# ECD in a Linear RF-Field without Buffer Gas

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## Overview

### Purpose

To obtain ECD spectra of peptides in a modified triple quadrupole instrument without the aid of a buffer gas.

### Method

- Triple quadrupole (Q-q-Q) instrument converted to Q-ECD-Q instrument
- Ring-filament placed at entrance of the ECD-cell (RF-only octapole)
- Filament and ECD-cell encased in a solenoid
- ESI of 50/50 methanol/$H_2O$ solution of substance P
- Doubly charged substance P [$M^{2+}$] used as precursor
- Electron energy less than 1 eV

### Result

Simultaneous transport of low energy electrons (< 1 eV) and ions through the ECD cell was demonstrated. ECD spectrum of substance P was obtained in the absence of a buffer gas.

## Introduction

In the past couple of years, Baba et al. [1] and Silivra et al. [2] independently succeeded in observing ECD in linear and three dimensional RF ion traps respectively. In both of these demonstrations, thermalization of the electrons was achieved by collision with a buffer gas (He). The possibility of hot electron capture dissociation [3] could not be excluded. More importantly, it was not possible to control the energy of the electrons precisely. We believe it is possible to achieve ECD without the intervention of a buffer gas.

## Method

- A triple quadrupole (Q-q-Q) instrument was converted to a Q-ECD-Q instrument (figure 1.):
  - A filament bent into 2mm diameter circle was placed coaxially at the entrance of the ECD-cell (RF-only octapole);
  - The filament and ECD-cell were encased in a two-part solenoid.
- Q1 was operated in a negative ion mode to observe the effect of magnetic field strength on the electron transmission efficiency:
  - Filament emission current ~ 1 μ A;
  - Electron energy < 1 eV.
- Q3 was operated to record an ECD spectrum of doubly charged substance P:
  - 10 μ M methanol/$H_2O$ ESI solution of substance P (MW:1347);
  - ESI optimized for strongest molecular-ion signal;
  - Magnetic field strength set at ~ 50 G
  - Spectra recorded as averages of 50 scans

## Results

- Carefully tuning the magnetic field strength of both parts of the solenoid and the electron energy produced an ECD spectrum of substance P (Figure 2).
- The doubly charged molecular ion (protonated and sodiated) was presented in the spectrum both with and without electrons.
- The backbone cleavage ions ($C_6$, $C_7$, $C_8$, $C_9$, and $C_{10}$ ) as well as the singly sodiated molecular ion were present in the spectrum only with electrons.
- Changing RF potential of the octapole affected electron transmission and ion transmission in opposite ways (Figure 3).

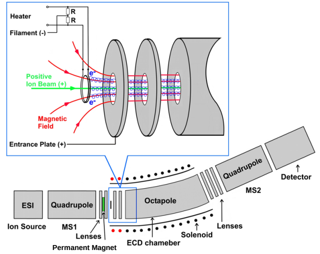

Figure 1. Schematic of Q-ECD-Q instrument.

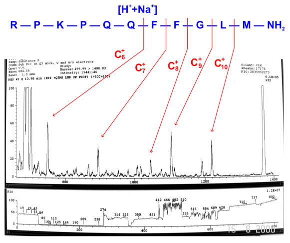

Figure 2. ECD spectrum of substance P

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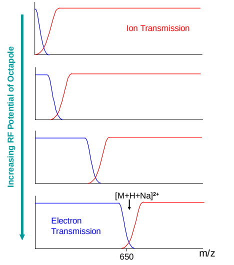

Figure 3. Electron and ion transmission with increasing RF potential of octapole (magnetic field strength and octapole RF frequency kept constant)

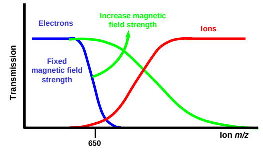

Figure 4. Effect of magnetic field strength on electron transmission efficiency with fixed octapole RF frequency and potential of octapole.

**Reference**

1. Baba T.; Hashimoto Y.; Hasegawa H.; Hirabayashi A.; Waki I. Electron capture dissociation in a radio frequency ion trap. *Anal. Chem.* **2004**, *76*, 4263-4266.
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3. Kjeldsen F.; Silivra O. A.; Ivonin I. A.; Haselmann K. F.; Gorshkov M.; Zubarev R. A. C alpha-C backbone fragmentation dominates in electron detachment dissociation of gas-phase polypeptide polyanions. *Chemistry* **2005**, *11*, 1803-1812.a

## Discussion

The spectrum shown (Figure 2) is the average of 50 single scans (3 s/scan); however, single scan spectra were similar to the averaged spectrum except that the S/N was not as good. ECD occurred efficiently without resorting to a buffer gas. It was possible to tune the average kinetic energy of the electrons while maintaining a narrow distribution of energies about this average. This opens the door to the possibility of using electron energy to achieve selectivity in fragmentation.

The magnetic field is the key parameter for this experiment. The RF potential of the octapole (ECD cell) affected the transmissions of electrons (checked in Q1 negative ion mode) and ions (checked in Q3 positive mode) in opposite ways (Figure 3). Specifically, increasing the potential of the octapole RF increased the transmission efficiency of electrons but also increased the low mass cut off of ions. Consequently, it was not possible to simultaneously transmit electrons and ions through Q2 with high efficiency. To overcome this hurdle, it will be necessary to increase the magnetic field strength (Figure 4).

## Conclusion

An ECD spectrum of substance P could be obtained in a modified triple quadrupole instrument without the intervention of a buffer gas. It should be possible to increase the efficiency of the ECD-reaction by increasing the magnetic field strength; however, this was not possible with the current instrument due to limitations placed by the geometry and size of its optical train. Therefore, the possibility of increasing the magnetic field strength is being explored on another instrument.