

Characterization of the Fragmentation by Collision Induced Dissociation in a MALDI Tandem Time-of-Flight Mass Spectrometer

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Most tandem mass spectrometric analyses of peptides are performed in the low-energy fragmentation regime wherein multiple collisional events (typically sub 100eV lab frame) result in the slow heating of the ion. Eventually, enough internal energy is imparted into the ion to induce charge-directed fragmentation resulting in the amide bond breakage and the formation of traditional γ - and b -ion types. The recent introduction of a MALDI tandem time-of-flight mass spectrometer (AB 4700 Proteomics Analyzer) now gives the researcher a new tool for MS/MS analyses. This instrument is capable of high-energy CID thereby exposing alternative fragmentations including the charge-remote fragmentation traditionally observed in sector instruments. Flexibility in the deposition of energy from the MALDI ionization, the selection of the collisional energy, gas pressure and gas type has been designed into this TOF/TOF mass spectrometer, allowing the fine tuning of the fragmentation pathways and observed patterns. Herein we describe the effects of varying these parameters to characterize the fragmentation pathways that are observed under different operating conditions.

The lab frame collisional energy was varied from 0.5-3kV by changing the potential on the collision cell and associated optics. He, Ne, Ar, N₂ and SF₆ were examined using the multiple gas inlet ports available on the 4700. The pressure regime for each gas was mapped (at 5 points) over a decade. Replicate spectra at each condition were collected and the data plotted in Spotfire. By examining the relative abundance of sequence specific ions, internal fragments, immonium ions and tradition high energy ions formed within each of these regimes a fragmentation map was made allowing researchers to tune the spectrometer into the optimal regime for various application requirements.
