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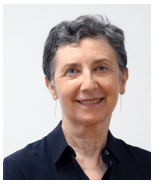


*In a context of considerable societal expectations regarding the innocuous nature of new products and the protection of the environment, analytical chemistry is a major scientific discipline that guarantees the acceptability of research and its applications, helping us understand phenomena* via *the characterization of materials and products in complex matrices.*

*No scientific field can ignore the contributions of the characterization of objects/reactions of interest. Hence, the scientific ambition of the Physics and Analysis division is* "to see the invisible and give IFPEN projects a head start"*, in mature fields as well as new energy technologies. As such, it plays an essential role in technological innovations.*

*To achieve this ambition, our researchers exploit analytical techniques and methodologies to their maximum, combining different pairings, mathematically extracting the information of interest from thousands of signals, using both prototype instrumentations and major national instruments. All significant progress made is also the result of dialog with IFPEN researchers and multidisciplinary academic teams.*

*This issue illustrates a few examples.*

*I hope you enjoy reading this issue,*

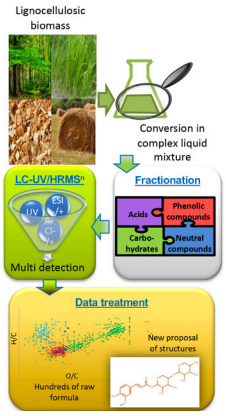
*Nathalie Schildknecht,*
*Head of the Physics and Analysis Division*

# Multiplying analytical dimensions to identify bio-based molecules

IFPEN is actively involved in the development of innovative processes for the conversion of lignocellulosic biomass into bio-based fuels and molecules. However, in chemical terms, the products generated are highly complex and it is necessary to know their detailed composition in order to relate it to the reactivity observed during the conversion process.

A multi-dimensional analytical approach has been developed to conduct an advanced characterization of samples resulting from biomass conversion (figure). It combines successive liquid-liquid extractions (LLE), liquid-phase chromatography coupled with ultraviolet detection (LC-UV) and high-resolution mass spectrometry (HRMS) in different ionization modes, associated with multi-stage fragmentation experiments (MSn). LLEs make it possible to organize the sample into four fractions according to the chemical family of the compounds. Each fraction is then analyzed by LC-UV/HRMSn[a].

As a result, original molecule structures were proposed, thanks uniquely to the simultaneous exploitation of the information obtained, such as the nature of the chemical family of the LLE fraction considered, the LC retention time, the UV spectrum, the molecular formula obtained via HRMS along with structural information provided by fragmentation experiments. For example, structures involving sugars with carboxylic acid functions and lignin-carbohydrate complexes were identified.




The information was partially concatenated using van Krevelen diagrams on which an innovative approach, based on convergence lines, makes it possible to identify unknown chemical structures detected on the chromatogram[1].

a - Combination of the different techniques, including fragmentation experiments throughout the analysis

(1) ***C.Reymond,*** *A. Dubuis,* ***A. Le Masle,*** *C. Colas,* ***L. Chahen,*** *E. Destandau,* ***N. Charon,*** *Journal of Chromatography A, Vol. 1610, (2020). DOI: 10.1016/j.chroma.2019.460569*

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# Analysis of the inorganic contaminants in bioethanol, from source to end product

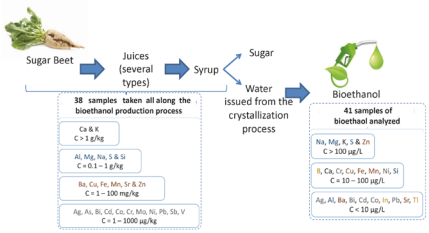
The use of renewable carbon-based biofuels is a solution aimed at reducing the climate impact of combustion engine vehicles. However, the diversity of potential biomass sources requires a characterization of any potential pollutants contained within the biomass that may prove harmful from an environmental or technical point of view.

