Collision Cross Section Calibration with Structures for Lossless Ion Manipulations

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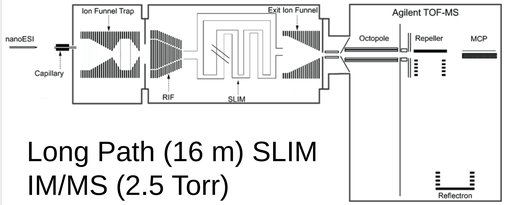
Overview

- First demonstration of traveling wave structures for lossless ion manipulations (TW-SLIM) collision cross section measurements.
- Used ion mobility (IM) calibrants commonly described in literature.
- IM collision cross sections (CCS) were measured for metabolite and peptide standards and compared to drift tube values.

Introduction

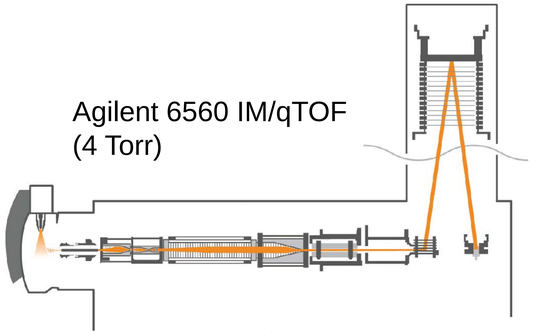
- Rotationally-averaged collision cross sections (CCS) reflect the 3D size and shape of gas-phase ions.
- CCS have been used to compare gas-phase ion structures to solution structures[1] and to aid in identification[2].
- SLIM have shown great increases in separation power over traditional drift tube and TWIM separations.
- TW does not allow for direct measurement of CCS.
- This project contains the first efforts towards using known CCS standards to calibrate for CCS measurements[3] in long-path TW-SLIM-IM.

Methods

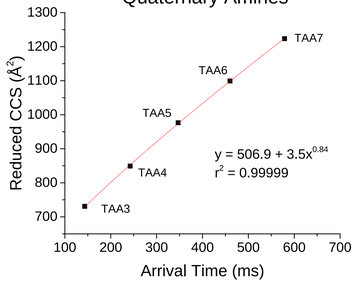


Long Path (16 m) SLIM IM/MS (2.5 Torr)

Agilent 6560 IM/qTOF (4 Torr)



Quaternary Amines



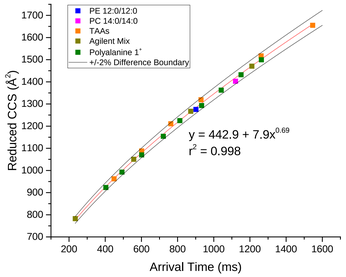
$$Reduced\ CCS = \frac{CCS}{z\sqrt{\frac{1}{\mu}}}$$

where z is charge and μ is reduced mass.

Example calibration curve for CCS determination from arrival time.

Results

Simple Standards Mixture, (30 V, 88 m/s)

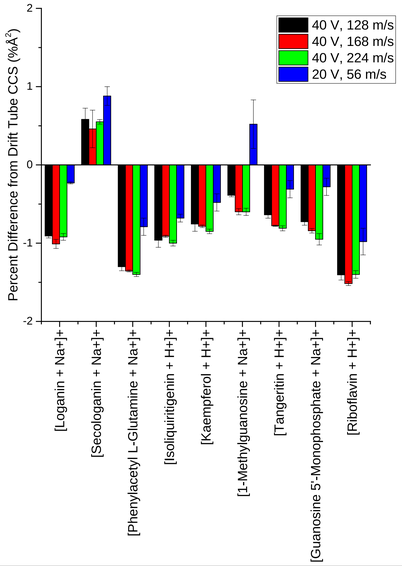


Reduced CCS measured by drift tube vs arrival times measured by SLIM.

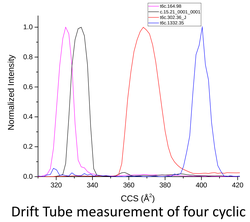
Analyte	m/z	CCS Drift Tube (Å²)	CCS SLIM (Å²)	%Difference	%CV
[Loganin + Na⁺]⁺	413.143	194.6	194.2	-0.23	0.76
[Secologanin + Na⁺]⁺	411.121	190.9	192.6	+0.88	0.73
[Phenylacetyl L-Glutamine + Na⁺]⁺	287.101	171.1	169.0	-0.79	0.91
[Isoliquiritigenin + H⁺]⁺	257.086	164.2	163.1	-0.68	0.90
[Kaempferol + H⁺]⁺	287.060	164.0	164.3	-0.48	0.91
[1-Methylguanosine + Na⁺]⁺	320.100	179.8	180.7	+0.52	0.81
[Tangeritin +H⁺]⁺	373.129	186.9	186.3	-0.31	0.73
[Guanosine 5'-Monophosphate + Na⁺]⁺	386.048	177.0	176.5	-0.28	0.82
[Riboflavin + H⁺]⁺	377.146	189.8	190.6	-0.98	0.74

Calibrants	m/z	CCS Drift Tube (Å²)
Tetrapropylammonium (TAA3)	186.227	148.1
Tetrabutylammonium (TAA4)	242.289	169.4
Tetrapentylammonium (TAA5)	298.351	192.9
Tetrahexylammonium (TAA6)	354.411	215.7
Tetraheptylammonium (TAA7)	410.472	238.9

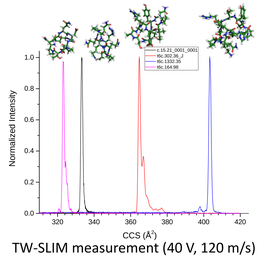
Comparison of CCS from drift tube and SLIM (20 V, 56 m/s) for a mix of metabolite standards.



Deviation (%difference) from drift tube measurements for SLIM measurements acquired at 40V and TW speeds 128, 168, and 224 m/s, and 20V at 56 m/s.



Drift Tube measurement of four cyclic synthetic D residue-containing peptides.



TW-SLIM measurement (40 V, 120 m/s) of four cyclic synthetic D residue-containing peptides. Structures are from NMR.

Conclusions

- Demonstrated IM CCS determination in SLIM through calibrating to known standards.
- Measurements of a limited set of metabolite standards were most accurate using lowest fields and TW speeds.
- Future work will investigate a greater diversity of chemical compounds and the need to use class-specific calibrants.

Acknowledgements

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