Computer Simulation of the Gap-Tripole Ion Trap with Linear Injection, 3D Ion Accumulation, and Versatile Packet Ejection

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The behavior of a completely new ion trap is shown with SIMION 7.0 simulations. The simulated trap, which was a mix of a linear and a 3D trap, was made by axially setting two ion guides with a gap between them. Each guide consisted of three rods with three symmetrically delayed radio frequency (rf) voltages (tripole). The “injected” ions were linearly contained by pulsed potentials on the entrance and exit plates. Then the three-dimensional (3D) rf field in the gap, which was created by the tripole special rod arrangement, could trap the ions when the translational energy was dampened by collisions with low-pressure nitrogen. Because the injected ions were trapped in the small gap, the trapping cycle could be repeated many times before ion ejection, so a high concentrated ion cloud could be obtained. This trapping and accumulation methodology is not possible in most conventional multipole linear traps with even number of poles. Compared with quadrupole linear trap at the same rf amplitude, tripole lost more ions due to strong charge repulsion in the ion cloud. However, tripole could catch up the ions at higher voltage. Radial and axial mass-independent ejection of the ions localized in the tripole gap was very simple, compared with conventional linear ion traps that need extra and complicated electrodes for effective axial ejection. (J Am Soc Mass Spectrom 2008, 19, 1367–1374) © 2008 American Society for Mass Spectrometry

For analytical sciences, high sensitivity is one of the key points for success. In many types of mass spectrometers, the signal-to-noise ratio increases considerably by analyte accumulation, and the linear ion trap (LIT) concept has been widely used for ion accumulation in hybrid instruments [1–7]. The LIT has been suitable for the construction of miniature mass analyzers, gas-phase reactions, atomic spectroscopy, precursor fragmentation, and beam physics experiments [8–16]. In the case of quadrupole LIT, it can perform ion trapping and mass analysis, all in a single package [17]. The LIT is considered to have higher trapping efficiency and capacity than conventional 3D quadrupole ion trap (3D QIT or Paul Trap). The trapping efficiency for LIT is very high (~100%) compared with the 5% range for QIT when high-speed ions are externally injected [2, 18, 19]. Compared with the 3D QIT, space-charge repulsion is minimized in LIT because the charges can be dispersed in its big central volume.

We have proposed a new ion optics, called “tripole” which consists of three parallel rods, carrying three rf voltages with symmetrically delayed phase shifts [20]. The rotating electric field of the tripole showed stable ion guiding for wide ranges of AC amplitude, better

collisional focusing than hexapole and octapole, and similar focusing as quadrupole (rod pole). Also, the ion optic showed interesting mass filtering potential [20]. We would like to propose here another new potential of this tripole to perform a high efficient unique ion trap.

There have been many technological and conceptual advances both in LIT and 3D traps. For example, the four-electrode rectilinear ion trap (RIT) had an axial pseudopotential, however, its trapping efficiency was lower than a 6-electrode RIT with pulse DC in the z-electrodes [21, 22]. Also, axial focusing DC fields have been created in the quadrupole LIT by mounting extra electrodes or decreasing the axial length [23, 24]. The cylindrical ion trap has a longitudinal symmetry but its 3D electric field suffers the same trapping inefficiencies as any other Paul trap [25].

For repeated ion injections, the segmented LIT and ring electrode traps [26, 27] was proposed, which can compartmentalize the first ion bunch in one or more segments and finally ion injection can be repeated. However, their constructions are complicated and expensive due to their inherent multiple sections, segments mounting, rf, and DC voltage supply. Since the ion ejection of the axially distributed beam was not always completely effective [28], the axial focusing of the beam was improved by adding special extra electrodes [23, 24].

Under certain conditions, ion motion within the inhomogeneous rf field of the LIT can be described by the

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pseudo- or effective potential theory [29–36]. The pseudo-potential can be calculated and expressed as electric potential with the eq 1 (H. G. Dehmelt equation) [35].

$$\psi = (e/4m\omega^2)E_0^2 \quad (1)$$

where m is the ion mass (kg), e is the ion charge (Coulomb, C), ω is the AC voltage frequency (rad/s), and E_0 is the amplitude of the AC electric field.

