Coaxial Ion Trap Mass Spectrometer: Concentric Toroidal and Quadrupolar Trapping Regions

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ABSTRACT: We present the design and results for a new radio-frequency ion trap mass analyzer, the coaxial ion trap, in which both toroidal and quadrupolar trapping regions are created simultaneously. The device is composed of two parallel ceramic plates, the facing surfaces of which are lithographically patterned with concentric metal rings and covered with a thin film of germanium. Experiments demonstrate that ions can be trapped in either region, transferred from the toroidal to the quadrupolar region, and mass-selectively ejected from the quadrupolar region to a detector. Ions trapped in the toroidal region can be transferred to the quadrupolar region using an applied ac signal in the radial direction, although it appears that the mechanism of this transfer does not involve resonance with the ion secular frequency, and the process is not mass selective. Ions in the quadrupolar trapping region are mass analyzed using dipole resonant ejection. Multiple transfer steps and mass analysis scans are possible on a single population of ions, as from a single ionization/trapping event. The device demonstrates better mass resolving power than the radially ejecting halo ion trap and better sensitivity than the planar quadrupole ion trap.

INTRODUCTION

Radio-frequency (rf) ion traps are among the most widely used mass analyzers, combining several advantages including high sensitivity, reasonable mass resolution, high duty cycle, compact size, tandem capability, and reasonable cost.1–5 Besides the original Paul-type quadrupole ion trap, several geometrical variants, such as linear,6–8 rectilinear,9,10 cylindrical,11,12 and toroidal ion traps13,14 have been developed, each with unique attributes resulting from the trapping geometry. For instance, the ion trapping capacity is larger in the linear, rectilinear, and toroidal ion traps compared with the quadrupole trap due to the extended axial dimension of the trapping volume.

The toroidal ion trap, invented by Bier and Syka13 and developed by Lammert et al.,14 represents a geometric variation on the quadrupole ion trap. The toroidal trapping region provides a larger ion capacity than that in quadrupole traps. A toroidal ion trap has recently been included in a commercial, portable GC-MS system — an application in which ion capacity and corresponding sensitivity are important considerations.15 Austin et al.16 described a device called the Halo ion trap, in which a toroidal trapping field was made using two planar electrode substrates. A set of 15 concentric ring electrodes was lithographically deposited on each substrate, which were then covered with a thin film of germanium. The two plates were mounted facing each other to form the trap. Appropriate rf voltages were applied to each ring using a capacitive voltage divider, with the amplitude on each ring chosen to establish the desired fields within the trap. Ions were resonantly ejected toward the center of the device and then pushed out toward a detector. A more recent version of the Halo ion trap included annular slits in the ceramic plates.17 Ions were ejected axially, that is, parallel to the axis of geometric rotation — the same ejection direction as was employed in the toroidal ion trap described by Lammert. Because of the improved ejection, mass resolution was better relative to the original Halo ion trap. Both versions of the Halo ion trap retained the large storage volume of the toroidal ion trap.

Zhang et al.18 used this same two-plate approach to create and demonstrate a quadrupole ion trap called the planar quadrupole trap mass analyzer. In the planar quadrupole trap, a capacitive voltage divider provided different rf amplitudes to each of 24 lithographically patterned rings on each plate resulting in a quadrupolar potential distribution. Higher-order multipoles could be individually controlled and adjusted to optimize performance.19,20 Although the large trapping volume of the toroidal geometry was lost, the equations of ion motion are better understood in the quadrupole geometry. As a result, the planar quadrupole trap demonstrated significantly higher mass resolution than either design of the Halo ion trap.

These two-plate ion traps demonstrate a novel, general method for producing electric fields for ion traps or other
devices. The use of microlithography allows devices and fields to be relatively free of the physical limitations imposed by machining tolerances, surface roughness, electrode alignment and placement, and similar obstacles. In addition, using a number of independent electrodes allows substantial variability and opportunity for creating electric fields. In essence, field geometry using this approach is not constrained or limited by substrate geometry, in contrast to conventional ion traps. Within limits, any potential distribution can be created using the correct combination of electrode patterns and applied voltages.

