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Fast and Sensitive Detection of Oligosaccharides Using Desalting Paper Spray Mass Spectrometry (DPS-MS)
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Conventional mass spectrometry (MS)-based analytical methods for small carbohydrate fragments (oligosaccharides, degree of polymerization 2–12) are time-consuming due to the need for an offline sample pretreatment such as desalting. Herein, we report a new paper spray ionization method, named desalting paper spray (DPS), which employs a piece of triangular filter paper for both sample desalting and ionization. Unlike regular paper spray ionization (PSI) and nanoelectrospray ionization (nanoESI), DPS-MS allows fast and sensitive detection of oligosaccharides in biological samples having complex matrices (e.g., Tris, PBS, HEPES buffers, or urine). When an oligosaccharide sample is loaded onto the filter paper substrate made mostly of cellulose, oligosaccharides are adsorbed on the paper via hydrophilic interactions with cellulose. Salts and buffers can be washed away using an ACN/H₂O (90/10 v/v) solution, while oligosaccharides can be eluted from the paper using a solution of ACN/H₂O/formic acid (FA) (10/90/1 v/v/v) and directly spray ionized from the tip of the paper. Various saccharides at trace levels (e.g., 50 fmol) in nonvolatile buffer can be quickly analyzed by DPS-MS (<5 min per sample). DPS-MS is also applicable for direct detection of oligosaccharides from glycosyltransferase (GT) reactions, a challenging task that typically requires a radioactive assay. This work suggests that DPS-MS has potential for rapid oligosaccharide analysis from biological samples.