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Selected case studies presenting advanced methodologies to study food and chemical industry materials: From the structural characterization of raw materials to the multisensory integration of food

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ABSTRACT

Agricultural resources give us food but also potential sources of feedstocks for the chemical industry. As demand from the growing human population rises, the food industry and the chemical industry face similar problems of scaling operations while sourcing the largest possible amount of at least reasonable-quality raw materials. Food is composed of complex structures formed from molecular assemblies (*e.g.* particles, fibres, crystals) whose properties depend in part on the molecular species present. In this context, investigations are needed to better understand raw material structure and structure transformation mechanisms in order to improve manufacturing processes and the properties of the final product (*e.g.* food), which means dedicated methodologies need to be developed. This review presents case studies illustrating advanced technologies designed for characterizing biopolymers, supramolecular complexes, cell membranes, enzymatic degradation of food matrices and biopolymers, flavor release dynamics during eating, cerebral multisensory integration of food and eating behavior.

Earth's biosphere is a tremendous source of materials that support human activities, like food, fibre, fuel and chemicals, but it also is a finite space, hence the need to improve our use of this precious resource. Agronomy is the science addressing the goal of improving the production and use of the resources offered by the biosphere. It is a combination of sciences (biology, chemistry, ecology, geosciences, economics and genetics) covering different fields of application, such as food or chemical resources for energy and industry. Each of these fields has an array of specific issues to face. Food research has to address important challenges to enhance the nutritional composition of farmed production for poor and developed countries and improve the formulation of foods for better health outcomes while ensuring product acceptability. In parallel, there is chemical industry demand for new feedstock solutions. These two topics of research both use biological material for numerous human activities: foods, feeds, the majority of materials and chemicals, heat, electricity, and more. Fossil energies are equally important in human activities, and are also a result of the transformation of biological raw materials. Controlling the transformation of biological raw material is thus a major challenge for human activities—and requires advanced knowledge on the structure of these materials. Biological organisms are organized according to a hierarchy of complex biological structures from nanoscopic up to macroscopic scale, which we can call ‘biological object’. Each level of structure takes the unit from the previous level, thus adding layers of increasing complexity to the organization, which expands from atoms up to biosphere.

Understanding the organization of organisms and characterizing the structure and properties of the different objects composing them at different scales is fundamental in order to gain a better understanding not only of their potential for use as raw materials or feedstocks for food

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or chemicals, but also the biological processes in which they are involved. For instance, cognitive and behavioral neurosciences require knowledge on neurons. The study of these different objects requires the development of dedicated methodologies and techniques. These developments have to address multiscale analysis, increase the resolution and specificity of the analytical techniques, improve the ability of the techniques to work under native conditions in order to preserve the integrity of fragile biological objects and develop non-invasive techniques to perform *in vivo* investigations. Furthermore, these techniques and methods also have to be able to record the studied phenomena over time.

This review presents a handful of illustrative examples of the new techniques that hold most promise to study agronomic objects and address specific challenges. Using various examples connected to food science and the chemical industry, we take you from the simplest molecule to behavioral sciences *via* newly-developed instrumental methodologies.

As both food and chemical industries use raw materials coming from agriculture, they are facing similar challenges. The huge variability intrinsic to agricultural products due to genetic and environmental factors can impact the quality of the product, the processes involved in making it, and the efficiency of their conversion. In this context, fundamental investigations are needed to better understand raw material structure and structure transformation mechanisms so as to improve manufacturing processes and the properties of the final product (*e.g.* food), which means dedicated methodologies need to be developed from other fields.