In previous work [20], we proposed the first new ion guide (tripole), and the next step is to convert this ion guide to an ion trap by setting entrance and exit apertures plates. Previously, it was observed that the tripole edge presented a retarding axial field or fringing field. For the same reason, if a small gap is cut in the middle of the tripole, the pseudopotential should smoothly and axially decrease from the tripole edge to the center of the gap, creating a trapping rf field. If the axially trapped ion loses kinetic energy due to inelastic collisions with neutral gas particles, it would be confined into the areas at low pseudopotential in the gap [37]. Multipole LITs and ion guides with phase-shifted rf voltages have already been used [38, 39], but none of them has included a gap for ion confining.

In this work, we propose a new concept of gap-tripole ion trap, which includes axially-focused performance, high ejection efficiency, and high duty cycle. The study was done by computer simulations using the software SIMION ver. 7.0 and with the pseudopotential theory.

Computational Methods

Ion Movement Simulations

The gap-tripole ion trap (Figure 1) comprised two rf tripoles with 25 mm length each, which were separated by a gap of 3 mm. The radius ratio of electrode to inner field (r_e/r_0) was 2.3 and $r_0 = 3$ mm, which were optimum parameters for tripole [20]. The trap was simulated in a 3D potential array with a scaling factor of 0.125 mm/gu, where gu is the software distance unit. As with the previous work [40], three rf voltages with the

Figure 1. Scheme of the gap-tripole linear ion trap. Two tripoles separated by a gap with entrance and exit aperture plates covered with grid. The trap consists of three electrode sets (rod pair with equal phase shift). The painted electrode-pair is an example of one electrode set. The x - y plane is the radial direction, and z axis, the longitudinal axis.

same amplitude and with symmetrically delayed phase-shifts (ϕ) were applied to each tripole electrode. The radial position of the rods of tripole “B” was rotated 120° with respect to that of tripole “A” rods. The trap consists of three pairs of electrode sets with the same rf voltage phase in tripoles “A” and “B” as dotted in Figure 1. The entrance and exit aperture plates with grids to which a pulse voltage was applied were set at 1 mm from the tripoles. Also another pulse voltage was applied to specific electrodes to eject the ions from the trap. The flight of single charged ions of which the initial kinetic energy was set at the low value of 5 eV was started from the entrance plate with initial direction parallel to the z -axis.

Theory and Calculation

Collisional Focusing Model

We chose the ion/neutral hard sphere collision model developed by Manura [41]. This model includes approaches that simulate real systems such as thermal broadening, background gas velocity with Maxwell-Boltzmann distribution, scattering angle, “rear-end” and “head-on” elastic collisions. The ion-gas collision cross-sections were approximated by $\sigma = Km^b$ [18], where “ m ” is the ion molecular mass in Da. The constants K and b , 2.41 Å² and 0.664, respectively, were obtained by fitting the cross section values from the mass-dependent database of Valentine et al. [42].

Calculation of the Electric Potential and Field

The calculation methodology for electric potential (V), radial field (E) and pseudopotential (ψ) within the tripole has been treated elsewhere [20]. The composite potential in the tripole gap space can be obtained by the arithmetical addition of the contribution of three electrode sets (superposition principle)

$$V(x, y, z) = V1(x, y, z) + V2(x, y, z) + V3(x, y, z) \quad (2)$$

Equation 2 changes to eq 3 by defining the normalized potential of the electrode set ($V_{i\eta}$) as the electric potential at certain position inside the gap in the case that the voltage in the “ i ” electrode set is 1 V and the other two sets are grounded. The definition of electrode set is explained in Figure 1.

$$V(x, y, z) = [V1_{\text{set}} \cdot V1_{\eta}(x, y, z)] + [V2_{\text{set}} \cdot V2_{\eta}(x, y, z)] + [V3_{\text{set}} \cdot V3_{\eta}(x, y, z)] \quad (3)$$

where V_{set} is the electrode set time-dependent voltage. The negative gradient of eq 3 leads to the electric field components:

$$E_u = -[V_0 \sin(\omega t) \times \dot{V}1_{\eta u}] - [V_0 \sin(\omega t + \phi_2) \times \dot{V}2_{\eta u}] - [V_0 \sin(\omega t + \phi_3) \times \dot{V}3_{\eta u}] \quad (4)$$

