**Applications of partial hydrolysis for the structural analysis of polysaccharides**

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The technofunctional properties of polysaccharides are decisively influenced by their molecular structure which is highly complex in most cases. Polysaccharides can be composed of various monomeric units which are interconnected by many different glycosidic linkages. Furthermore, a polysaccharide backbone may be substituted with side chains of varying composition and length. This structural diversity is a significant challenge for the analysis of polysaccharides. Methods such as monosaccharide analysis, linkage analysis, or NMR spectroscopy often only provide an incomplete picture of the molecular structure, because they yield no or limited information on, for example, side chain lengths or the presence of copolymers. In addition, their applicability in complex matrices is limited.

These limitations can be overcome by analyzing the oligo- and polymeric products which are obtained from partial hydrolysis of the polysaccharides. Although there are many possibilities for partially hydrolyzing polysaccharides, the use of highly specific enzymes is particularly promising. In most cases, the enzymes are used for the hydrolysis of defined glycosidic linkages within the backbone of homopolysaccharides. For example, the hydrolysis of dextrans with endo-dextranase yields isomaltose and glucose from the linear, α-1,6-linked areas, but also branched oligosaccharides. After the characterization of the branched oligosaccharides, an HPAEC analysis can rapidly provide detailed information on the structure of different dextrans. The fingerprints obtained from this approach can also be used to differentiate dextrans that can hardly be discriminated by using other methods. Furthermore, a combination of partial enzymatic hydrolysis with HPSEC and HPAEC can help to identify larger sections with other glycosidic linkages in the α-glucan backbone. Partial enzymatic hydrolysis in combination with different chromatographic techniques can also be applied for the analysis of bacterial fructans which also exhibit remarkable structural complexity. Furthermore, it is possible to analyze complex heteropolysaccharides after partial enzymatic hydrolysis, although their hydrolysis usually requires the application of multiple enzymes. Because the necessary enzymes are often not commercially available and because side activities must be avoided, it is in many cases necessary to produce them in recombinant form. The obtained enzymes can then be applied to gain detailed information on the structural architecture of, for example, hybrid carrageenans. Furthermore, specific hydrolytic enzymes can be applied to deepen the understanding of the structure of gum arabic. Although many polysaccharide-degrading enzymes have been described, it is sometimes not possible to apply this approach. This is especially true for heteroexopolysaccharides which show enormous structural diversity. However, partial chemical hydrolysis can be applied in such cases. Due to the high structural variability, it is typically possible to detect diagnostic fragments and to utilize them for structural elucidation. Hyphenated techniques such as HPAEC-PAD/MS are especially useful for this approach. Partial chemical or enzymatic hydrolysis can also be used to analyze the occurrence of different polysaccharides in complex food matrices such as yoghurt, beverages, or sourdough. Due to the high specificity of the hydrolytic enzymes, the sample workup can often be simplified. However, the application of suitable analytical techniques can also allow for the detection of individual polysaccharides in complex mixtures after less specific chemical hydrolysis. Altogether, partial hydrolysis offers a range of possibilities for the characterization and analysis of polysaccharides. The main challenge for the future will be to translate this potential into quantitative approaches for polysaccharide analysis.