This article describes a surprising twist to this approach: the ability to produce multiple, linked trapping regions simultaneously between two such plates. A toroidal region is formed using the outer rings, and a quadrupolar trapping region is formed in the center. The two trapping regions share a common axis of symmetry — hence the name coaxial ion trap — and can be operated more or less independently of one another due to the independent nature of the rings. In addition to trapping and mass analysis, ions can be transferred between the two trapping regions. After ions are ejected from the toroidal trapping region into the quadrupole trapping region, they can be collisionally cooled down in the center region and mass-selectively ejected. The arrangement of the two trapping regions and the electric fields in the coaxial ion trap are shown in Figure 1. An ion trap with two or more trapping regions may combine the advantages of both trapping geometries and demonstrate unique opportunities for experiments in tandem mass analysis, quantum computing, and ion–ion reactions.

**METHODS**

**Fabrication and Assembly of Device.** The coaxial trap is made using plates identical to those used in the previously described planar quadrupole trap mass analyzer. Fabrication details are provided in section 1 of the Supporting Information. The trap consists of two ceramic plates mounted 6 mm apart, the facing surfaces of which are imprinted with concentric metal rings (Figure 2). Appropriate rf potentials are applied to each ring producing trapping fields in the space between the plates.

Each trapping plate was patterned with 24 aluminum rings ranging in radius from 0.5 mm to 13.2 mm in increments of 0.5 mm. All but the innermost ring were 0.1 mm wide. Because of processing constraints, the innermost ring extended from the center hole to a radius of 1.8 mm and was therefore much wider than any other ring. The center hole in each plate, through which ions are ejected, was 1 mm in diameter. The deposited aluminum layer extended throughout the inside of the central hole to maintain a well-defined electric potential as ions eject from the trap. The holes for vias, 0.127 mm in diameter, were positioned to fall immediately beneath the corresponding rings. Aluminum patterning on the backside of each plate consisted of connections from each via a contact pad. Each ring had its own contact pad for independent control. Backside connections between vias and contact pads were 0.25 mm wide.

Each trapping plate was controlled using a printed circuit board (PCB). The contact pads on the backsides of the substrates were connected to the PCBs using spring-loaded (pogo-style) pin connectors as shown in Figure 2. A voltage divider consisting of a series of capacitors was soldered onto each PCB. The value of the capacitors between each ring was determined by the potential intended for each ring while maintaining a constant overall capacitance for each plate (25 pF).

**Calculating and Optimizing Electric Fields.** The choice of potential values for each ring was made by modeling the electric fields using SIMION 8.0 (SIS, Ringoes, NJ). The electric field within the trap volume is a result of the potential distribution on the germanium layer, which in turn is determined by the underlying rings. The potential of the germanium immediately above a given ring is the same as the ring itself. The potential between rings can be solved using Ohm’s Law and integrating over the radius. This can be done in SIMION using a previously described method.
The trapping field of the radial direction (along \( z = 0 \)) in the coaxial ion trap was simulated to approximate the radial field in the toroidal ion trap\(^{22,23} \) and planar quadrupole ion trap.\(^{18} \) The field in the axial direction was selected to be similar to the axial field of the planar quadrupole ion trap (working within the constraints of the Laplace equation). Several sets of potential functions were identified as feasible during the optimization process. For the potential distribution used for this article, the rf amplitudes applied to each ring are given in Figure S1 of the Supporting Information. A series of capacitors, acting as an rf voltage divider, determined the rf amplitude applied to each ring.

Figure 3 shows the time-independent electric potential and field distributions within the coaxial trap, as calculated using SIMION. In part a of Figure 3, equipotential lines indicate the two trapping regions. Part b of Figure 3 shows the axial potential function and electric field, which is the direction in which ions are ejected out from the quadrupolar trapping region. The higher-order component of the axial field is shown Figure S2 of the Supporting Information — these components are expected to have a significant effect on the resolving power of the quadrupolar trapping region.\(^{22,23} \) In part c of Figure 3, the radial potential function and the resulting electric field are shown. This is the direction in which ions are transferred between the trapping regions. Note that the two trapping regions have opposite polarity. Because the field along the radial direction spans two trapping regions, the high-order components of the field in the toroidal trapping region and quadrupolar trapping region need to be studied separately as shown in Figure S2 of the Supporting Information. In both trapping regions, the electric fields deviate somewhat from the ideal toroidal and quadrupolar fields. Part of this deviation is a result of the necessity of field continuity between the trapping regions. In addition, the small ratio of plate spacing to ejection hole size increases field imperfections in the quadrupolar trapping region, as is also the case with conventional ion traps.\(^{24,25} \)