With this in mind, an investigation of the inorganic contaminants contained in different sources of bioethanol was conducted, in partnership with Alicante University[1], using atomic spectrometry techniques (ICP/OES[a] and ICP/MS[b]). It covered a broad range of bioethanols used as a fuel base, but also in the petrochemicals sector. Across all of the samples analyzed, the contents measured were systematically comparable or indeed below those of a commercial gasoline (< mg/kg).

The analyses were conducted throughout the manufacturing process in order to identify the origin of these contaminant traces in bioethanol derived from beetroot[2]. It turns out that most of the metals present in the end product were already present in the original biomass (figure) rather than the result of process-induced contamination. Above all, an improvement is observed at the distillation stage, which is particularly effective when it comes to eliminating these contaminants, with concentrations reduced by a factor of 10,000 in bioethanol!

Finally, complementary research using isotope analysis of ultra-trace lead (Pb)[3] demonstrated that it was possible to identify the resource employed to produce the bioethanol: wheat, wine, beetroot, cane or non-food residues (2nd generation).

a - Optical emission spectrometry combined with ICP (Inductively Coupled Plasma)
b - Mass spectrometry combined with ICP




(1) *C. Sánchez, **C.-P. Lienemann**, J.-L. Todolí, Spectro Chimica Acta Part B, 124, (2016), 99-108. DOI: 10.1016/j.sab.2016.08.018*

(2) *C. Sánchez, **C.-P. Lienemann**, J.-L. Todolí, Fuel Processing Technology, 173, (2018), 1-10. DOI: 10.1016/j.fuproc.2018.01.001*

(3) *C. Sánchez, E. Bolea-Fernández, M. Costas-Rodríguez, **C.-P. Lienemann**, J.-L. Todolí, F. Vanhaecke, J. Anal At. Spectrom, 33, (2018), 481-9. DOI: 10.1039/c8ja00020d*

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# Spectrometry and chemometrics supporting processes

As a result of the deterioration in the quality of crude oils and the tightening up of environmental standards, refiners are modifying their processes in order to meet the growing demand for light cuts and middle distillates. They must also meet eco-efficiency criteria, all of which requires a detailed chemical characterization of these various cuts.

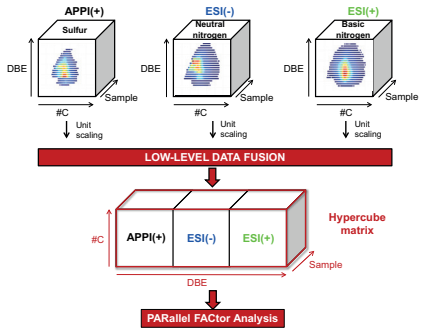
Oil products contain hundreds of thousands of compounds, including nitrogen-, oxygen- and sulfur-type heteroatoms. Their characterization requires cutting-edge, sensitive and robust analytical methods – methods that have been the focus of increasing research at IFPEN –, based on high-resolution mass spectrometry (FT-ICR/MS[a]).

This analysis technique was deployed, *via* three different ionization modes, for several Vacuum Gas Oils (VGO) derived from various refining processes[1]. It was used to identify differences in composition between the samples from these diverse origins and monitor the evolution of nitrogen[2] and sulfur[3] species during hydrotreatment steps.

Since FT-ICR/MS analyses generate considerable and complex data spectra, their exploration was conducted using chemometric approaches, making it possible to categorize samples from the identification of the various chemical species.

