

## Principle of Electron Capture Dissociation Mass Spectrometry

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### DESCRIPTION

In addition to the more established tandem mass spectrometry methods, the new fragmentation method known as Electron Capture Dissociation (ECD) is used in Fourier transform ion cyclotron resonance mass spectrometry. Disulfide bonds are preferentially broken in ECD even though they are typically stable to vibrational excitation. After backbone bond dissociation, fragmentation occurs quickly, specifically, and labile post-translational modifications and non-covalent bonds frequently stay intact. In polypeptides, ECD offers greater sequence coverage, and at higher electron energies, even isoleucine and leucine may be distinguished. The top-down verification of DNA-predicted protein sequences, de novo sequencing, disulfide bond analysis, and the combined top-down/bottom-up investigation of post-translational modifications are expected to be the key areas of ECD use in biotechnology.

The dissociative recombination of protonated polypeptide molecules with low-energy electrons (0.2 eV) is the foundation of the relatively new ion activation method known as ECD. By bombarding trapped ions with low-energy electrons, often from a heated filament electron gun or an indirectly heated dispenser cathode, ECD is utilised in FT-ICR MS. Because of the trapping requirements-ions and electrons must be held concurrently for dissociation to take place-ECD is challenging to apply in other mass spectrometers. The precursor ion must have at least two positive charges in order to observe product ions after electron capture; this decreases the overall charge by one.

### Principle

The concepts and methods used in peptide and protein structure analysis using Electron Capture and Transfer Dissociation (ECD/ETD or ExD) Mass Spectrometry (MS). ExD MS depends on interactions between gas phase protein and peptide ions bearing multiple positive charges and either free low-energy (1 eV) electrons or reagent radical anions carrying an accessible

electron for transfer. ECD generates more extended sequence fragments than more traditional fragmentation methods, including Collisionally Activated Dissociation (CAD), while preserving labile modifications during backbone fragmentation-a crucial characteristic for identifying post-translational modifications.

A multiple protonated molecule often interacts with a free electron to generate an odd-electron ion during electron-capture dissociation. The resultant ion fragments as the electric potential energy is released. The frequency of ion-electron fragmentation reactions and the quantity of ions present in an ion-electron interaction volume both influence the rate of electron capture dissociation. The cross-section of the ECD and the electron current density are directly inversely related to the fragmentation frequency. A dispenser cathode that has been indirectly heated produces a greater electron current and a larger emission surface.

There are two types of ECD devices. It can either operate in flow-through mode, where dissociation occurs as analyte ions flow continually through the ECD zone, or it can trap analyte ions during the ECD stage. A benefit of the flow through mode over other modes is that almost the whole analyte ion beam is employed. However, that makes ECD less effective in flow through mode. ECD differs significantly from other MS/MS fragmentation techniques like Electron-Detachment Dissociation (EDD), Collision-Induced Dissociation (CID), and infrared multiphoton dissociation in terms of the types of fragment ions it generates. There are two types of ECD devices. It can either operate in flow-through mode, where dissociation occurs as analyte ions flow continually through the ECD zone, or it can trap analyte ions during the ECD stage. A benefit of the flow through mode over other modes is that almost the whole analyte ion beam is employed. However, that makes ECD less effective in flow through mode. ECD differs significantly from other MS/MS fragmentation techniques like Electron-Detachment Dissociation (EDD), Collision-Induced Dissociation (CID), and infrared multi photon dissociation in terms of the types of fragment ions it generates.

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