Figure 2. (a) Macromotion and (b) micromotion of an ion trapped in the tripole gap. $V_0 = 100V$, $\omega = 1$ MHz, $r_0 = 3$ mm, m/z 1000.

where $\dot{V}i_{\eta u} = (\partial V i_{\eta} / \partial u)$ is the derivative of the normalized voltage with any of the Cartesian directions ($u: x, y, z$) created by the “i” electrode set. For the tripole used in this work, $\dot{V}i_{\eta u}$ was calculated by the software SIMION (version 7.0, D. A. Dahl, ID National Engineering Laboratory, Idaho Falls, ID) at each (x, y, z) position. Using eq 4 to solve the algebraic procedure $|E| = \sqrt{\sum_{u=x,y,z} E_u^2} = \sqrt{E_x^2 + E_y^2 + E_z^2}$, we can write the total electric field as:

$$|E(u, \phi, t)| = V_0 \sqrt{[A \sin^2(\omega t) + B \sin(\omega t) \cos(\omega t) + C \cos^2(\omega t)]} \quad (5)$$

where

$$\begin{aligned} A(u, \phi) &= \sum_{u=x,y,z} \dot{V}1_{\eta u}^2 + \cos^2(\phi_2) \left(\sum_{u=x,y,z} \dot{V}2_{\eta u}^2 \right) \\ &\quad + \cos^2(\phi_3) \left(\sum_{u=x,y,z} \dot{V}3_{\eta u}^2 \right) \\ &\quad + 2 \cos(\phi_2) \left(\sum_{u=x,y,z} \dot{V}1_{\eta u} \dot{V}2_{\eta u} \right) \\ &\quad + 2 \cos(\phi_3) \left(\sum_{u=x,y,z} \dot{V}1_{\eta u} \dot{V}3_{\eta u} \right) \\ &\quad + 2 \cos(\phi_2) \cos(\phi_3) \left(\sum_{u=x,y,z} \dot{V}2_{\eta u} \dot{V}3_{\eta u} \right) \\ B(u, \phi) &= 2 \sin(\phi_2) \left(\sum_{u=x,y,z} \dot{V}1_{\eta u} \dot{V}2_{\eta u} \right) \\ &\quad + 2 \sin(\phi_3) \left(\sum_{u=x,y,z} \dot{V}1_{\eta u} \dot{V}3_{\eta u} \right) \\ &\quad + 2 \cos(\phi_2) \sin(\phi_2) \left(\sum_{u=x,y,z} \dot{V}2_{\eta u}^2 \right) \\ &\quad + 2 [\cos(\phi_2) \sin(\phi_3) \\ &\quad + \cos(\phi_3) \sin(\phi_2)] \left(\sum_{u=x,y,z} \dot{V}2_{\eta u} \dot{V}3_{\eta u} \right) \\ &\quad + 2 \cos(\phi_3) \sin(\phi_3) \left(\sum_{u=x,y,z} \dot{V}3_{\eta u}^2 \right) \\ C(u, \phi) &= 2 \sin(\phi_2) \sin(\phi_3) \left(\sum_{u=x,y,z} \dot{V}2_{\eta u} \dot{V}3_{\eta u} \right) \\ &\quad + \sin^2(\phi_2) \left(\sum_{u=x,y,z} \dot{V}2_{\eta u}^2 \right) \\ &\quad + \sin^2(\phi_3) \left(\sum_{u=x,y,z} \dot{V}3_{\eta u}^2 \right) \end{aligned}$$

Calculation of the Tripole Pseudopotential

The typical plot of the time-dependent electric field of the tripole trap gap, obtained from eq 5, at certain x, y, z position is similar to previous work [40]. Equation 5 consists of a phase-shifted oscillating field with frequency “ ω ” and the direction of the field that periodically shifts to the opposite one. The resulting waveform is not sinusoidal, but it is a combination of squareform and waveform components of which respective amplitudes are related with the positional-dependent coefficients A, B , and C . In this oscillating field, the ions are trapped and oscillate in a combination of a fast micromotion and a slow macromotion, see Figure 2. These observations allowed us to apply the pseudopotential theory to the tripole gap space. The zero to peak field amplitude (E_0), obtained from the plot of eq 5, was placed in eq 1 to calculate the tripole pseudopotential $\psi(x, y, z)$ as shown in Figure 3.