Data were also merged *via* PARAFAC[b] analysis, making it possible to evaluate the combined impact of nitrogen and sulfur compounds on different refining processes[1]. This original approach (figure) provides access to molecular descriptors essential for modeling and optimizing conversion processes.

a - Fourier-transform ion cyclotron resonance mass spectrometry
b - Parallel Factor Analysis




*Analytical methodology for the characterization of sulfur compounds in Vacuum Gas Oils.*

(1) ***J. Guillemant, A. Berlioz-Barbier, F. Albrieux, L. Pereira de Oliveira, M. Lacoue-Nègre, J.-F. Joly,** L. Duponchel. Analytical Chemistry, Vol. 92, n° 3, (2020). DOI: 10.1021/acs.analchem.9b05263*

(2) ***J. Guillemant, F. Albrieux, L. Pereira de Oliveira, M. Lacoue-Nègre,** L. Duponchel, **J.-F. Joly.** Analytical Chemistry, Vol. 91, n° 20, (2019). DOI: 10.1021/acs.analchem.9b01702*

(3) ***J. Guillemant, F. Albrieux, M. Lacoue-Nègre, L. Pereira de Oliveira, J.-F. Joly,** L. Duponchel. Analytical Chemistry, Vol. 91, n° 18, (2019). DOI: 10.1021/acs.analchem.9b02409*

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# *In situ* characterization of the genesis of the active sites of hydrotreatment catalysts by X-ray Absorption Spectroscopy

Meeting environmental standards governing the sulfur content of oil-based fuels hinges around the optimization of hydrotreatment processes (HDT), involving, in particular, the development of more efficient catalysts. Catalyst efficiency depends on the activation of catalytic sites, a step produced by a sulfurization treatment, before use, within an industrial reactor.

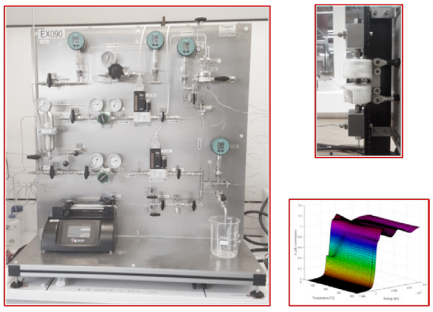
The characterization of this phenomenon in the laboratory is generally carried out *via* a gas phase treatment[a]. Not representative of liquid phase[b] industrial treatment, it does not always make it possible to correlate the physicochemical characteristics of the sulfur phase formed with catalytic performances in real operating conditions.

In order to study the *in situ* sulfurization mechanism of HDT catalysts in industrial conditions, a Quick-XAS[c] analysis unit making it possible to reproduce such an operating environment was developed at IFPEN (figure), and then installed at the SOLEIL[d] synchroton's ROCK beamline to characterize the structure of the active phases formed during activation.

Direct observation during the liquid phase sulfurization process helped to explain the changes in the active phase and their effect on catalytic performances.

Industrial activation conditions lead to the initial formation of well-dispersed and depolymerized[e] oxide species on the alumina surface. With the massive release of $H_2S$ at 225°C, the nucleation of oxysulfide occurs almost instantaneously, before that of MoSx species.

This mechanism may be the source of the slight morphological differences observed under the microscope on the final $MoS_2$ phase, i.e., small-sized and better dispersed slabs leading to improved catalyst activity.



In situ *analysis unit for the Quick-XAS monitoring of catalyst activation in industrial conditions.*

a - $H_2S/H_2$, 1 bar
b - Diesel/$H_2$/sulfurizing agent, under pressure (30 bar) and at a temperature of 350°C
c - XAS = X-ray Absorption Spectroscopy
d - French synchrotron radiation center, a major multidisciplinary instrument and research laboratory
e - Thus converted into simpler species

(1) ***C. Lesage, E. Devers, C. Legens, G. Fernandes,*** *O. Roudenko, V. Briois. Catalysis Today, Elsevier, 2019, 336, pp.63-73. https://doi.org/10.1016/j.cattod.2019.01.081*

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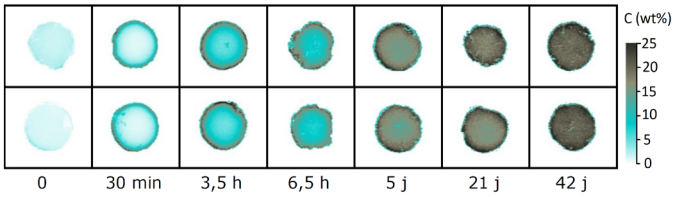
# Rapid elementary metal mapping *via* LIBS

Effectively detecting the presence of very low quantities of elements in industrial materials is a major challenge. One such example is heterogeneous catalysis where contamination and poisoning of catalysts by some elements present in small quantities adversely affect their properties and process performance.

