Supporting Information for

High Sensitivity combined with Extended Structural Coverage of Labile Compounds via nanoElectrospray Ionization at Subambient Pressures

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The following supplementary figures are included

Figure SI1: Plot of elution time vs. degree of polymerization from LC-MS analysis of colominic acid.

Figure SI2: Plot of polymer monoisotopic mass vs observed charge state

Figure SI3: Mass spectra of a sialic acid containing N-glycan, $Hex_6HexNAc_5NeuAc_3$ from various interface configurations.

Figure SI1. Plot of the elution time vs. the degree of polymerization observed from the LC-MS analysis of colominic acid via a conventional ESI source operated with capillary temperatures of 300 °C (b), and 150 °C (c) and the SPIN source (d).

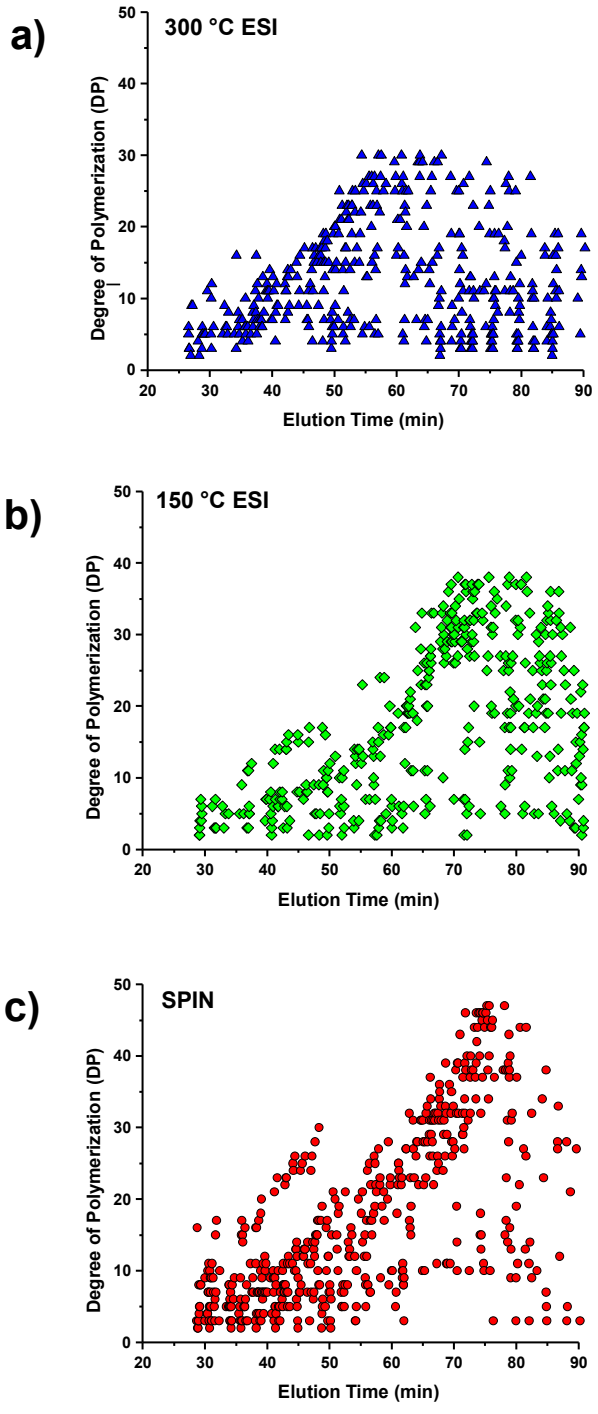
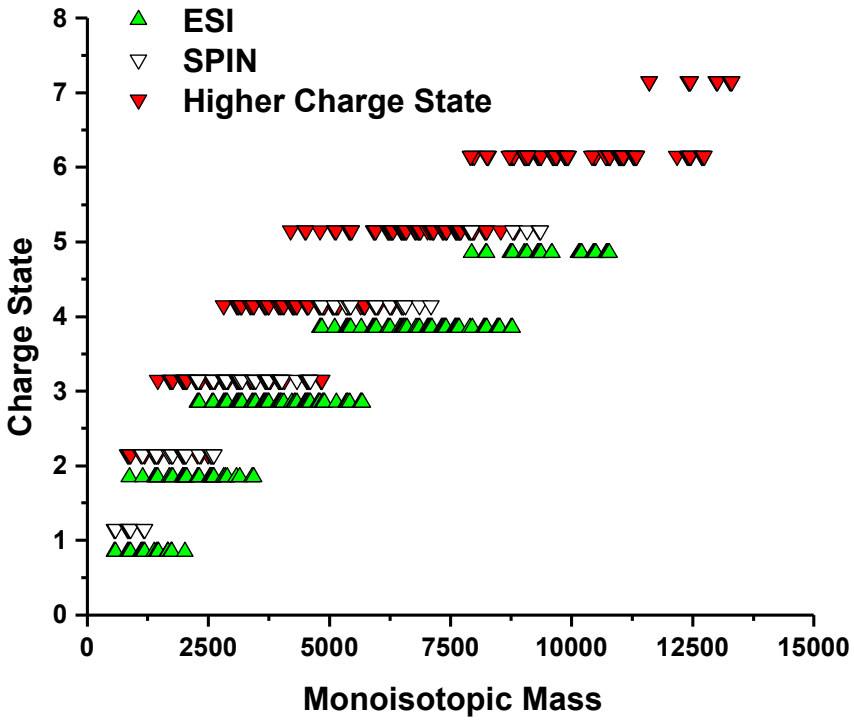


Figure SI2. Plot of the observed charge states for all colominic acid polymers detected with conventional ESI with a capillary temperature of 150 °C (green triangles) and SPIN (white and red triangles). Polymers observed in a higher charge state in SPIN than ESI are shown by red triangles. Charge states have been shifted from their integer values for clarity.



As an additional example from the LC-MS analysis of N-glycans containing sialic acid identified in human serum, figure SI2 shows the mass spectra for the N-glycan $Hex_6HexNAc_5NeuAc_3$ (2881.03 Da) obtained with different MS interface configurations. The spectrum in Figure SI2a was obtained using the ESI source with the capillary temperature at 300 °C showing predominantly fragment peaks. The 2+ intact glycan at 1441.53 *m/z* was observed at very low abundance. When the capillary temperature was lowered to 150 °C, as shown in Figure SI2b, the relative intensity of all the fragment ions decreased significantly whereas the abundance of the intact glycan peak increased. In addition, the 3+ intact glycan at 961.36 *m/z* was observed as the base peak in Figure SI2b. The mass spectrum with the SPIN-MS interface is shown in Figure SI2c. The sialic acid containing fragment ions present in the ESI interface spectra (at 819.29 *m/z*, 657.24 *m/z*, and 292.10 *m/z*) are noticeably absent in Figure SI2c while the intensity of the intact glycan increases substantially and the 4+ intact glycan at 721.27 *m/z* is clearly visible.

Figure SI3. Mass spectra of a sialic acid containing N-glycan, $Hex_6HexNAc_5NeuAc_3$ (2881.03 Da), from the LC-MS analysis of human serum obtained with the conventional ESI interface operated at the inlet capillary temperatures of 300 °C (a) and 150 °C (b) and with the SPIN interface (c). The red arrows represent the 4+, 3+, and 2+ charge states of the observed intact glycan. CFG nomenclature was used to illustrate putative glycan structure with the modification that white circles represent a generic hexose.