistry), where they are among promising candidates to possibly fulfill requirements as substitutes of crude oils as primary sources of chemical energy feedstock.

This contribution investigates different aspects of lipid analysis in rich-lipidic samples and oleaginous feedstock, as: i) extraction; ii) fatty acids derivatization and analysis; and iii) investigation of minor lipid components.

The first part is devoted to the applicability of a microwave-assisted extraction (MAE) methodology using methyl-tert-butyl ether (MTBE) as a one-step organic solvent extraction or in mixture with methanol and water compared to conventional extractions for lipid analysis such as Soxhlet and Matyash methods. Extraction yield and fatty acid in terms of methyl esters derivatives (FAMEs) were statistically compared.

In the second part, a one-step microwave assisted lipid extraction/fatty acid derivatization method was compared with two official methods from the American Oil Chemical Society in terms of FAME profile analyzed by comprehensive two-dimensional (GC × GC)-flame ionization detector (FID).

In the last part, a preparative column liquid chromatography followed by a GC×GC-HRMS (high resolution mass spectrometry) was employed for a deeper investigation of minor lipid components, mainly oxygen-containing compounds, in oleaginous feedstock (animal fat).

Comprehensive and Quantitative GCxGC Combined with Property Modeling to Support the Development of Sustainable Aviation Fuels

Patrick Le Clercq [1], Hannes Lüdtke [1], Florian Pütz [1], Thomas Gröger [1], Uwe Bauder [1], Georg Eckel [1], Patrick Oßwald [1], Markus Köhler [1]

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The commercial aviation industry is committed to achieving net-zero CO_2 emissions by 2050. In addition to improving aircraft and engine technologies, and promoting fuel efficient air traffic operations, the majority of future aviation scenarios conclude that the highest CO_2 emissions reduction potential will come from the development and deployment of sustainable aviation fuels (SAF). The International Civil Aviation Organization report, concerning the feasibility of long-term aspirational goal, states a 51% reduction in 2050 w/r 2019 level in the most ambitious scenario. SAF made from renewable or waste-derived feedstocks meet rigorous sustainability criteria together with the transformation process. Similar to conventional fossil aviation turbine fuel in their chemical composition, SAF yield substantially lower greenhouse gas emissions from a life cycle analysis perspective than fossil jet fuel – typically around 80% with an aspirational goal of 100% before 2050. There is a wide range of feedstocks available, from bioresources such as non-food crops to waste sources, and eventually to recycled or directly-captured CO_2 and low-carbon electricity to produce power-to-liquid fuels.

Aviation turbine fuels, including synthesized hydrocarbons (e.g. SAF) contain several hundred individual species distributed in different chemical groups. Safety being the most important aspect in commercial aviation operations, SAF must meet very stringent technical requirements to become a safe replacement to conventional aviation turbine fuels. Currently, eight synthetic blending component production pathways have been approved according to the ASTM D4054 evaluation process and each one has its respective annex in the ASTM D7566 specifications.

Certain SAF have additional benefits. Actually, substantial reduction in soot particle emissions for ground and in-flight operations can be observed when burning SAF produced from hydroprocessed esters and fatty acids, when compared to fossil Jet A-1. This leads to the reduction in contrail cirrus, one major climate forcing component and non-CO_2 effect of aviation. It also leads to an improvement in local air quality.

We support the development of new SAF production pathways and the ramp-up of those already qualified. In particular, we are developing the pre-screening of SAF candidates at early-stages to support decision making and de-risking. More generally, our technical fuel assessment method applicable from lab-scale samples to SAF from commercial plants, includes evaluating aforementioned additional benefits. This method relies initially on combining chemical analytics and property models to reliably determine the quantitative composition and derive key physico-chemical properties.

In the present work, comprehensive two-dimensional gas chromatography (GC×GC) is performed for chemical fuel analysis.

The method performs well in terms of carbon number and hydrocarbon group separation (both conventional and synthetic fuel mixtures) by reduction of coelution. Quantification of the total composition is done with a flame ionization detector (FID). A quadrupole mass spectrometer (qMS) can additionally support structural and group-type identification such as *n*-, *iso*- and *cyclo*-alkane groups as well as *mono*- and *polycyclic*-aromatic (mostly naphthalene) compounds.

Fuel properties can be derived from this quantitative compositional characterization. Some safety-relevant physical properties, such as viscosity and freezing point and some pollutant-formation relevant chemical properties, such as the concentration of soot precursors depend on isomeric structure differences, which remain an open problem in chemical analytics. Using a model based on molecular descriptors, we predict the retention behavior of the isomers within the *iso*-alkane family. This enables individual structures to be divided into subgroups, thereby achieving a higher level of detail in the determined composition. These results can provide important input for property predictions. In addition, this technique allows a differentiation of fuels based on their degree of branching. By using this input as an extension of the weighted average model approach we achieve improvements in fuel property predictions, which can support technical assessment of SAF.

