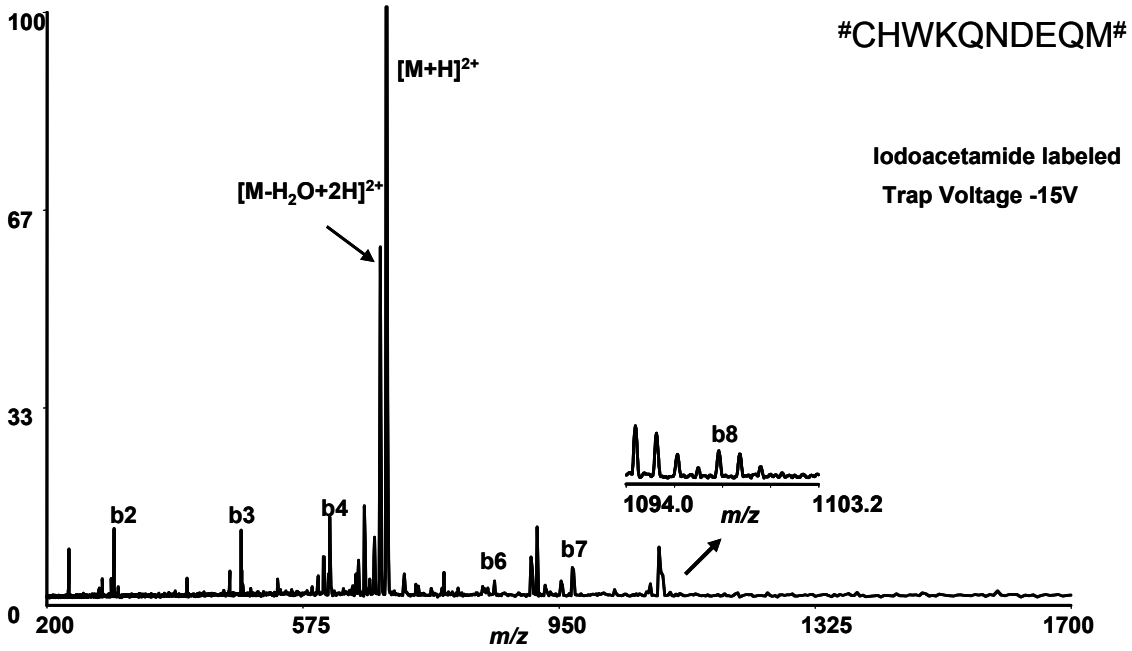
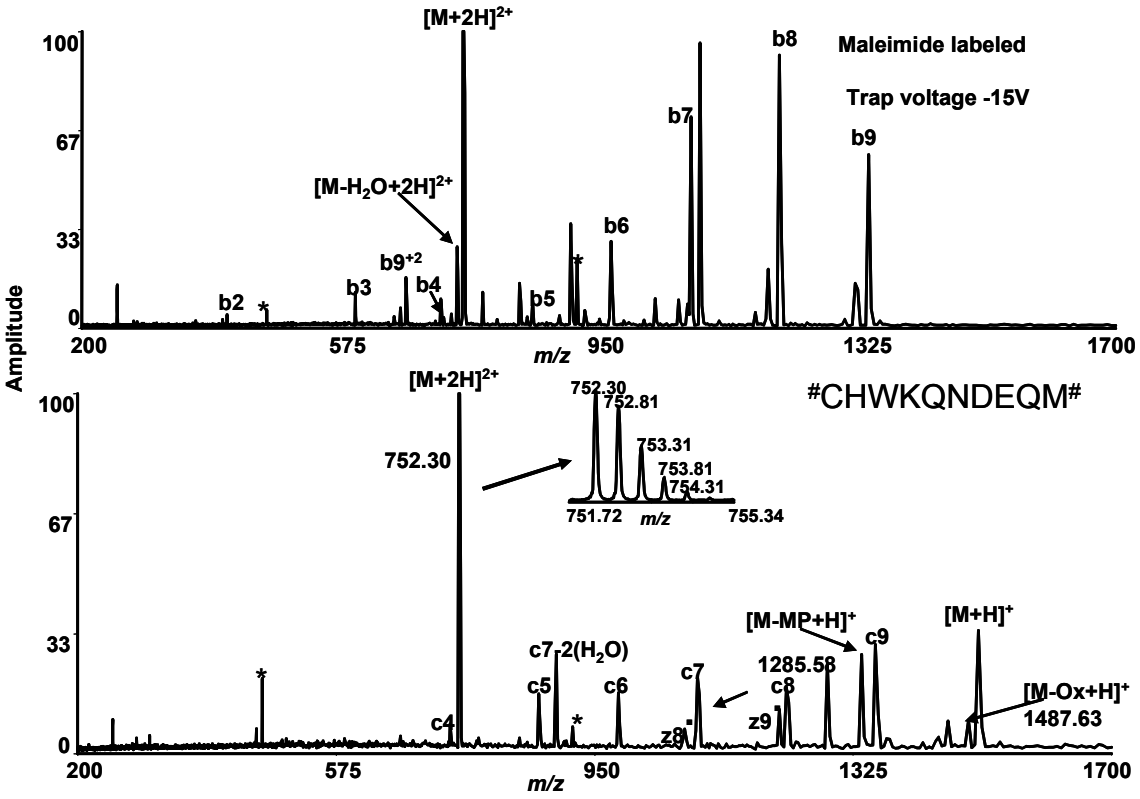
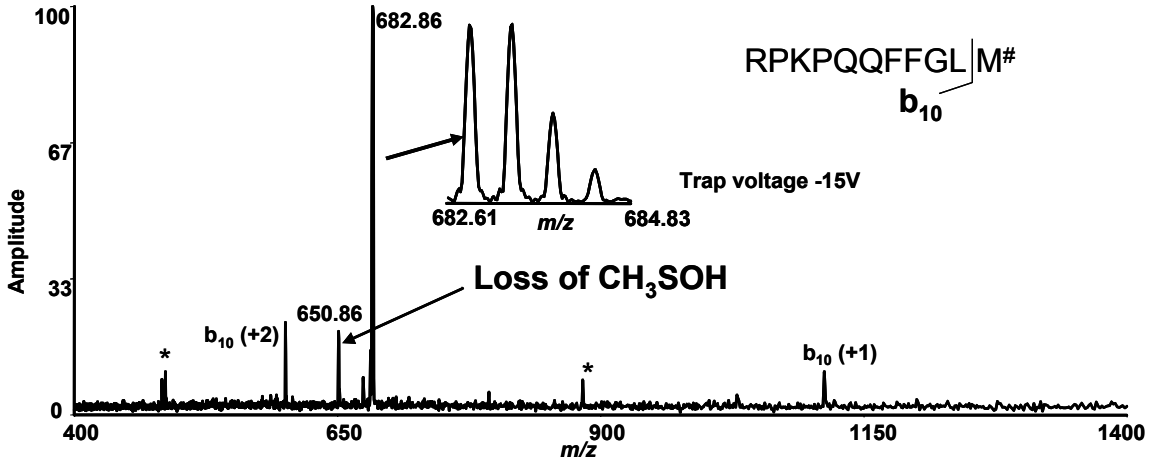
Supplementary Data:



Supplementary data 1: ESI-FTICR-MS/MS spectrum of an iodoacetamide labeled un-oxidized peptide. Several 'b' ions confirmed that N-terminal cysteine was modified with iodoacetamide. The methionine sulfur residue was oxidized to sulfoxide under this modification reaction. Collisional trap voltage was -15V. No low energy signature ion was observed for un-oxidized modified peptide.



Supplementary data 2: ESI-FTICR-MS/MS and ECD spectra of un-oxidized modified cysteinyl peptide (CHWKQNDEQM). Cysteine was modified with 3-maleimido propionic acid. A) CID-FTICR-MS spectra of modified peptide. Several 'b' ions confirmed the labeling of maleimide group on the N-terminal cysteine. Methionine was oxidized during the modification reaction. Trap voltage was -15V. No low energy signature ions were observed for un-oxidized modified peptide B) ECD-FTICR mass spectra of modified peptide. Several 'c' ions confirmed the labeling of maleimide group on the N-terminal cysteine.



Supplementary data 3: ESI-FTICR-MS/MS spectrum of methionine-oxidized Substance P. The ions at *m/z* 650.38, correspond to the loss of CH_3SOH fragment from the oxidized peptide.