**Experimental Setup.** An rf power supply (PSRF-100, Ardara, North Huntingdon, PA), operated at 1.43 MHz and 500 V\(_{p-p}\) provided the trapping rf. Supplemental time-varying signals were provided by a function generator (SRS, DS345, Sunnyvale, CA), which controlled the timing of ionization and the ejection ac signals. An ac signal used for axial resonant ejection from the quadrupole trapping region was provided by an arbitrary waveform generator (Agilent, Model 33250A, Santa Clara, CA) and was applied at the central hole. Another ac signal (used to transfer ions from the toroidal region to the quadrupole region) was provided by a function generator (SRS, DS345, Sunnyvale, CA). A custom-made electron gun and the two function generators mentioned above were triggered by two pulse generators (BNC, Models 565 and 575, San Rafael, CA). These two pulse generators and the rf power supply were synchronized by another function generator (Figure S3 of the Supporting Information).

The two plates comprising the ion trap were mounted using a grounded, 6 mm thick metal spacer to maintain accurate plate spacing and alignment. Holes in the spacer allowed introduction of the ionizing electron beam, helium gas, and two Teflon tubes connecting to the sample inlet and to a Pirani gauge (Kurt J. Lesker, Clairton, CA). The entire assembly (Figure 2) was contained within a small vacuum chamber, and high vacuum was maintained using a 70 L/s turbomolecular pumping system (Leybold, BMH70 DRY, Export, PA). A continuous-dynode electron multiplier (DeTech, Palmer, MA) was mounted near the ejection hole of one plate.

All test samples were HPLC grade or were >99% pure. The headspace vapors of samples were introduced directly into the trapping region via precision needle leak valves (Nupro/Swagelok, Solon, OH) and heated transfer lines. Sample pressure was normally 2 \( \times 10^{-3} \) Torr (uncorrected), and helium buffer gas was admitted into the vacuum chamber to cool the ions via the same precision needle leak valves to a nominal pressure of about 3 \( \times 10^{-3} \) Torr.

Basic instrument functionality was demonstrated using the procedure shown in Figure 4. Ions were produced in situ within both the toroidal and quadrupolar trapping regions using an electron gun and ionization time of 12 ms. The electron beam was directed tangential to the toroidal region. Following ionization, the ions in the quadrupole trapping region were analyzed using dipole resonant ejection mass analysis. This was followed by a short period in which ions were cooled by collisions with background helium. The quadrupole region was then scanned again to verify that all ions initially trapped in the quadrupole region had been ejected, and that the quadrupole region was empty. This second quadrupole scan was followed by another cooling period. Next, an ac signal (25 V\(_{p-p}\)) was applied to the outermost rings of the toroidal trapping region to transfer ions into the quadrupole region. These ions were then trapped and cooled within the quadrupole region, then resonantly ejected through the center hole in the substrate and onto the electron.

Figure 3. (a) Isopotential contours in the coaxial ion trap, (b) potential function and field along axial (\( z \)-) direction in quadrupolar region, (c) potential function and field along the radial (\( r \)-) direction through both trapping regions.
multiplier detector. The ac signal used for resonant ejection had amplitude of 1 Vp-p and was applied to the innermost ring on one of the plates, whereas keeping the corresponding ring on the other plate grounded, analogous to dipole ejection in conventional ion traps. The frequency of the ac signal applied to the toroidal region was 1100 kHz, and the ac signal applied to the quadrupole region was scanned from 800 to 50 kHz over a period of 100 ms, providing mass-selective ejection. The signal was amplified by a current sensitive amplifier (EG&G PARC, Model 181, Oak Ridge, TN) and then recorded by a digital oscilloscope (LeCroy, WaveRunner 6050A, Chestnut Ridge, NY). Figure 4 illustrates ion movement inside the trap at each scan step: creation of ions inside the trap, cleaning of ions inside the quadrupolar region, transfer of ions from the toroidal region to the quadrupolar region, and mass selective ejection of ions from the quadrupolar region to the detector. This sequence is also represented in part a of Figure 5.

Any combination of quadrupole and toroidal scans is possible with this setup. For instance, part b of Figure 5 shows an experiment in which three transfer steps were applied in sequence (using a single ionization step) with a quadrupole scan subsequent to each transfer. The ion capacity of the toroidal trapping region was investigated using this multiple-transfer process, with a single sampling/ionization event followed by up to 30 repetitions (i.e., 30 toroidal scans each followed by a quadrupole scan).