Combustion-MS to Enhance GC-MS Features with Selective Detection of all Major Elements and Quantification without Specific Standards

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Electron Ionization Mass Spectrometry (EI-MS) is acknowledged as the most powerful detector in Gas Chromatography (GC) as it can provide compound characterizing information and very sensitive and quantitative species-specific information when operated in SCAN and SIM modes, respectively. Its only restraints are the need of specific standards for quantification of every individual compound and the lack of element-selective information to screen for the families of potential target N-, S-, O-containing compounds of interest present in complex samples. It is clear that a new detector able to overcome such limitations while maintaining the already powerful MS features would be absolutely welcome, becoming a ground-breaking approach, in a wide variety of scientific fields (e.g., metabolomics, clinical, environmental sciences) and industrial applications (e.g., hydrocarbon processing, new energies, natural gas and biogas, and pharmaceutical, chemical, and additive manufacturing).

Recently, a new detection system called GC-combustion-MS was introduced allowing elemental-based quantification of organic compounds while maintaining the structural elucidation capabilities of MS by simply actuating a switching valve.[1,2] A combustion interface, located in between the GC and MS instruments, with the on-line addition of an oxidizing flow (0.4 mL/min of 0.3% O_2 in He), results in the quantitative conversion of each and every organic compound eluting from the column into $\underline{C}O_2$, $\underline{H}_2O$, $\underline{S}O_2$, and $\underline{N}O$, opening the gate to simultaneous C-, H-, S-, and N-selective detection. Notably, the use of isotopic oxygen (95% abundance ^{18}O) as oxydizing gas,3 and operated in a Pt-shielded ceramic combustion tube, makes Oxygen detection possible as well under the same operational conditions.

Peak area ratios computed in the individual GC separated peaks allows their fast and accurate classification as S-, N- and O-containing compounds. Simple compounds containing only C and H are grouped together. Interestingly, their H:C ratios measured as the individual *m/z* 20:12 ($^{18}O\underline{H}_2$:$^{12}\underline{C}$) peak area ratios, facilitates their further classification as a function of their aromaticity degree. It is crucial to note that, as final MS detection of all the individual separated GC compounds is performed through the same volatiles species generated after their combustion ($\underline{C}O_2$, $\underline{H}_2O$, $\underline{S}O_2$, and $\underline{N}O$, and their corresponding EI fragments), the signal obtained is inherently equimolar permitting their generic quantification using simple generic standards.

Another exceptional feature is that LODs obtained for each target C-N-S-O-H element are significantly lower than the LODs offered by the corresponding commercially available element-selective detectors (i.e. FID, NCD, SCD, O-FID), which in turn only offer detection of one single element.

In summary, GC-combustion-MS has the potential to provide full elemental fingerprint for individual compounds in complex samples, only limited by the chromatographic capacity to separate all of them. However, such limitation could be overcome when combined GC-combustion-MS with the huge separation power of multidimensional GC or exhaustive sample preparation procedures to fractionate the complex samples in advance. The new instrumental advances (Pt-shielded combustion tube operated at high temperature and flow rates) and new analytical strategies (highly discriminating normalized peak area ratios) will surely boost the potential application of the recently commercially available GC-combustion-MS Shimadzu instrument4 in many scientific fields and industrial applications.

1 Laura Freije *et al.*, Chem. Commun., 2020, 56, 2905
2 Javier García *et al.*, Anal. Chem., 2023, 95, 11761
3 Javier García *et al.*, Anal. Chem., 2024, 96, 10756
4 ELEM-SPOTTM - https://www.shimadzu.com/an/products/gas-chromatography/application-specific-system-gc/elem-spot/index.html

Enabling Online Monitoring of Sustainable Aviation Fuels through Data-Driven and Sensor Integration

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The accelerated adoption of sustainable aviation fuels (SAF), driven both by the urgent need to reduce aviation's climate impact and by regulatory measures such as the EU SAF blending mandate (ReFuelEU Aviation), is diversifying aviation fuel supply through new production pathways. This shift from fossil crude oil to sustainable feedstocks such as biomass and renewable energy inevitably alters the chemical composition of the final product. As a result, greater variation in the physical and chemical properties of aviation fuels is expected. While strict monitoring remains essential to ensure compliance with existing technical standards, this transition also creates opportunities to exploit beneficial fuel characteristics—such as higher specific energy or reduced aromatic content—for added value. An example could be the flexible adjustment of the fuel uplift during refueling based on the actual energy specific energy of the available fuel, rather than relying on mean values. With the higher specific energy expected from SAF, this would result in a reduced fuel uplift and thereby save in weight and, ultimately, CO_2 emissions.

