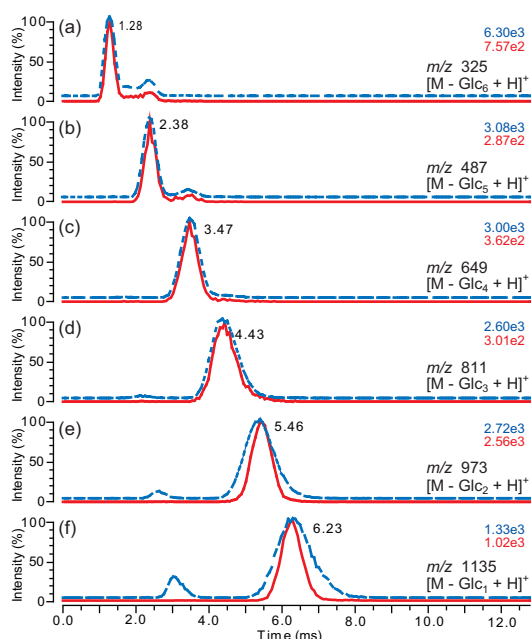


Peak Width-Mass Correlation in CID MS/MS of Isomeric Oligosaccharides Using Traveling-wave Ion Mobility Mass Spectrometry

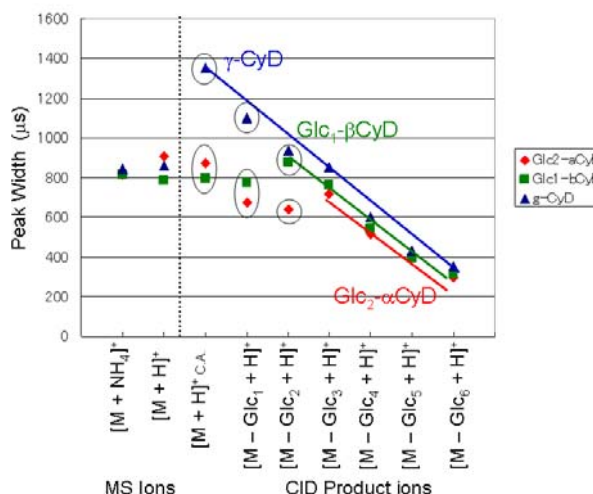
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Ion mobility-mass spectrometry (IM-MS) has been applied to biomolecule analyses such as peptides, proteins, sugar chains and etc. Ion mobility spectrometry is a separation technique based on the drift-times of the molecules against the collision with gas. All applications of biomolecules separations with IM-MS were the drift time-mass separation and correlation methods. Until now, there is no research for peak-width of ion mobility spectra. In this study, it was revealed that the IM peak-width includes structure information, and we applied the IM peak-width mass correlation to the identification of the isomeric oligosaccharides structures. Isomeric oligosaccharides γ -cyclodextrin (γ -CD), glucosyl- β CD (Glc_1 - β CD), and maltosyl- α CD (Glc_2 - α CD) were analyzed by traveling-wave ion mobility (IM) mass spectrometry. Their multicharged multimers' formation differed from each other, but their drift times were almost the same. The drift times of the product ions in collision induced dissociation (CID) MS/MS correlated to their mass and/or chain length, and the differences among the three isomers were small, specifically the drift-time mass correlation of their product ions. In contrast, the ion mobility peak widths were sensitive to structural differences of the isomeric product ions. The IM peak width of the product ions $[\text{M} - \text{Glc}_n + \text{H}]^+$ ($n = 0\sim 6$) of γ -CD correlated linearly with their masses; the large and/or long chain product ions had wider peak widths than did the small ones. This was a novel and useful "trend line" to discriminate between the three isomers. Plots of the $[\text{M} - \text{Glc}_{2-6} + \text{H}]^+$ of Glc_1 - β CD and $[\text{M} - \text{Glc}_{3-6} + \text{H}]^+$ of Glc_2 - α CD product ions' plots were on the same trend line of γ -CD. The plots of $[\text{M} - \text{Glc}_1 + \text{H}]^+$ of Glc_1 - β CD and $[\text{M} - \text{Glc}_{1,2} + \text{H}]^+$ of Glc_2 - α CD strayed from the γ -CD line; their peak widths were narrower than those of γ -CD. These results indicated that product ions from those chemical species of Glc_1 - β CD Glc_2 - α CD retained their CD structure. Analyses of the IM peak width enable us to elucidate the structures of the product ion.



The IM spectra of the product ions of γ -CD (blue dotted lines) and Glc_2 - α CD (red lines). The Glc_2 - α CD red lines of $[\text{M} - \text{Glc}_{1,2} + \text{H}]^+$ were narrower than those of γ CD blue lines.



The correlation plots between IM peak width and the number of sugar residues and/or mass value of the product ions. Plots to the left of the dotted line are the peak widths of the ions without the CID energy.