Polysaccharides are important biopolymers from e.g. plant, marine, yeast and bacterial origin. In their natural habitat, a huge structural variation of molecules belonging to the same class of polysaccharides may exist, all having their own contribution to the techno-en biofunctionality of the mixture. After industrial extraction of specific groups of polymers, such structural variation may even become bigger.

During the last years, strategies have been developed to characterise different classes of complex polysaccharides in great detail. Firstly, the sugar composition and the presence of non-glycosidic substituents will be measured. In addition, enzymatic fingerprinting methods using pure and well defined enzymes have been developed to split the polymer in diagnostic oligosaccharidic fragments which can be separated, identified and quantified using LC and LC-MS approaches.

During the presentation, the chemical structure of two complex polysaccharides, pectin and alginate, will be discussed in detail and the distribution of methyl esters and acetyl groups (pectin) as well as the distribution of the two alginate building blocks (guluronic acid and mannnuronic acid) over de backbone will be highlighted. Enzymatic digests will be analysed using Maldi ToF MS, HILIC-Iontrap-MS and HILIC-Ion Mobility MS, while different detection systems will be discussed briefly. Examples how to use the obtained in formation in descriptive parameters will be given.