However, current fuel supply chains and refueling infrastructures are limited in their ability to detect and leverage these advantages, as they rely primarily on offline chemical analytics rather than real-time, in-flow measurement techniques. While some basic properties can in principle be monitored in flow, advanced characteristics—such as energy specific energy remain challenging to measure online, especially when moving beyond the well-established experience base of conventional aviation fuels.

At the same time, data-driven modeling approaches offer a flexible means of predicting key fuel properties, either by linking compositional information to properties or by correlating properties with more complex properties. When combined with physical sensors that capture easily accessible properties in real time, such models form the basis of hybrid sensing systems capable of online characterization of aviation fuels at multiple points across the supply and distribution chain.

This contribution presents recent progress in the development and demonstration of such hybrid sensors, supported by the SimFuel software platform under development at the German Aerospace Center's Institute of Combustion Technology, which provides a comprehensive environment for the data-driven assessment of sustainable aviation fuels. For the present work, a key element is the unique and comprehensive SimFuel database, which encompasses both conventional and alternative aviation fuels and forms the foundation for the formulation and training of machine learning–based property–property models. On this basis, predictive models for energy density from readily measurable bulk properties have been derived. Complementing the software developments, a flexible hardware testbed has been established to integrate and evaluate different sensor types and modeling approaches. This testbed has been deployed within the fueling infrastructure at Copenhagen Airport, enabling the collection of real-world operational data.

Session 6 – Electrical Storage and Batteries

Ba-K1 1:30-2:10	**Christian Masquelier** ***University of Picardie*** Crystal Chemistry of Important Polyanionic Materials Used as Cathodes in Sodium-Ion Batteries: the Decisive Impact of Synchrotron X-Ray Diffraction
Ba-K2 2:10-2:50	**Lauriane d'Alençon** ***Syensqo*** Analytical Challenges in Sulfide Solid Electrolytes from Large Scale Manufacturing to Use in Systems
2:50-3:20	Coffee break and poster session
Ba-K3 3:20-4:00	**Yan-Yan Hu** ***Florida State University*** Magnetic Resonance Insights into Interface Chemistry and Ion Transport in Batteries
Ba-O1 4:00-4:20	**Remi Dedryvere** ***University of Pau and Adour Countries*** *In situ* and Operando Chemical Analysis of Interfaces in Batteries by X-Ray Photoemission Spectroscopy
Ba-O2 4:20-4:40	**Klaus Lips** ***Helmoltz Berlin*** *In situ* Monitoring of Lithium Metal Dendrites Using EPR-on-a-Chip (EPRoC)
Ba-O3 4:40-5:00	**Mathieu Freville** ***ESPCI*** Surface Evolution Monitoring in Zinc Air Batteries

Crystal Chemistry of Important Polyanionic Materials Used as Cathodes in Sodium-Ion Batteries: the Decisive Impact of Synchrotron X-Ray Diffraction

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Polyanionic materials (phosphates in particular) are of special interest as positive electrodes for Li-Ion or Na-ion batteries since they offer competitive performances compared to sodiated or lithiated transition metal oxides [1,2]. They are based upon stable frameworks which provide long-term structural stability thanks to a unique variety of atomic arrangements.

The fluorinated vanado-phosphate $Na_3V_2(PO_4)_2F_3$ possesses quite extraordinary features in terms of performances at very high rates and for extensive electrochemical cycling and is now developed by the company TIAMAT as their cathode material in commercialized batteries. Very early preliminary studies conducted in ALBA Synchrotron gave us the opportunity to determine its real crystal structure and to reveal subtitle phase transformations upon Na+ extraction [3-4].

The NASICON structural family, on the other hand, with its large panel of compositions, $Na_xMM'(PO_4)_3$ ($0 < x < 4$; M,M' = Ti, Fe, V, Cr, Mn) is among the most widely investigated due to its 3-D framework structure which generates high Na+ mobility [1]. Among them $Na_3V_2(PO_4)_3$, $Na_4MnV(PO_4)_3$ and $Na_4FeV(PO_4)_3$ are of particular interest [5-10]. We will present several new structures that we determined, from pristine powders or for intermediate compositions spotted by operando synchrotron XRD.

