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Structural Elucidation of Intact Rough-Type Lipopolysaccharides using Field Asymmetric Ion Mobility Spectrometry and Kendrick Mass Defect Plots

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Abstract : Lipopolysaccharide (LPS) is a hallmark virulence factor of Gram-negative bacteria. It is a complex, structurally heterogeneous mixture due to variations in number, type, and position of its simplest units: fatty acids and monosaccharides. Thus, LPS structural characterization by traditional mass spectrometry (MS) methods is challenging. Here, we describe the benefits of field asymmetric ion mobility spectrometry (FAIMS) for analysis of intact R-type lipopolysaccharide complex mixture (lipooligo- saccharide; LOS). Structural characterization was performed using Escherichia coli J5 (Rc mutant) LOS, a TLR4 agonist widely used in glycoconjugate vaccine research. FAIMS gas phase fractionation improved the (S/N) ratio and number of detected LOS species. Additionally, FAIMS allowed the separation of overlapping isobars facilitating their tandem MS characterization and un- equivocal structural assignments. In addition to FAIMS gas phase fractionation benefits, extra sorting of the structurally related LOS molecules was further accomplished using Kendrick mass defect (KMD) plots. Notably, a custom KMD base unit of [Na-H] created a highly organized KMD plot that allowed identification of interesting and novel structural differences across the different LOS ion families, i.e., ions with different acylation degrees, oligosaccharides composition, and chemical modifications. Defining the composition of a single LOS ion by tandem MS along with the organized KMD plot structural network was sufficient to deduce the composition of 181 LOS species out of 321 species present in the mixture. The combination of FAIMS and KMD plots allowed in-depth characterization of the complex LOS mixture and uncovered a wealth of novel information about its structural variations.

Keywords : lipopolysaccharide, ion mobility MS, Kendrick mass defect, Tandem mass spectrometry
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