A wire-ion-guide ICR cell for low-magnetic-field FTICR MS

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OVERVIEW

Fourier transform ion cyclotron resonance mass spectrometry (FTICR MS) is the leading MS method in terms of mass accuracy and resolution. This work is a continuation of our research on the use of low-field-strength magnets in FTICR to produce cheaper, smaller (benchtop-size) and easier-to-maintain FTICR MS [1,2]. However, in biological applications such as proteomics, the highest performance of this technique is observed only for a mass range of up to about m/z = 2000, which is even less with more convenient and less costly magnets of low field strength (1 - 5 T). A novel method involving the introduction of a central wire electrode into the ICR cell in order to achieve electric field modifications favorable for higher performance is investigated in this work. This design is called a wire-ion-guide (WIG) ICR.

INTRODUCTION

In 1994, Russell and coworkers published pioneering work on the WIG FTICR MS [3]. This early WIG cell was designed to trap high energy- high m/z ions produced by MALDI because the high voltages (>10 V) required to decelerate these ions entering a traditional ICR cell also produced a large radial electric field which had the adverse effect of pushing the ions outward from the cell center. In the typically employed setup with an ESI ion source and quadrupole ion guides, the kinetic energy of the ions introduced into the ICR cell is minimized [1,2]. Our approach in this project is to adjust the total radial electric field (the sum of the outward directed radial electric field due to the trapping electrodes and the inward directed radial electric field due to a negative potential (relative) on the wire), so that the m/z limit and the mass resolution of our low-magnetic-field FTICR method may increase. The potential energy surface created in the ICR cell with a negative (relative to the trapping voltage) voltage on the wire is illustrated in Figure 1. It has also been previously demonstrated that the presence of a central electron beam inside the ICR cell may improve the performance in a fashion similar to the suggested WIG ICR cell [4].

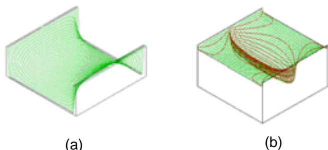

Figure 1. SIMION 7.0 simulations of the potential energy surfaces of the (a) unmodified (b) WIG ICR cells. Trapping voltage = 3.0 V, wire voltage = 1.0 V.

INSTRUMENTATION

A 1” cylindrical ICR cell consisting gold plated copper electrodes and a wire electrode (0.12 mm diameter, Cu) centered along the z-axis and isolated from the trapping electrodes (see Figure 2) has been designed and fabricated. The same ion optics as reported earlier were used where ions were formed by electrospray and transported through several pumping stages guided by rf quadrupole fields. Ions are trapped and gated using a linear ion trap (LIT) prior to introduction into the ICR cell [1,2].

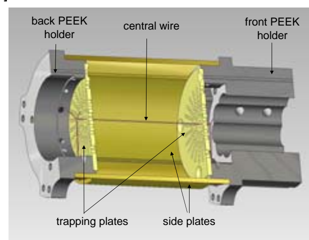

Figure 2. A cut-off view of the wire-ion-guide cell showing the central wire mounted on the two PEEK holders using supporting mounting wires

PRELIMINARY RESULTS

In our initial WIG ICR experiments, the peptide ions produced by electrospray ionization were introduced into the WIG cell in-line with the wire to avoid major modifications to the front-end ion optics system. Figure 3 is a mass spectrum of bradykinin ions obtained with the WIG cell, when the pressure in the ICR cell was in the region of 10^{-8} torr. The resolution obtained in this experiment is 3000 (at FWHM). However, this signal was observed only with a specific combination of voltages as shown in Figure 4 and the optimization of these conditions are still under investigation. Notice that the wire voltage was initially at – 2.0 V in order to attract the ions into the cell. When the excitation started, this voltage was pulsed to 3.6 V for a duration of 10 μs to assist the ions to “pull away” from the wire. The wire voltage was then adjusted to a value that yielded the best signal in terms of resolution and sensitivity. With only constant voltages (including 0.0 V) applied to the wire, either no signal was observed or the performance (resolution/ sensitivity) decreased.

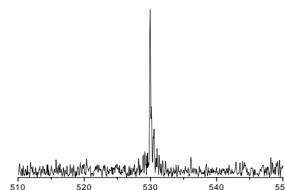

Figure 3. A WIG FTICR spectrum of electrosprayed bradykinin 2+ ions. Voltage conditions employed for this experiment are shown in Figure 4.

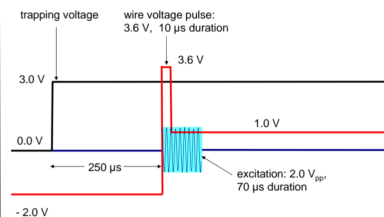

Figure 4. A schematics of the voltage steps involved in the WIG experiment that resulted in the spectrum shown in Figure 3 (not to scale).

The maximum trapping time prior to excitation (the period of time from the raising of the trapping voltage to the beginning of the excitation event) obtained was about 250 μs. Longer trapping times yielded either no or worse signal than shown in Figure 3. Simulations revealed that this is mainly due to the ions tending to collide with the wire during this trapping period. This short trapping time may be the main hurdle in the implementation of this specific WIG design and voltage configurations since insufficient relaxation of the ions prior to the excitation may have resulted in short time domain transients (about 50 ms for the spectrum in Figure 3). In order to overcome this, we are currently investigating the possibility of further changes to the wire voltage during the trapping period such as continuously increasing the voltage on the wire to a more positive value. Another suggested experiment is to introduce the ions off-axis to the wire, instead of using the current in-line ion introduction system. Our simulations showed that by implementing off-axis ion introduction, trapping times as long as seconds can be obtained.

CONCLUSIONS AND FUTURE DIRECTIONS

Our initial experiments showed the feasibility of the use of a WIG cell for the low field magnet ICR MS. The resolution of the initial design was limited by the short trapping times achieved prior to excitation. This is attributed to the in-line ion introduction used resulting in ion loss to the wire (implemented to demonstrate proof-of-concept experiments without introducing major modifications to the instrumental setup). A future modification in order to obtain longer trapping times will focus on off-axis introduction of the ions to the WIG ICR cell.

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