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Analytical Challenges in Sulfide Solid Electrolytes from Large Scale Manufacturing to Use in Systems

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Among the various post Li-ion technologies, All Solid State Batteries (ASSB) offer a promising future as they provide breakthrough performances in terms of capacity, fast charging, safety, and cost [1-5].

Many technological solutions have been explored in the last twenty years and sulfides materials appear as the best compromise for the solid electrolyte due to intrinsic properties such as ionic conduction, compatibility with active materials and easiness to be integrated in batteries manufacturing processes leveraging the Li-ion industry know-how [6-9].

However, development of sulfide based ASSB technology relies on deep analyses of each ingredient of the batteries (from definition of the product to final use in the battery) and their interfaces in order to leverage the full capacity of the system. Thus many challenges occur due to the specificity of the materials and of the application.

In this presentation, as european front-runner in sulfide-solid-electrolyte manufacturing at lab and pilot scale, we will present some precise illustrations of these challenges.

We will then develop the following categories : a first part is related to product definition and purity. A second part is linked to manufacturing of the product from lab to large scale with the same accuracy. Then we will focus on the capacity to validate the characteristics and performances in-situ at industrial level. The last part will be dedicated to analyses during battery life in order to feed back and refine the product definition. In fact, the solid state nature of ASSB means that interfaces between sulfides solid electrolyte and other materials in the battery (active materials, electronic conductors, binders…) are buried solid-solid interfaces: characterization of such interfaces is then challenging but critical to control long term performances of ASSB and failure mode detection. [10]. Moreover, transversely to all these challenges, we will show how reactivity of some ingredients can be a limitation to standard analyses, which might then need some new developments to overcome this difficulty.

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Magnetic Resonance Insights into Interface Chemistry and Ion Transport in Batteries

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Understanding charge transport mechanisms and interfacial phenomena in solid-state batteries is critical to achieving performance enhancement yet challenging. With a complement of advanced magnetic resonance techniques, including *ex/in situ* nuclear magnetic resonance spectroscopy (NMR), magnetic resonance imaging (MRI), and electron paramagnetic resonance (EPR), we can non-invasively track ion transport and examine interfacial processes with temporal and spatial resolution. Compositional, structural, and dynamical entropy on different length scales, from atomic to micron, is shown to have varied effects on ion transport. We have identified lattice dynamics conducive to fast ion transport *vs.* those with little or no effects on transport. We have shown ion dynamics within grains *vs.* at grain boundaries are distinctively different, which influence overall transport and metallic microstructure formation in solid electrolytes. These new insights have guided the synthesis and discoveries of new inexpensive solid electrolytes and electrode-electrolyte composites with improved transport properties. The fundamental understanding of the complex interfacial phenomena advises strategic measures to improve interfaces for enhanced ion transport, limited electron transport, and minimized dendrite formation in solid-state batteries.

In situ and Operando Chemical Analysis of Interfaces in Batteries by X-Ray Photoemission Spectroscopy

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Mastering the electrode/electrolyte interfaces in batteries is a key point to obtain their good performances, long term stability and safety. It is often the major factor limiting the development of new batteries. The so-called Solid Electrolyte Interphase (SEI), which is formed at the interface between a graphite negative electrode and a liquid electrolyte in a Li-ion battery is the most famous example. However, the recent development of new battery chemistries, like Li all-solid-state batteries, or Li-sulfur, or batteries using other elements as an alternative to Li (e.g. Na, K, Mg), etc... leads scientists to solve emerging problems addressing the chemical reactivity of new kinds of interfaces.

After 40 years of research on electrode/electrolyte interfaces, they are far to be completely understood, because of their structural and chemical complexity depending on many parameters, such as electrolyte composition, impurities, cycling conditions, temperature, etc. Moreover, the chemical analysis of passivation layers and interphases is very difficult because they are only a few nanometers thick and extremely moisture- and air-sensitive. New characterization approaches of interfaces are necessary, since classical *ex situ* experimental conditions do not correspond to the true conditions existing in a battery during its operation, where the electrodes are constantly in contact with the electrolyte.

X-ray Photoemission Spectroscopy (XPS), as a surface-sensitive analysis technique, is a major analytical technique to improve our knowledge of electrode/electrolyte interfaces, and more generally to all surface phenomena and redox mechanisms at electrodes surfaces in batteries. Some recent developments, like Hard X-ray Photoemission Spectroscopy (HAXPES) and Near-Ambient Pressure Photoemission Spectroscopy (NAP-PES), allowed the emergence of *in situ* and *operando* approaches, opening new possibilities to understand the chemistry of interfaces in batteries.

In this talk, I will present the *in situ* and *operando* characterization of interfaces in Li-ion batteries with a liquid electrolyte, and in Li all-solid-state batteries, taking advantage from these new developments.