Results and Discussion

The tripole-gap pseudopotential is shown to explain the trapping capability. Later, the ion trajectory for one ion is presented to illustrate the tripole trapping mechanism compared with a conventional even-rod-number quadrupole LIT. Finally, the trapping efficiency of many ions under strong space-charge repulsion is examined, and the whole novel ion accumulation-ejection concept is explained.

Gap Pseudopotential Field

Figure 3 shows that the center of the gap is the point of the lowest pseudopotential and the pseudopotential increases radially and axially depending on the dimension and voltage magnitude. This is the “bowl” shape field or “well” as called elsewhere [26, 43], where the ions flying in the axial direction turns back. Since the iso-pseudopotentials in Figure 3b are concentric, the trapping capability acts in all the directions.

The pseudopotential in the x - y plane of the gap showed that the iso-pseudopotential lines formed the tripole electrode shape and were parallel to the

Figure 3. Tripole gap pseudopotential for $V_0 = 100\text{V}$, $\omega = 1\text{ MHz}$, $r_0 = 3\text{ mm}$, $m/z = 1000$. The origin of the longitudinal and radial directions is located in the center of the gap. (a) 3D representation; (b) 2D map representation of the pseudopotential in the x - z plane at $y = 0$; (c) 2D map representation of x - y plane at $z = 0$.

electrodes to prove the correct potential calculation procedure.

In our previous work about tripole ion guide [36], neither the axial field nor the squareform field was taken in the pseudopotential calculation. For these reasons, concentric circles were obtained in the pseudopotential of the 2D tripole guide. In this work, however, tripole-shape lines were gained in the radial direction.

In short, the pseudopotential field shape explains why the ions can be trapped when their kinetic energy is dampened by the collisions to around one tenths of electron volts.

Linear and 3D Trapping in the Gap-Tripole

Linear trapping. The trapping simulations of one ion were carried out to show qualitatively the behavior of an ion beam (Figure 4). The synchronized injection was started at time " T_i " when the entrance was opened (grounded) and finished after the ion was being reflected back by the exit plate but before it returned to the entrance (around $100\text{ }\mu\text{s}$). The entrance voltage was pulsed to trap the first bunch of ions.

3D accumulation. Tripole presents an axial retarding field at the entrance edge that raises the axial pseudopotential between the entrance plate and the tripole edge. The magnitude of this pseudopotential raise is very similar to that of the pseudopotential raise from the gap center to the tripole edge (Figure 3). However, this 3D field is so low and gentle that it decreases the momentum of the injected ions. When the linearly trapped ions slow down by collisions, they can be confined in the gap without rejection. This contrasts with QIT that rejects slow ions [18]. The ion was trapped in the gap in 200 to 300 μs .

The time to dampen its oscillation was around 900 to 1000 μs [a minimum (T_c) in Figure 5a]. Then the entrance can be opened again to accumulate more ions without losing the trapped ions in the gap. Figure 2 shows the harmonic oscillations of the trapped ion in radial and axial directions. The radial and axial micromotion frequencies are roughly 1 MHz, which is almost equal to the driving rf frequency. The radial and axial macromotion frequencies tend to be similar and are much smaller than the micromotion frequency. The radial oscillation amplitude is smaller than the axial one; therefore the radial pseudopotential should be higher than the axial part. These behaviors correspond to Figure 3b and are comparable to QIT pseudopotential in which axial depth is the double of the radial depth [44].

