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Addressing the challenges of lignin oligomer analysis by liquid-based separation techniques
From universal quantification to multidimensional separations

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Lignin is the second most abundant biopolymer on Earth after cellulose, found in virtually all plants where it is responsible for rigidity, hydrophobicity and mineral transport. For a long time, it has been considered a waste in the paper production process and incinerated for its energy content. However, with the depletion of crude oil reserves, it has been found to have a large potential to become a candidate to alleviate the transition to a more sustainable economy by replacing oil as a raw material in many industrial processes including the production of fine chemicals, fuels and plastics. This discovery induced a rapidly increasing interest in lignin valorization. At the same time, the development of existing and new procedures to exploit lignin requires reliable chemical analysis to identify and quantify phenolic compounds along the whole stream. Lignin samples have proven to be challenging to analyze since they contain hundreds of phenolics of vast complexity regarding size, functionality and concentration. On the top of this, reference materials are commercially available only for monomers, further hindering the research of oligomers, especially in terms of quantitative analysis. To improve the quality of the data by providing selectivity to the analysis method, separation techniques are critical components of lignin analysis prior to detection. In this thesis work, liquid-based chromatographic techniques were employed to address the difficulty of separating technical lignin samples. Efforts were centered around applying supercritical fluid chromatography and gel permeation chromatography. Supercritical fluid chromatography was utilized to achieve a high-resolution separation of lignin compounds prior to detection. This was particularly important when a universal detector was employed, which lead to the proposal of a single-calibrant approach to quantify lignin dimers. This way, our methodology addressed the challenge of the lack of dimer standards to build calibration curves. Furthermore, insights into the retention of lignophenolics were collected regarding the selectivity differences between various stationary phases and the role of analyte functionality. Gel permeation chromatography was thoroughly investigated in terms of the trueness of the molecular weight determination. Combining results from diffusion-ordered NMR, mass spectrometry and partial least squares regression it was found that although it yields in a considerable error for monomers, linear polystyrene still provides reliable results for a large part of the molecular weight distribution curve. Additional observations regarding the stability of lignin solutions and repolymerization were recorded. Multidimensional chromatography, the ultimate answer to the separation challenge of complex samples, was applied to characterize lignin compounds in technical lignins. A combination of GPC and SFC, not reported before, was explored, with specific attention to compatibility, modulation and the achievable peak capacity. Conventional hyphenation utilizing stationary-phase assisted modulation did not yield a practically useful method. Hence, valve-based solutions were employed to expand the separation space and combined with ion mobility mass spectrometry, it increased the selectivity of the method, allowing for the analysis of large lignin oligomers which have been less in the focus of earlier works. Furthermore, the creative use of valves also addressed a few hindrances identified in the literature regarding the expansion of orthogonality and increasing the peak capacity.