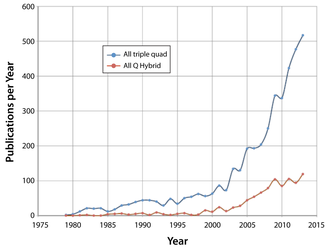
# LOW ENERGY COLLISION INDUCED DISSOCIATION (LE-CID): A POPULAR TOOL IN TANDEM INSTRUMENTS

**As in many fields of science,** when a new concept or piece of instrumentation overcomes the initial resistance to acceptance, researchers begin to adopt, modify, improve and otherwise change the concept to suit their special needs. Thus, it is not surprising that within years of acceptance, the rf-only LE-CID cell underwent a variety of modifications and was made a crucial element in a wide variety of tandem instruments. The growth in the use of rf-only LE-CID in both quadrupole and hybrid tandem instruments began to accelerate around the year 2000. While the majority of researchers used all quadrupole instruments, the rf-only LE-CID cell became an important element in hybrid instruments with non-quadrupole mass analyzers.

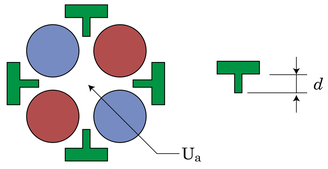
**Graph of publications using rf-only LE-CID in all-quadrupole and hybrid tandem instruments as a function of time**




High energy CID (HE-CID), as performed in sector instruments with ion accelerating potentials of many keV, and LE-CID in rf-only multipoles and ion traps differ in several important regards. Interaction of the mass selected ion in HE-CID can be described most readily in terms of classical physics scattering analysis. Furthermore, product ions are created with sufficient translational energies to enter MS2 directly. Rf-only LE-CID occurs at kinetic energies 2 to 3 orders of magnitude lower than HE-CID and for optimal performance, product ions – particularly those of lower mass – may need 'assistance' in exiting the rf-only collision cell because of their low translational energy. In addition, LE-CID in ion traps generally involve enhancing fragmentation of a mass selected ion, using its resonant, or secular, frequency to elevate its kinetic energy; the fragment ions formed can be different than those produced without resonance excitation, providing the analyst with another tool for the investigation of the ion of interest. The use of these low energy collision processes for tandem MS analyses has spread beyond the classical QqQ configuration to other mass analyzers such as the quadrupole ion trap and the ion cyclotron resonance instrument.

One of the earliest modifications of the rf-only LE-CID cell was to experiment with the number and shape of the rods from four to six, and even eight. In addition, the use of tapered rods as well as resistive rods was introduced to create an axial potential with the aim of increasing the mass range of ions transmitted to MS2. The non-linear field created by such elements helps to efficiently transport the slow ions to the exit of the rf-only LE-CID cell.

**The LINAC II rf-only collision cell from an end-on view**




## ONE "OCTOPOLE" AMONG MANY

An interesting approach to rf-only LE-CID cell modification was developed at the University of Manitoba. The additional 'T' shaped elements are used to impress an electric field between the quadrupole rods.

By varying the dimension d in a non-linear fashion along the length of the 'T' shaped rods, a fixed voltage applied to these rods results in a varying axial field in the collision cell. This helps to shorten the drift time of ions in the rf-only LE-CID cell and also increase the mass range of ions transmitted to MS2.

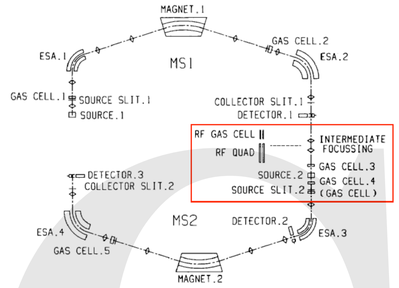
*From Loboda, A.; Krutchinsky, A.; Loboda, O.; McNabb, J.; Spicer, V.; Ens, W.; Standing, K., Novel LINAC II electrode geometry for creating an axial field in a multipole ion guide, Eur. J. Mass Spectrom. 2000, 6, 531-536.*

Probably the most popular hybrid tandem instrument today is the Q-ToF, or more correctly, the Qq-ToF, where q symbolizes the rf-only LE-CID cell. When combined with an electrospray ion source, this powerful hybrid combination provides an excellent interface for a liquid chromatograph as sample inlet. The high resolving power of the modern ToF provides mass spectra well suited to studies of a wide variety of biomolecules. Another hybrid combination that is competing with the Qq-ToF replaces the ToF analyzer with an Orbitrap. Here again the high resolving power of MS2 makes the combination attractive in the rapidly expanding area of biological applications.