Compared with a conventional quadrupole 2D linear trap with a gap in the center and without extra electrodes, the ions could not be trapped in the gap and continued oscillating longitudinally (Figure 4b). Since quadrupole has no axial trapping rf electric field, some ions will escape when quadrupole entrance is opened. In contrast, the tripole trap repeats as many trapping cycles as the space charge allows. There exist the inherent differences between the axial fields of an odd-number and an even-number rf ion optics.

Optimization of the configuration of gap-tripole trap. All the remarks described in this paper were obtained with the optimized tripole configuration. In this configuration, the axis of one tripole was rotated by 120° relative to the other. Simulations showed that the radial trapping field in the gap in the 0° configuration was the weakest and that in the 60° configuration was the second. In the 0° , the electric field between two rods in one electrode set was null. Consequently the pseudo-

Figure 4. Trapping process in tripole and quadrupole linear traps with gaps. Gap width 3 mm, ion mass m/z 1000, trapping DC = 25 V, rf 1 MHz, 130 V_{0-pr} , N_2 gas 3 mTorr. (a) Ion oscillating along the tripole z -axis. The ion oscillations are dampened and confined in the gap. (b) Ion oscillating along the quadrupole z -axis. The ion is not confined in the gap even for high DC voltage applied to the entrance and exit plates.

potential field that enclosed the gap weakened in the radial direction. Also in the 60° or any other angle between 0° to 120° , the enclosure field was debilitated in the radial direction because an unnecessary free space and asymmetric system were created. The length of the gap was extended to 3 mm to maximize the trapping volume. Some simulations showed that for longer gaps, for example 5 mm, the radial field was feeblers and many ions escaped through the free space. The radial containment was almost impossible for our conditions with a gap of longer than 5 mm. Also, it was observed that the gap could be longer if the field radius was increased with keeping the described proportion. Finally, the optimization of the ratio of electrode to field radius was shown in a previous tripole linear ion trap work [40].

Effect of the Space Charge on the Trapping Efficiency

Repulsion effects were estimated by distributing an arbitrary total charge among the ions with the algorithm of SIMION [hereafter called beam charge in coulombs (C)]. This algorithm is useful for the estimation of the onset of space-charge [45]. Again, it is interesting to compare the natures of a tripole (odd-number) with that of a conventional quadrupole (even-number) of rods with the same simulation accuracy. The quadrupole trapping onset was found in a beam at total charge of ions about 1×10^{-12} C (inflexion point in Figure 5a). At this repulsion value, the beam expands from its birth and some ions crash the rods. Tripole contains lower beam charge at the trapping onset. It has lower trapping capacity than the quadrupole on the condition that they have the same voltage. The tripole trapping field and its pseudopotential are inherently weaker than those of the quadrupole. Thus, the tripole voltage must be increased to trap the same amount of ions as the quadrupole LIT.

Figure 5. Effect of space charge repulsion in the gap trapping efficiency. Injection: one bunch of 500 ions (m/z 1000), kinetic energy 5 eV, beam diameter 1.5 mm, 3 mTorr N_2 , rf 1 MHz, 130 V_{0-pr} , trapping DC = 30 V. Ions counted after 2000 μ s. (a) Continuous line: both traps with equal rf voltage; discontinuous line: tripole conditions, 10 eV, rf 300 V_{0-pr} and trapping DC = 40 V (high rf voltage). (b) Axial ion distribution with 1×10^{-13} C space repulsion. (c) Transversal view of the trapped beam with a shape similar to the tripole pseudopotential lines (1×10^{-12} C and high rf voltage).

Figure 5b shows that tripole concentrated and localized dense ion bunches in the gap space. Due to the repulsion induced by high charge density, some ions radially escaped through the gap or axially moved outside of the gap. Figure 5c shows that the shape of the trapped and dampened ion-cloud at high space-charge is similar to the pseudopotential field shape. In contrast, the ion cloud takes a circular shape and the ions concentrate near the center at lower charge-repulsion (not shown). The calculated pseudopotential shape (Figure 3) is congruent with SIMION simulation.

In short, the gap-tripole ion trap combines the high trapping efficiency of a linear 2D trap with that of the gap 3D trapping field. The gap-trapping field is strong enough to keep a dense ion cloud.