With the emergence of electrospray ionization (ESI) and matrix-assisted laser desorption ionization (MALDI) allowing the ionization of intact biomolecules, mass spectrometry (MS) is becoming a technique of choice for the characterization of biomolecules. The advantages of MS are speed, sensitivity and specificity. Moreover, ESI-MS can easily be coupled with liquid chromatography, adding a dimension of separation as a function of the molecule's affinity for the stationary phase. MS gives access to the molecular weight of the molecules. Additional structural information can be obtained by using MS/MS, which can fragment the precursor ion into product ions. The most common fragmentation technique is collision-induced dissociation (CID). Other activation techniques have been introduced, such as electron-capture dissociation (ECD) and photodissociation (PD), as they can generate different product ions, bringing different structural information. A promising new fragmentation technique called dissociative photoionization (DPI), which uses vacuum ultraviolet (VUV) photons, has recently been introduced by coupling MS to synchrotron radiation (SR) (Milosavljevic et al., 2012). Here we highlight the potential of this technique to bring crucial structural information on biopolymers and their interactions *via* a study on the structural characterization of specific oligosaccharides and noncovalent supramolecular edifices forming between a salivary protein and polyphenol food compounds involved in astringency sensation. In this study, MS was also coupled to ion mobility and small-angle X-ray scattering (SAXS) experiments, bringing additional information on the structure of the salivary protein and on the supramolecular complexes formed during the interaction. SAXS is one of the most powerful methods for assessing protein dimensions and shape. The scattered intensity is sensitive to the size of the protein in solution, but also to the conformational properties of the polypeptide chain.

MS methods of fragmentation can also be used to generate a specific product ion from a selected precursor ion. This product ion provides absolute structural specificity for the analyte, allowing it to be selectively quantified, even in a complex mixture. This type of advanced methodology enabling accurate quantification is illustrated through the study of plant polyphenols, which are highly complex and reactive biopolymers.

Another advantage of MS is its speed, which makes it possible to follow dynamic processes over time. One of the current challenges in food perception is to follow flavor release *in vivo* during food consumption, so coupling an MS to the nasal cavity of human subjects makes it possible to follow aroma release *in vivo* and thus investigate the effect of food matrix or subject physiology. Recent insights on aroma release using this technique are presented here.

Another challenge regards monitoring dynamic processes such as enzymatic activities in biological samples without labeling, as the addition of a chemical label to biomolecules can potentially affect their distribution and interactions within their biological environment. A powerful tool to address this challenge is autofluorescence microscopy, which a technique of choice for molecular histology and for following metabolic processes. Moreover, the recent development a synchrotron-coupled DUV microspectrofluorimeter has extended the range of wavelengths for fluorophore excitation in the UV and deep-UV domain (Jamme et al., 2013). Here we illustrate the potential of this technique in two examples. The first example concerns the study of the degradation of dairy gels during gastric digestion by label-free microscopy coupled to SAXS experiments, which brought additional information at the nanometer scale. The second example concerns a study on *in cellulo* enzymatic cell-wall degradation, where the label-free fluorescence microscopy approach was coupled to infrared microspectroscopy to also follow changes in polysaccharides.

Another challenge for investigations on food is to understand how the different sensory cues stimulated during eating are integrated at brain level to form flavor perception. Functional MRI (fMRI) is now a reference method for analyzing this kind of cerebral process, and we also spotlight a study case that illustrates the latest developments in this technique.

1. Characterization of biopolymers

Biopolymers are probably the most important biological objects, as they are at the base of the organization of living organisms. They are crucially important due to their functions, their properties, and the percentage of biomass that they represent. These objects are polymers that contain monomeric units covalently bound to one another. The function of these biopolymers is strongly tied to the composition and organization of the monomers in the backbone, their potential modifications, and the folding of the polymeric chain into a well-defined structure. Biologists have led intensive research into three main types of biopolymers: polynucleotides, which are biopolymers composed of nucleotide monomers (RNA and DNA); polypeptides or proteins, which are polymers of amino acids; and polysaccharides, which are polymeric carbohydrate molecules composed of long chains of monosaccharide units. Other big classes of biopolymers are also an important part of agronomic resources, such as lipids that are essential components of biological membranes, polyphenols that constitute a large and diverse group of plant secondary metabolites such as including lignin, an insoluble polymer component of plant cell walls, and several types of soluble compounds (*e.g.* anthocyanin pigments, tannins, and many more).

1.1. Investigation on plant polysaccharides: an example of prospective molecules for the chemical industry

Polysaccharides are the most abundant biopolymers on Earth. They have a wide variety of structures and properties and, as such, provide a large pool of molecules of putative interest in several industrial sectors, including “green chemistry” and biorefining (Persin et al., 2011). Seaweeds offer a rich and profuse source of various polysaccharides. Among different strategies to degrade these molecules, “green” degradation, which uses enzymes to transform the biological raw materials, is one of the most sustainable. However, the “green” degradation of marine biomass into high-added-value oligosaccharides remains limited by a lack of available degrading enzymes with known and controlled activities. Among seaweed polysaccharides, galactans, which