ASMS 2022, TP297

One-minute quantitative separation of complex carbohydrates for food analysis using direct infusion ESI-TIMS-QTOF mass spectrometry

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Ion Mobility Separation of Structural Isomers

Trapped ion mobility spectrometry (TIMS) offers fast and accurate analysis of complex mixtures with effective fragmentation rates beyond 100 Hz. TIMS provides accurate collisional cross section (CCS) values for further sample separation and identification and enhances the sensitivity of quadrupole time-of-flight (QTOF) mass spectrometry. We have developed a quantitative method using direct infusion of samples for analysis of di-, and trisaccharides and malto-oligosachhrides (4-10 monomer length). Malto-oligosaccharide separation was demonstrated over a wide mobility range while high ion mobility resolution enabled identification off differently branched compounds. This method provided baseline mobilogram separation of di-, and tri-saccharides with an analysis speed drastically faster than existing methods, decreasing analysis time from hours to one minute.

Saccharide	Lit. value (Na+)	Number of Lit. Values	timsTOF Result (Na+)
Nigerose	-	-	173.9, 175.6, 178.5
Gentiobiose	180.5	1	178.4
Isomaltose	177.7 ± 0.3	2	178.0
Maltulose	181.3	1	175.6, 178.5, 180.0
Glucose	145.2 ± 7	5	145.2, 147.2
Raffinose	209.6 ± 1.1	4	208.7
Maltotriose	212.2 ± 1.4	4	212.9
Sucrose	173.0 ± 2.96	4	173.9
Maltose	178.3 ± 0.9	5	179.2
Lactose	178.3 ± 0.9	5	176.3

Fig. 1 - Literature collisional cross section values (CCS) in Å² were obtained from ccsbase.net. Experimental timsTOF CCS values demonstrate close agreement with established literature measurements.

Methods

Mixtures of glucose, nigerose, gentiobiose, isomaltose, and maltulose with concentrations in range of 0.4 to 62 ppm were infused to evaluate separation. Similarly, mixtures of disaccharides sucrose, maltose, and lactose were infused at 5 ppm each, and trisaccharides raffinose and maltotriose at 6-7 ppm each. Malto-oligosaccharides DP4 to DP10 and DP6 to DP16 was also infused to resolve the mixtures. All samples were loop injected with no chromatographic separation into a Bruker timsTOF Pro QTOF mass spectrometer for ion mobility separation and quantification.

Results

- High accuracy CCS values produced by the timsTOF are in excellent agreement with reported literature values
- Di- and tri-saccharides were baseline separated with high resolution ion mobility, with resolving power of 120 or greater
- This high resolution is possible at scan speeds of 1 Hz, allowing for a fast loop injection
- Malto-oligosaccharide series were clearly detected and visualized using a mobility-m/z heat map

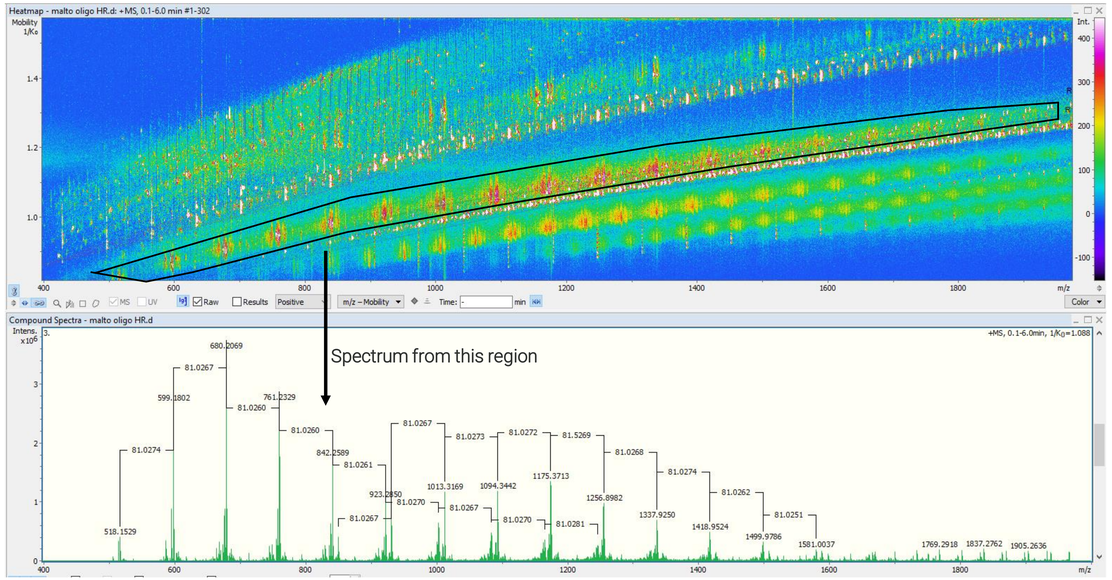

Fig. 2 – Malto-oligosaccharides were infused and data was displayed on a mobility vs. m/z heatmap to visualize the sample. Different series are visible in the heatmap, representing different charge states. These series can be isolated and extracted into discrete spectra in software to deconvolute a complex sample without the need for chromatography.

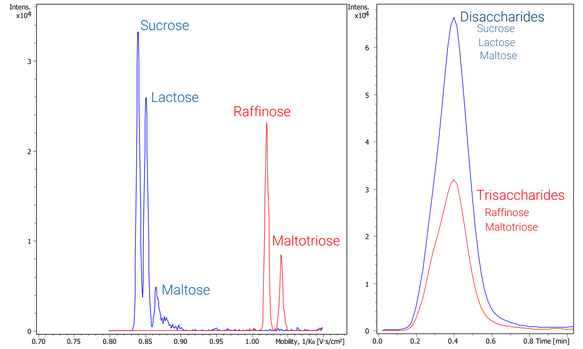

Fig. 3 – Disaccharides and trisaccharides are fully separated in the mobilogram (left) despite fully coeluting (right). These mobilograms are quantitative and repeatable, allowing an analysis to be run in under one minute.

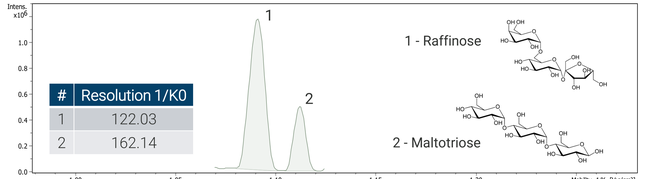

Fig. 4 – Raffinose and maltotriose, two isomeric trisaccharides, show baseline separation in a mobilogram.

Conclusions

- Ion mobility enables separation of sugars in the absence of lengthy chromatography
- Mobilograms are repeatable and quantitative
- Total analysis can be performed in one minute, saving time and increasing throughput

Bruker timsTOF Ion Mobility QTOF MS