Axial and Orthogonal Mass-Independent Packet Ejection

On trapping, almost all the ions are localized and significantly focused in the gap. Therefore, each axial and orthogonal ejection is simple by applying only DC offset to specific electrodes (Figure 6). In the axial ejection, an offset bias is applied to only one tripole or DC offset ramp is applied to the entrance, tripoles “A”, “B”, and the exit plate. In the orthogonal ejection, extracting ring-electrodes should be added to keep the ejected beam focused.

In contrast, a conventional multi-pole LIT has narrow slits between poles to eject ion beam to radial direction and wider axial central space to focus the beam in the central zone, and many improvements were performed [23, 27, 46–49]. Another ejection method for LIT is simply to apply a very high DC voltage to the entrance and exit plates. This technique creates an ion beam with very high kinetic energy spread but is not effective to eject all the ions [5, 50].

Tripole Trapping Concept

Figure 7 illustrates the scheme of the pulse voltage for different steps. At the time of zero (T_0), the voltage at

Figure 7. Tripole linear ion trap voltage scheme. (a) Entrance plate pulse: while the entrance is zero (T_0 – T_1), the ions enter (injection cycle); in the lapse T_1 – T_c , the entrance voltage rises and the ions remain in the trap (synchronized linear trapping). (b) After accumulation (final T_e), an offset voltage rises and the ions are pushed out (ejection). (c) At the same time (T_e), the exit voltage becomes zero and the ions escape. (d) Ion counting in the whole trap and in the gap. Five beams of 100 ions were injected every 0.2 ms (five trapping cycles).

the exit plate is positive (positive mode) and the entrance voltage is zero, thus the ions enter (injection) and are reflected by the exit grid. After a synchronized short injection time (T_i), the voltage of the entrance is pulsed to positive, and the positive ions are linearly trapped. From this time, the ions oscillate in the longitudinal direction or z-axis by gradually losing their kinetic energy by the low-pressure gas and when their speed is low enough and the gap 3D electric field finally catches the ions (gap trapping). When the time (T_c) is reached, the entrance voltage falls to zero again and the trapping step is repeated.

Trapping new bunches of ions can be repeated in cycles as many times as the space charge allows. This process is called “accumulation”. Figure 7d shows that

Figure 6. 3D and transversal views of the axial and orthogonal ejection modes from the tripole gap after a trapping time of 2000 μ s. (a) Orthogonal: 40 V ejecting DC offset is applied to electrodes A1 and B1. (b) Axial: 40 V ejecting DC offset is applied to all the electrodes of tripole “A”. The same simulation conditions as Figure 5 are used except for no space-charge repulsion.

the number of linearly trapped ions increases with the cycles. The number of ions trapped in the gap increases slowly because the ion injection rate is faster than the speed of transition between fast linearly-trapped ion state and the slow gap-trapped state. Figure 7d shows that not all the ions that enter the trap are trapped in the gap because some ions lose all their kinetic energy before arriving at the gap area. After “ n ” cycles, a period of time ($T_g - T_c$) is set to allow a maximum amount of ions to get trapped and “cooled” in the gap. Finally, an offset DC voltage is applied to the tripole electrodes and the ions are ejected. Figure 7d shows that all the ions trapped in the gap are effectively ejected by axial electric fields.

Conclusions

An easy-to-mount hybrid linear and 3D gap-tripole trap is proposed. The ions can be efficiently confined in the tripole gap because the beam is first linearly trapped and then the ion speed is dampened through ion-gas collisions to trap the ions in the gap 3D rf field. We showed the trapping mechanism of the tripole gap by its bowl-shape pseudopotential by computer simulations.

The main advantage of this trap is repeated ion accumulation. The trapping cycle can be repeated many times and a high, dense ion cloud can be obtained. In contrast, this situation cannot be obtained with a conventional quadrupole linear trap with an even number of rods. In addition, it is very simple to radially or axially eject a well-focused ion packet. The tripole trap also has potential use in miniaturization, beam spectroscopy, negative-positive ion reaction, and to feed mass analyzers such as the ICR and TOF.

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