At one time, developers of the QqQ instrument were advised that sufficient collision efficiency could only be obtained from high energy, keV collisions, using cells similar to those in magnetic sector instruments. This would require acceleration of the mass selected ion from Q1, injecting that ion into a collision cell, and subsequently decelerating the dissociation products prior to entry to a second quadrupole mass filter. Obviously, the rf-only quadrupole was found to be quite capable of producing fragment ions at eV energies, and the need for the introduction of a high energy collision cell was found to be unnecessary.

In fact, the opposite approach has since been found useful in hybrid tandem MS sector instruments. Thus, high energy ions in the sector mass spectrometer are decelerated, injected into an rf-only LE-CID cell, and dissociation products subsequently re-accelerated into the next mass analyzer.

## COLLISION CELL 'TURNABOUT'




Six sector tandem MS for NRMS or CAD experiments. Ion optical elements in red box can be swapped with each other between MS1 and MS2.

*From Bateman, R. H.; Brown, J.; Lefevere, M.; Flammang, R.; Haverbeke, Y. V., Applications in gaseous ion and neutral chemistry using a six sector mass spectrometer. International Journal of Mass Spectrometry and Ion Processes 1992, 115, 205-218.*

# HYBRID INSTRUMENTS CREATE MORE ALPHABET SOUP

While ToF and Orbitrap analyzers utilizing rf-only LE-CID cells have become very popular tandem instruments, the cell is amenable to use in almost any analyzer combination that can be imagined. Combinations with Fourier transform ion cyclotron resonance instruments and various arrangements with magnetic sector instruments, both before, in the middle, and after high energy analyzer sectors have been reported. Some of the reported combinations are listed here:

**QqHQC**
**BEqQ**
**BEQ**
**EBEqQ**
**qQq-FTICR**
**QqTOF**
**QqLIT**

**Where:**
**Q = quadrupole mass filter**
**q = LE-CID Cell**
**H,B = magnetic sector**
**C, E = electric sector**
**FTICR = Fourier Transform Ion Cyclotron Resonance**
**TOF = time-of-flight**
**LIT = linear ion trap**

Paul and Steinwedel's 1953 publication describing *"A New Mass Spectrometer without Magnetic Field"* began a revolution in mass analysis that continues to this day. Considered at the time to be more of a curiosity than a mass analyzer, the dedicated work of numerous workers in many different areas of research over the last six decades has created a powerful tool that will continue to provide innovative scientists with new approaches to study ion-molecule chemistry in an ever widening range of molecular species.

*Paul, W.; Steinwedel, H., A new mass spectrometer without magnetic field. Z. Naturforsch. 1953, 8a, 448-50*

**1980** — November Patent 4,234,791 issued. Enke, Yost, and Morrison Inventors. Research Corporation assignee.

**1980** — Hiller & Vestal report tandem quadrupole in photodissociation study

**1982** — Energy resolved CID provides means of differentiating isomers

**1984** — Stafford and co-workers creates new analytical possibilities by adding collision gas to ion trap

**1985** — Energy resolved MS provides insight to character of phosphorous oxy acids

**1987** — $MS^n$ in ion trap described

**1989** — Reactive collisions of GC eluates studied in LE-CID cell

**1994** — High pressure LE-CID cell characteristics reported

**1995** — CID efficiencies in the quadrupole ion trap reported

**1998** — Electron capture dissociation (ECD) for LE-CID described

**2000** — Comparison of tandem MS spectra from EBE, ion trap and QqQ instruments reported