**RESULTS AND DISCUSSION**

Instrument performance was tested using several volatile organic compounds, including bromopentafluorobenzene, toluene, trichloroethylene, and tetrachloromethane with the above procedure. Part a of Figure 6 shows the resulting spectra of bromopentafluorobenzene at a pressure of 2 × 10⁻⁵ Torr (helium pressure 3.45 × 10⁻³ Torr). The spectra were obtained by sweeping the resonant ejection frequency from 800 to 50 kHz in 100 ms for the mass analysis in the central region and applying 1100 kHz ac signal in 100 ms for the transfer process from the toroidal region to the quadrupole region. Mass assignments are based on calculated secular frequencies for the quadrupolar trapping region. During the first quadrupole scan, peaks with mass-to-charge ratio (m/z) of 98, 117, 129, 136, and 168 were detected, as shown in parts b and c of Figure 6, matching well with the standard mass spectrum of bromopentafluorobenzene.²⁶ Because the applied ac for resonant ejection out of the quadrupole trap relied on a linear scan of frequency, the mass resolution drops at higher masses when plotted as a mass-domain spectrum. Mass resolution in this device is better than that previously demonstrated by radial ion ejection in the halo ion trap, which is similar to the toroidal trapping region in the present device acting alone. Mass spectra for other compounds are available in Figure S4 of the Supporting Information and show similar performance and the expected patterns for each compound.
As shown in part a of Figure 6, no ions were ejected from the quadrupole region during the second quadrupole scan indicating that the quadrupole region was empty prior to the first transfer step. After the first toroidal transfer step, ions were detected during the next quadrupole scan demonstrating that these ions had been transferred from the toroidal trapping region to the quadrupole trapping region.

Following the first transfer step and subsequent mass analysis, additional toroidal transfer scans and quadrupole mass scans on the same population of ions (i.e., from one ionization event) showed additional ejected ions (part a of Figure 6). These ions presumably were trapped in the toroidal region, were not transferred to the quadrupole region during the first transfer scan, and were subsequently transferred. Multiple sets of toroidal and quadrupole scans showed the same result implying (1) that the toroidal region had trapped many more ions than the quadrupole region, as the populations of ions do not appear to be depleted after three transfer scans, and (2) that the transfer of ions from the toroidal region to the quadrupole region was either not very efficient or proceeded only until the quadrupole region had reached a certain population. Slight mass discrimination may be observed during the transfer process by comparing the mass spectra obtained from the first quadrupole scan and third quadrupole scan after a toroidal transfer process as shown in parts b and c of Figure 6.

In part a of Figure 6, the baseline during the toroidal scans is elevated due to electrical noise. This elevated baseline is present whether ions are analyzed or not and does not diminish after repeated scans from a single ionization event.

The originally intended mode of operation using this device was to employ resonant transfer of ions, that is, the radial secular motion of ions in the toroidal region would be resonantly excited by the ac signal applied to the outside rings. Had this been the case, mass-selective transfer should have been observed. However, we observed that a wide range of masses was transferred, even if only one frequency of applied ac was used. In addition, applied ac with a frequency higher than the secular frequencies of any trapped ion was also effective at transferring ions. From these results, we conclude that resonant excitation was not responsible for the observed ion transfer.

To determine the mechanism of observed ion transfer, we next studied the relationship between the phase of the drive rf and the phase of the ac applied to the outer rings during the toroidal transfer step. In general, and in the work described above, these frequencies are not exact multiples of each other, and the phase relationship between them is random. However, reports by Harden and Wagner,27 by Mastoris,28 and by Dawson and Lambert29 describe the possible importance of synchronizing the ejection pulse to the ring electrode in quadrupole ion traps. They concluded that relative efficiencies of ejecting different masses would be dependent on the phase relationship between the drive rf and the ac signal applied for resonant ejection. Many experimental systems30–32 have been employed to test this “pulse/rf synchronization circuit” on the performance of ion traps both as an ion source and as mass analyzers. In those experiments, an output trigger pulse gated to a specified phase angle of the drive potential was used. This triggered pulse activated the ejection pulse generator, and the phase angle was

![Figure 6](image_url)
was recorded in respect to the phase differences between trigger pulse and rf signal.

