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A simplified toroidal ion trap mass analyzer

Nicholas Taylor, Daniel E. Austin*

Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602, USA

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ABSTRACT

A radiofrequency toroidal ion trap mass analyzer comprised of four cylindrical electrodes is described. The ion trap consists of two RF electrodes and an AC electrode that surround a central electrode. Mass-analyzed ions are ejected through a slit in the central cylinder. A conversion dynode and electron multiplier are contained within the central cylinder for ion detection. The orientation of the RF and AC electrodes allows for inward-radial ejection of ions, removing the need for ion collection optics. Resolution of the toluene m/z 91 ion was determined for both a forward mass selective instability scan as well as for a reverse scan with resonant ejection. These experiments were performed in parallel with the stretching and compressing of the RF ring electrode spacing. Experimental resolution (Δm) values compare well with previous toroidal ion traps. The stability diagram for the toluene m/z 91 ion is also reported. The diagram possesses a slightly asymmetric profile due to asymmetry of the trapping dimensions as well as the curvature of the toroidal trapping region. Finally, the tandem (MS^2) mass spectrum of iso-butylbenzene is reported.

1. Introduction

Quadrupole ion traps (QIT) have for decades been successfully used as ion storage devices, reactors for ion/molecule reactions, and mass analyzers [1–5]. Since Wolfgang Paul first unveiled his ion trap in 1953 [1], much attention has been focused on the development of ion trap designs. In addition to novel designs, miniaturization of these devices has also been pursued. Naturally, certain complications arise when reducing the scale of a device. For the QIT mass analyzer, one issue lies with machining millimeter scale hyperbolic electrodes with acceptable tolerances. Thus, a new approach was required to make miniature mass spectrometers a successful reality.

In 1977, Bonner et al. reported on the construction of the first cylindrical ion trap (CIT) [6]. A simplified version of the QIT, the cylindrical electrode geometry allowed for acceptable machining tolerances and analytical performance relative to the QIT. However, it was soon realized that physically reducing the trapping dimensions also reduced the ion storage capacity due to space charge repulsion, putting a limitation on miniature mass analyzers. A solution presented itself in 1995 with the U.S. patent of the linear ion trap (LIT) by Thermo Finnigan [7]. A primary advantage offered by the LIT design over the QIT and CIT is its increased dimensionality, alleviating problems associated with space charge effects. This was realized by the Cooks group at Purdue University who in 2004 introduced the rectilinear ion trap (RIT) [8]. The RIT is a simplified LIT design in which the truncated hyperbolic electrodes are replaced with flat plates forming a rectangular box capable of ion storage. Despite its simplified design, a resolving power of 1200 was achieved at an m/z 502 for the compound PFTBA. Due to the RIT's increased dimensionality, a superior ion trapping capacity relative to a CIT was demonstrated. From this work, a portable mass spectrometer system equipped with a RIT mass analyzer has been reported [9].

In 2001, Lammert et al. [10] presented a novel ion trap mass analyzer that utilized a toroidal trapping volume. The design was based on the QIT; however, the axis of rotation was moved from the center of the end caps to a line outside of the cross section of the quadrupole trap. Similar to the LIT, the motivation for such a design was fueled by the need to increase trapping dimensionality while preserving the opportunity for miniaturization. Analogous to the LIT, the trapping capacity of a toroidal ion trap can be orders of magnitude higher than a standard QIT of equal trapping dimensions, greatly alleviating performance problems induced by space charge effects. Torion Technologies Inc. demonstrates this benefit with its Guardion-7 GC-TMS system [11,12]. This hand-portable system is equipped with a gas chromatography (GC) system coupled to a miniature toroidal mass analyzer based on the original design by Lammert.

In 2007, Austin et al. presented the Halo ion trap [13]. Unique compared to the systems described above, the Halo ion trap is based on the use of non-equipotential electrodes. The trapping region is established using two ceramic plates imprinted with concentric metal rings and coated with a thin layer of germanium. Using

* Corresponding author. Tel.: +1 801 422 1551.
E-mail address: austin@chem.byu.edu (D.E. Austin).

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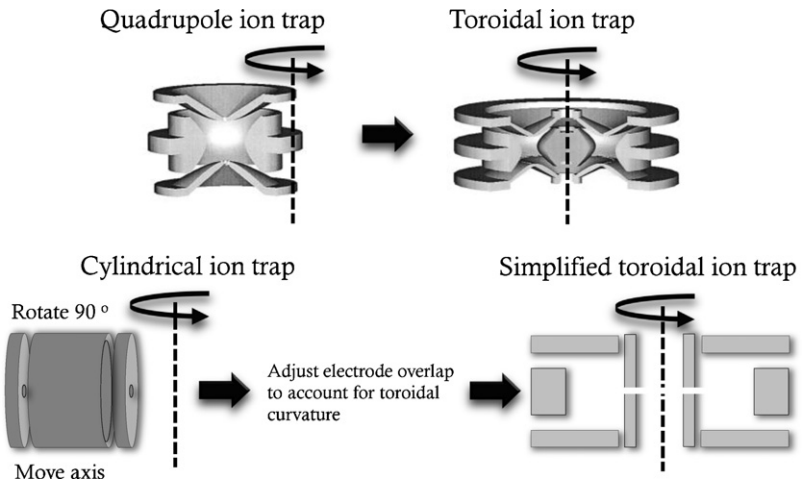

