

A compact FT-ICR mass spectrometer with a field-emission cathode



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INTRODUCTION

Recently, we have reported the first results obtained employing a bench-top FT-ICR mass spectrometer equipped with a permanent magnet (PM) [1]. In later work, we have presented the preliminary results on electron-capture dissociation (ECD) technique realized in a PM-FT-ICR instrument using a dispenser cathode [2]. However, a very high outgassing rate of the hot dispenser cathode in combination with a narrow bore of the vacuum system (restricted by the magnet bore i.d.) has resulted in an increase of the background pressure and thus has dramatically limited a mass resolution achieved routinely. Herein, we describe the initial results on ECD of peptides obtained using compact FT-ICR instrument equipped with a field-emission cold cathode.

METHOD

Experiments were performed using a home-built 1.25T permanent magnet FT-ICR mass spectrometer described elsewhere [1] equipped with a field-emission cold cathode (Model 102811, HeatWave, Inc with minor modifications) with ~ 1-2 mm active emission area. The timing accuracy (few milliseconds) for the irradiation event in these experiments was limited by a reed relay (model C3, Hermetic Switch, Inc.) used to apply high voltage potential to the extracting grid.

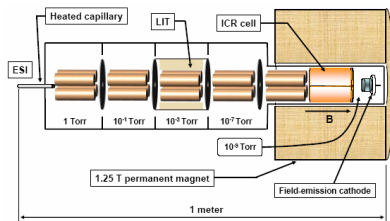


Figure 1. Schematic diagram of 1.25T PM-FT-ICR instrument.

The electron current and duration of the irradiation time were controlled by the application of a high extracting voltage to the grid located ~ 1 mm away from the cathode surface. The maximum value for electron current (up to 5 mA) was achieved at +1,800 V of the extracting voltage (in contrary to +600 V specified by manufacturer). The cathode surface was kept under a negative potential of 0-10 V in ECD experiments. In order to repel electrons (in a multiple pass mode), a negative potential was also applied to the electrostatic lens located 1 mm away from the orifice (i.e., from ESI side) trapping plate. A copper mesh (87% transparency) was placed ~1 mm away from the back trapping plate in order to avoid high voltage (from the extracting grid) penetration into the ICR cell region.

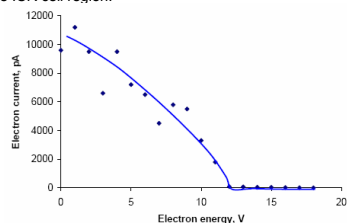


Figure 2. Electron energy distribution defined as a difference between potentials on the cathode and mesh electrodes. The electron current was measured on the detector plate placed in front (i.e., from ESI side) of the copper mesh. Extracting voltage on the grid was +1,800 V, cathode potential was -5 V and potential on the mesh was variable.

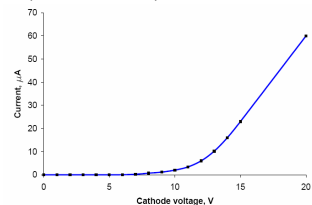


Figure 3. Electron current measured on the quadrupole ion guide as a function of cathode voltage (+1,500 V extracting voltage, +18.5 V mesh potential, both trapping electrodes were grounded).

RESULTS

Analyte ions, generated by the ESI source, were accumulated in the measuring cell of the permanent magnet FT-ICR mass spectrometer and irradiated with electrons produced by the field-emission cold cathode. The set of peptides was investigated under ECD conditions. Efficient fragmentation of doubly and triply-charged precursor ions was observed for a majority of compounds tested including Substance P, Bradykinin, Angiotensin II etc.

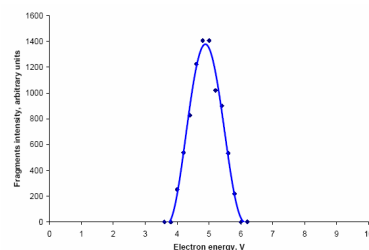


Figure 4. Abundance of fragment ions (obtained from the Substance P $[M+2H]^{2+}$ ions) in the ECD mass spectrum as a function of cathode voltage (+4V trapping voltage, 300 ms electron irradiation time, multiple pass mode).

In the multiple pass mode, a potential of +4 V was applied to the trapping electrodes during an electron irradiation event (100-300 ms long), then lowered to +0.8 V for another 500 ms and then to +0.3 V immediately before the ion excitation/detection event. Interestingly no ion signal was observed if the second event (at +0.8 V) was less than 500 ms. We propose that this delay is required to remove electrons from the ICR cell [3, 4]. No significant electron clean-up delay was required in the single pass mode. The observed fragmentation efficiency in the multiple pass mode was ~10-20 times higher than that of the single pass mode.

In all ECD experiments, an extracting voltage of +1,800 V was applied to the cathode grid electrode, +3 V to the mesh and -4.2 V to the cathode surface.

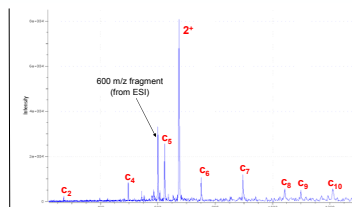


Figure 5. ECD mass spectrum obtained from Substance P $[M+2H]^{2+}$ ions.

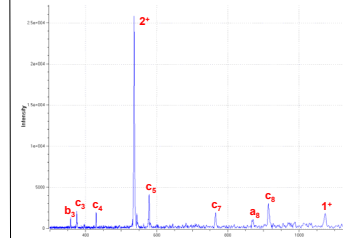


Figure 6. ECD mass spectrum obtained from Bradykinin $[M+2H]^{2+}$ ions.

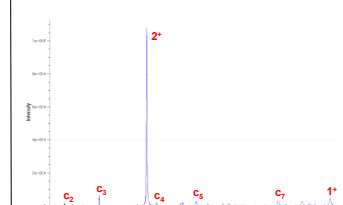


Figure 7. ECD mass spectrum obtained from Angiotensin II $[M+2H]^{2+}$ ions.

CONCLUSIONS AND FUTURE DIRECTIONS

ECD with a cold field-emission cathode has been successfully demonstrated in the permanent magnet FT-ICR mass spectrometer. The observed fragmentation efficiency is comparable with that of the full-scale FT-ICR instruments [3].

On the other hand, even at ultra high vacuum conditions (1×10^{-9} Torr) the signal durations of the product ions were found to be very short (~ 15 ms). This can be assigned to the extensive magnetron expansion of ions caused by the presence of high intensity electron beam along the centerline of the small volume (cubic 1") FT-ICR cell located in a low magnetic field (1.25T). In order to reduce the extent of the ion's magnetron expansion, in the future work we plan to minimize the delay time required for electron clean-up procedure. An alternative way of electron clean-up can be, for instance, realized through a suspending trapping event where the trapping potentials are lowered to negative potentials for a very short period of time [4].

It is noteworthy that significant improvement in the instrument's overall performance is expected after the ongoing installation of a new sub-compact magnet with a higher field (5T).

ACKNOWLEDGEMENTS

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