In order to characterize these phenomena, IFPEN has developed the use of LIBS[a], in partnership with the Institut Lumière Matière (Institute of Light and Matter) in Lyon. The principle is to focus a laser beam on the material to be analyzed in such a way as to apply enough energy to ablate some of the matter and convert it into plasma. The light emitted by the latter, with wavelengths characteristic of the atoms ablated, makes it possible to measure the local composition of the material and thus reconstruct a map of the elements for the sample as a whole, with a very fast measurement and visualization speed[(1)].

LIBS was used to locate metals such as vanadium and nickel, present in oil feeds and known to poison catalysts, even in extremely small amounts (0.001% weight). Usually difficult to identify and visualize, their distribution in catalyst grains was obtained in a few minutes, thanks to the sensitivity of the technique[(2)].




*Carbon map on two sections of catalyst grain over time when in contact with oil feed.*

Another example: the capacity of LIBS to produce a quantitative image of carbon. In some refining processes, a carbon residue known as coke can form on the surface of catalysts thereby reducing their efficiency. The use of LIBS, associated with a non-contaminating preparation method[b], made it possible to overcome the limits of conventional analysis techniques and monitor the evolution of carbon locations in the grains at various points over the time the catalyst was operating[(3)].

a - Laser Induced Breakdown Spectroscopy
b - Packing of grains in a copper film, then coating in a resin and mechanical polishing

(1) ***L. Jolivet****, M. Leprince, S. Moncayo,* ***L. Sorbier, C.-P. Lienemann****, V. Motto-Ros, Spectrochim. Acta Part B 151 41–53 (2019). https://doi.org/10.1016/j.sab.2018.11.008*

(2) *F. Trichard,* ***F. Gaulier, J. Barbier, D. Espinat, B. Guichard, C.-P. Lienemann, L. Sorbier****, P. Levitz, V. Motto-Ros, J. Catal. 363 183–190 (2018). https://doi.org/10.1016/j.jcat.2018.04.013*

(3) ***L. Jolivet****, V. Motto-Ros,* ***L. Sorbier, T. Sozinho, C.-P. Lienemann****, J. Anal. At. Spectrom. 35 896–903 (2020). https://doi.org/10.1039/c9ja00434c*

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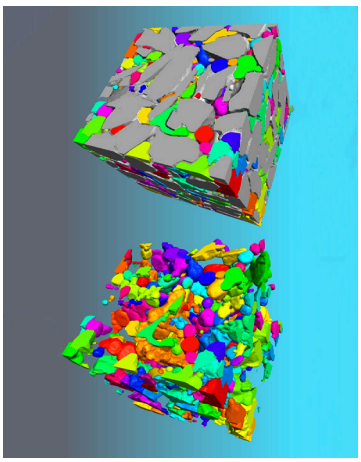
# *In situ* study of the detailed structure of a foam flowing in a real porous medium

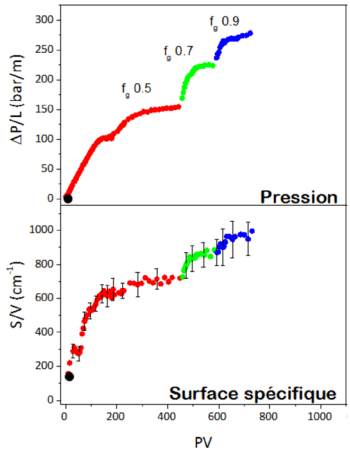
Foam injection during oil production or ground remediation is aimed at overcoming problems of gravity segregation and viscous fingering[a] created by fluid injection. Improving this practice requires knowledge of the detailed structure of a foam flowing in a real porous medium. A multi-scale approach using complementary characterization techniques, in terms of resolution (space and time) and field of view[b], made it possible to access this information *in situ*, by combining conventional petrophysical measurement equipment with different observation cells.