Fig. 1. Conceptual illustration of the simplified toroidal ion trap mass analyzer based on the rotation of a cylindrical ion trap. Not drawn to scale. Top images "reprinted from *International Journal of Mass Spectrometry*, vol. 212, Stephen A. Lammert, Wolfgang R. Plass, Cyril V. Thompson, Marcus B. Wise, Design, optimization and initial performance of a toroidal rf ion trap mass spectrometer, 25–40, 2001, with permission from Elsevier."

a capacitive voltage divider, a toroidal trapping region is created between the two ceramic plates. Trapped ions are radially ejected into the center of the device, in contrast to axial ejection employed in previous toroidal ion traps. A benefit of a non-equipotential electrode design is the ability to achieve any desired higher order field strength by simple adjustment of the voltages applied to each ring. A later design of this instrument utilized axial ejection of ions through slits machined in the ceramic plates [14].

Up until now no effort has been reported to simplify the electrode geometry of the toroidal ion trap as has been done with the QIT and LIT. Part of the reason for this stems from an electrode asymmetry required in the toroidal design and described by Lammert et al. [10]. Because of the curvature of the trapping region, electrode surfaces exterior the trapping center are "viewed" by trapped ions as having a larger solid angle, and therefore a larger effect on potential than electrodes closer to the axis of rotation. In the asymmetric design by Lammert, the asymptote angles of the electrodes were modified so that the outer ring electrode is sharper and the inner ring electrode broader. Implementing such an asymmetry in a toroidal trap with simplified (i.e., cylindrical) electrode surfaces is not obvious. However, the advantages of the toroidal ion trap make it an ideal candidate for miniaturization once the electrode geometry can be simplified.

We present a design for a toroidal ion trap in which asymmetric overlap of cylindrical electrodes satisfies the abovementioned asymmetry requirement. This study reports on the development and performance of this simplified toroidal design as an effective mass analyzer. Tandem mass spectrometry capabilities are also demonstrated.

2. Experimental

2.1. Mass analyzer design

Initial designing began by considering the rotation of a CIT rather than the QIT. As mentioned, one must also account for the asymmetry of the electrode surface area viewed by the trapped ions. This was achieved by adjusting the overlap of the electrodes as shown in Fig. 1. As a result, ions are ejected radially rather than axially allowing all ions to converge onto a single point, removing the need for focusing optics of analyzed ions. Simulations suggest that unidirectional ejection is achieved with this electrode orientation, eliminating ion losses in the outward radial direction. In addition, by moving the axis of rotation beyond the edge of the end cap a cavity is created into which ions can be ejected and subsequently detected. This also allows for a larger toroidal radius to be created, increasing the dimensionality of the mass analyzer. An illustration of the prototype design with gas/sample inlets, ionization, and detection components is shown in Fig. 2.

2.1.1. Field optimization and high order multipole evaluation

SIMION 8.0 (Scientific Instrument Services, Ringoes, NJ) was used to evaluate the contribution of higher order multipoles to the over-all trapping field. The method of obtaining the multipole components was achieved by using the method described in reference [14]. Briefly, this was accomplished by setting up a potential array representing the device, then determining the potential at every grid unit along the $z = 0$ ion ejection axis. The resulting function was then imported into MatLab (The MathWorks, Natick, MD) and fit to a 25th order polynomial. The coefficients obtained were then used to calculate the magnitude of the hexapole, octopole, and decapole components.

As mentioned in previous work [14], exact solutions to the Laplace equation in cylindrical coordinates do not exist for a toroidal ion trap in which the axis of rotation passes through an electrode. The electric field cannot be continuous and differentiable at the axis of rotation except for the case where $\nabla\Phi = 0$. Thus, strictly speaking, cylindrically symmetric multipoles representing electrical potential do not exist in any toroidal system. However, the electric field in the immediate vicinity of the trapping center, at some distance from the axis of rotation, can be approximated using higher-order terms (r^2, r^3, r^4, etc.) analogous to the set of multipoles used for all other quadrupole ion traps. In the interest of readability the higher-order terms will be referred to using the conventional mulitpole terminology (quadrupole, hexapole, octopole, etc.). Note, however, that ion motion does not respond exactly the same to these higher-order terms as it does in the higher-order multipoles of quadrupole ion traps.

Previous works with QIT's have shown that a near 0% octopole [15] or a slightly positive octopole [16] can yield enhanced mass resolution. How these observations translate to the toroidal geometry has yet to be determined. It is therefore, important that the octopole component be adjustable. Given the design in Fig. 2, the easiest way to adjust the octopole component is to stretch or compress the RF ring electrode spacing. This stretching and compressing was modeled with SIMION 8.0 and the results of the higher order multipole components can be seen in Fig. 3. It was found that an RF ring spacing of approximately 11.82 mm ($z_o = 5.91$ mm) generates