

IDENTIFICATION OF INTRAMOLECULAR AND INTERMOLECULAR DISULFIDE BRIDGED PEPTIDES USING NEGATIVE ION MASS SPECTROMETRY

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Peptide sequencing is predominantly conducted using positive ion mass spectrometry, although, negative ion mass spectrometry can provide complementary sequencing data. Positive ion MS however is ineffective at identifying and sequencing both intra- and intermolecular disulfide bridged peptides. In contrast, the formation of a pronounced $[(M-H)^- - H_2S_2]$ fragment anion under negative ion MS conditions immediately identifies an intramolecular disulfide bridge. Additional amide cleavages from this ion provide much of the sequence of the peptide. Intermolecular disulfide peptides also produce characteristic negative ion fragmentations with subsequent amide cleavages providing sequencing data. Theoretical calculations have been used to investigate the mechanisms of the characteristic negative ion disulfide cleavages.