I. Energy-Variable CAD of N-Terminated Sulfonate Peptides:

The success of the N-terminal sulfonation strategy for mass spectrometric characterization of peptides is due in part to the relative affinities of the N-terminal proton and the resulting protonated species. Energy-variable CAD studies confirm the importance of the N-terminal proton in dissociation of peptides. Resonance energy-variable CAD measurements were undertaken in order to define the domain of CAD energy-variable dissociation. In the case of the derivatives used here, the CAD energy range was set from 200 to 1000 mV.

Results

The overall advantage of the N-terminal sulfonation strategy for mass spectrometric characterization of peptides is due in part to the relative affinities of the N-terminal proton and the resulting protonated species. Energy-variable CAD studies confirm the importance of the N-terminal proton in dissociation of peptides. Resonance energy-variable CAD measurements were undertaken in order to define the domain of CAD energy-variable dissociation. In the case of the derivatives used here, the CAD energy range was set from 200 to 1000 mV.

Table 1 shows the location of each peptide within the protein along with the best-fit tryptic peptide sequences derived from the PEAKS software de novo algorithm.

Table 2 shows the location of each peptide within the protein along with the best-fit tryptic peptide sequences derived from the PEAKS software de novo algorithm.

Table 3 shows the location of each peptide within the protein along with the best-fit tryptic peptide sequences derived from the PEAKS software de novo algorithm.

Figure 1: Instrument diagram of the IRMPD modified LCQ Deca XP equipped with a CW laser to a depth of 5.6 μm.

Figure 2: N-Terminal Sulfonated Peptide.

Figure 3: Mass spectra showing the dependence of the complete peptide sequence and trypsinized Y ions for the energy- and voltage-variable CAD studies of a tryptic peptide (100 mV).

Conclusions

N-terminal sulfonation of peptides lowers the critical energy which facilitates IRMPD in a quadrupole ion trap.

IRMPD allows the mass cut-off providing a complete series of y sequence ions critical for de novo interpretation of N-terminal sulfonated peptides.

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References

1. Bin Ma, Kaizhong Zhang, Christopher Hendrie, Chengzhi Liang, Ming Li, Amanda Doherty-Kirby, Gilles Lajoie. Enhanced De Novo Sequence Interpretation of N-terminal Sulfonylated Peptides by Infrared Multiphoton Dissociation in a Quadrupole Ion Trap. The Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712.