On a core scale, the X-ray scanner is used to quantitatively monitor local fluid saturations (gas or liquid) with a time resolution of a few seconds[1]. On a smaller scale, the combination of spatial (1 µm) and temporal (1 s) resolutions provided by synchrotron X-ray microtomography gave access for the very first time to *in situ* 3D images of the structure of a foam trapped in a porous medium (figure a). The analysis of volumes over time highlighted the intermittent nature of the trapping[2].

Measurements on foam bubble and lamellae scales were conducted *via* SANS[c] using different contrasts. They provided information concerning the saturation of the medium by the fluids in place and S/V, the quantity of gas/liquid interfaces by unit of volume (figure b). Using this information on scattering objects, established on several scales, it was possible to describe transport mechanisms as well as the size of oil micro-droplets[3]. These measurements also make it possible to estimate the average size of bubbles for different foam qualities and different porous media.



(a)




(b)

*(a) 3D images obtained via synchrotron X-ray microtomography of foam in the porous medium[d] (volume 400 x 400 x 400 µm³) [2].*
*(b) SANS micro-macro correlation for different foam qualities ($f_g$)[e].*

a - Due to the low density and viscosity of the gas compared to the liquid
b - Solid angle seen by the sensor
c - Small angle neutron scattering
d - Each color corresponds to a bubble, separated by image analysis
e - Foam quality, defined as the ratio of the gas volumetric flow rate to the total volumetric flow (liquid + gas)


(1) ***C. Ouali, E. Rosenberg, L. Barré, B. Bourbiaux,*** *Oil Gas Sci. Technol. – Rev. IFP Energies nouvelles, 74 (2019) 33. https://doi.org/10.2516/ogst/2019005*

(2) ***R. Poryles, N. Gland,*** *A. King,* ***E. Rosenberg, L. Barré, T. Chevalier,*** *Soft Matter, 2020,16, 6354-6361. https://doi.org/10.1039/D0SM00392A*

(3) ***R. Poryles, T. Chevalier, N. Gland, E. Rosenberg, L. Barré,*** *Soft Matter, 2020, 16, 1771-1778. https://doi.org/10.1039/C9SM01936G*



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## News

• ***IFPEN and INRIA sign a strategic partnership agreement*** *to support the energy transition, focused on artificial intelligence and high-performance data analysis technologies.*

• ***The website of the CARMEN joint research laboratory*** *concerning the characterization of materials for new energies* ***is online.***

• ***François Kalaydjian,*** *Director of the Economics and Technology Intelligence Division, is appointed "Hydrogen Coordinator" at IFPEN.*

• *With 190 patent applications filed with the INPI in 2019,* ***IFPEN Group was ranked 3rd among French research bodies filing patents*** *(and was 13th in the 2019 rankings of patent filers in France).*

• ***The new "CARMA" chair (Carbon Management and negative $CO_2$ emissions technologies towards a low carbon future)*** *promotes and shares research and initiatives in the field of education in order to contribute to public and scientific dialog on major carbon-related issues. Jean-Pierre Deflandre (lecturer-researcher at IFP School) and Florence Delprat-Jannaud (manager of the CCS program at IFPEN) are joint chair holders.*

## Scientific visitor

• *The Geosciences Division is currently hosting* ***Doctor David Sebag****, lecturer at Rouen University and associate researcher at Lausanne University, for a period of one year.*

## Online Scientific events

• ***"Corrosion in Low Carbon Energies"*** *Scienc'Innov workshop, 3-4 November 2020 www.corrosion-lce.com*

• ***"Innovative Material: which Scale-up Methodology?"*** *Scienc'Innov workshop, 24-25 November 2020 www.scale4mat.com*


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