In situ Monitoring of Lithium Metal Dendrites Using EPR-on-a-Chip (EPRoC)

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Batteries based on lithium metal anodes offer a significantly higher specific capacity when compared to the graphite anodes currently used in lithium-ion batteries. However, lithium metal exhibits inhomogeneous plating during charging that leads to the growth of microstructures (e.g. dendrites), causing short-circuits and preventing its commercial use. To properly understand its growth mechanism, characterization methods that are particularly sensitive to lithium metal are advantageous. Several approaches based on electron paramagnetic resonance (EPR) spectroscopy have been recently demonstrated using commercial EPR systems for monitoring the growth and presence of lithium metal dendrites, but these require the design of intricate in situ cells. Our approach of using EPR-on-a-chip (EPRoC), however, allows the use of simple electrochemical cells and an active volume comprising only the plated lithium, thereby greatly simplifying the acquired signals and facilitating their analysis. In addition to its compact nature, EPRoC has great potential in terms of sensitivity, ease of use, price, and in situ compatibility. Using an EPRoC, we designed a simple electrochemical cell comprised of lithium metal and a copper current collector and monitored its EPR signal while charging. Using a physical model for conduction EPR (CEPR), we modeled the plated lithium metal and deduced a specific charging stage that manifested clear signs of dendrite growth and offered a deeper insight into the growth mechanism. This EPRoC proof of concept in the characterization of battery materials could open the door to many new research and industrial possibilities, considering its advantages over commercial EPR systems.

Surface Evolution Monitoring in Zinc Air Batteries

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Electrochemical layer deposition is an important process not only for coatings and microfabrication but also for energy storage applications, particularly those connected to renewable energy sources like solar and wind power. These energy sources are inherently intermittent, and as such, efficient storage systems are critical. Among promising storage systems, metal-air batteries — especially zinc-air batteries — stand out due to their high energy density and cost-effectiveness. However, one major limitation they face is dendrite formation during the charging process, which can lead to reduced battery life, internal short circuits, and safety risks.

Dendrite growth is a common problem across all types of metal-air batteries and remains a significant challenge for long-term commercial viability. Researchers have developed various approaches to address this, including mathematical modeling (both analytical and numerical), which helps in understanding the electrochemical and physical processes leading to dendrite formation. Several technological strategies have also been explored: using porous zinc electrodes, implementing polymer separators, adding electrolyte additives, applying pulsed charging currents, and even designing flow battery systems. While each of these techniques can reduce dendritic growth, none has yet completely eliminated the problem.

A more recent and promising avenue involves actively controlling the charging and discharging cycles and using electrode rejuvenation protocols when dendrites are detected. However, implementing such control requires effective diagnostic tools that can monitor the internal state of a battery in real time. These tools must be practical and scalable: ideally, they should be simple enough to integrate directly into battery management systems at manufacturing plants or be installed on consumer devices. Importantly, such tools should be capable of warning users about harmful operating conditions and potentially initiate corrective actions to prolong battery lifespan.

Current diagnostic techniques such as tomography and operando video microscopy provide valuable insights but are too complex and expensive for routine or industrial use. This has led researchers to explore alternative diagnostic tools based on electrochemical signals.

This work presents a novel approach based on linear sweep voltammetry (LSV) to monitor changes in electrode surface morphology. LSV is a relatively simple technique where the voltage is swept linearly over time while measuring the current response. The key insight is that zinc oxide deposits differently depending on the surface structure of the electrode — both in terms of nucleation behavior and deposition kinetics. The shape of the LSV curve, particularly how current varies with overpotential, provides critical information about the morphology and density of the oxide layer, which directly affects the diffusion of zincate ions. To utilize this relationship, we compiled a database of LSV curve shapes corresponding to various known electrode morphologies.

By comparing experimental LSV curves to this reference database, it becomes possible to infer the nature and effective surface area of the electrode in real-time. This advancement enables in situ diagnostics of the electrode's condition and may eventually allow for real-time monitoring and even repair of battery electrodes.

Overall, this study represents a significant step forward for the development of smart, durable metal-air batteries. The ability to monitor and diagnose electrode surfaces using LSV opens promising pathways for predictive maintenance, performance optimization, and possibly automated recovery protocols. Furthermore, the method's simplicity makes it a strong candidate for integration into commercial systems. The short scan times involved also minimize issues such as bubble formation on air electrodes, suggesting broad applicability across battery technologies.Examples of applications of this technique will be presented, including the monitoring of zinc-air battery cycling and the characterization of electrodeposition phenomena on segmented electrodes, which pave the way for faster and more efficient charging.