To investigate the effect of phase-synchronized ion ejection on the ion transfer process in the coaxial ion trap, a periodic dc pulse was applied to the outmost ring to replace the original ac signal applied during the toroidal transfer scan. This dc pulse was synchronized with the drive rf. The rf phase at which this dc pulse was applied, the repetition rate of the dc pulse, and the length of the dc pulse were explored for their effect on ion transfer. A short dc pulse produced by the same BNC 575 pulse generator with 24 ns width and 12 V amplitude was applied to the toroidal region at different rf phases. Square pulses with different widths from 24 ns to several rf wavelengths including $1.5 \lambda$, $2 \lambda$, and $3 \lambda$ were investigated, applied at different rf phases (Figure 55 of the Supporting Information). The relationship of peak intensity with rf phase angles when dc pulses were used for the transfer process is shown in Figure 7. When dc pulses were applied at certain rf phases, ions could not be transferred from the toroidal to the quadrupolar trapping regions, whereas at other phases transfer occurred. In addition, when the repetition rate of the dc pulses was reduced, the number of ions transferred decreased proportional to the number of pulses applied, as shown in Figure S6 of the Supporting Information, indicating that the transfer time also has an effect on the transfer process. Similarly, when using sinusoidal signals to effect ion transfer, the number of ions detected increases in proportion to the duration of the applied supplementary ac signal, at least up to the point of saturation. Although these results are consistent with the phase-synchronized ion ejection observed by previous groups, the lack of dependence on ac frequency points to a transfer mechanism in which ions are pushed, out of resonance, into the quadrupole trapping region. The amplitudes needed to affect this transfer are larger than those typically used for dipole resonant ejection in conventional quadrupole ion traps, further supporting this conclusion.

The time-independent electric fields shown in Figure 3 assume that the rf driving the two trapping regions is exactly 180° out of phase, with the same frequency. The center of the toroidal trapping region is of the opposite polarity as the center of the quadrupole region. Obviously, this is the simplest experimental approach, as a single rf power supply can be used to operate the device. Alternatively, it may be possible to operate the two trapping regions with separate frequencies or other phase relationships. The consequences of a two-rf-frequency coaxial trap remain to be explored.

A possible application of the coaxial device takes advantage of the higher ion storage capacity of the toroidal trapping region. Ions in a quadrupole trap are confined to a small volume in the trap center, leading to the onset of space—charge problems when the number of trapped ions becomes too large. In contrast, some trapping geometries, such as those used in linear, rectilinear, and toroidal ion traps, are extended in one dimension, allowing a greater number of ions to be analyzed. The coaxial ion trap uses a toroidal trapping geometry for initial ion trapping, and might thus take advantage of this feature. To characterize the increased trapping capacity of the coaxial trap relative to the central quadrupolar trap acting alone, up to 30 sets of toroidal transfer scans and quadrupole analysis scans were used on a single ion population (from a single ionization event). The ion signal did not diminish noticeably after 30 transfers. This is consistent with the larger trapping capacity of the toroidal region, which, based on geometrical arguments, can contain 100—200 times as many ions as the quadrupole region alone. This experiment could not be continued past 30 scans due to length limitations in the signal-recording electronics. Ensemble averaging of these spectra demonstrated improvement in the signal-to-noise ratio, sensitivity, and dynamic range of the device. Trapping ions from a single ionization event, with multiple subsequent analyses, might enable sensitive mass analysis and characterization of dynamic or transient systems.

CONCLUSIONS

The coaxial ion trap, combining quadrupolar and toroidal trapping regions, has been constructed and demonstrated. Ions can be transferred from the toroidal to the quadrupolar region, although the mechanism of this transfer is not clear, and is not based on resonant excitation of the radial secular motion of the trapped ion. Because of the larger ion trapping capacity of the toroidal region, more ions from a given ionization event can be trapped and mass analyzed, leading to an improvement in sensitivity and dynamic range over the planar quadrupole ion trap acting alone. Similarly, mass analysis using quadrupolar fields instead of toroidal fields produces higher mass resolution than the halo ion trap. It is notable that the physical device of the coaxial ion trap is identical to that of the planar quadrupole ion trap, the difference being only the rf amplitudes applied to each patterned electrode ring. This underscores the versatility of making electro-optic devices using this approach.

ASSOCIATED CONTENT

Supporting Information. Chart of rf potentials, figure of nonlinear high-order field components, chart of experimental set-up for coaxial ion trap, figure of coaxial ion trap spectrum, figure of short dc pulses applied at different rf phases, figure of detected signal intensities as a function of rate of dc pulses. This material is available free of charge via the Internet at http://pubs.acs.org.

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