# Ion Trap Array Mass Analyzer: Structure and Performance

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**An ion trap array (ITA) mass analyzer—a novel ion trap mass analyzer with multiple ion trapping and analyzing channels—was designed and constructed. Its property and performance were investigated and reported in this paper. The ITA was built with several planar electrodes including two parallel printed circuit board (PCB) plates. Each PCB plate was fabricated to several identical rectangular electric strips based on normal PCB fabrication technology and was placed symmetrically to those on the opposite plate. There is no electrode between any two adjacent strips. Every strip was supplied with an rf voltage while the polarity of the voltage applied to the adjacent two strips was opposite. So the electric potential at the central plane between two adjacent strips is zero. Multiple identical electric field regions that contain the dominant quadrupole plus some other high-order fields were produced between the two PCB plates. The multiple identical electric field regions will have the property of ion trapping, ion storage, and mass analysis functions. So an ITA could work as multiple ion trap mass analyzers. It could perform multiple sample ion storage, mass-selected ion isolation, ion ejection, and mass analysis simultaneously. The ITA was operated at both "digital ion trap mode" and "conventional rf mode" experimentally. A preliminary mass spectrum has been carried out in one of the ion trap channels, and it shows a mass resolution of over 1000. Additional functions such as mass-selected ion isolation and mass-selected ion ejection have also been tested. Furthermore, the ITA has a small size and very low cost. An ITA with four channels is less than 30 cm³ in total volume, and it shows a great promise for the miniaturization of the whole mass spectrometer instrument and high-throughput mass analysis.**

The ion trap mass spectrometer is one of the most popular scientific instruments, and it is widely used in the investigation of chemical and biochemical components in different samples, drug discovery, and environmental protection. In comparison to other types of mass analyzers, the ion trap has its own advantages such as structural simplicity, compact size, and the abilities to perform tandem mass spectrometry and operate at a relatively higher pressure. These advantages make the ion trap an ideal candidate for miniaturization and field portability. Besides operating as stand-alone mass spectrometers, ion traps can also be combined with other mass analyzers in hybrid instruments[1–3] and used to accumulate and store the sample ions, to isolate mass-selected ions, to perform MS[n] experiments, and to study ion–molecule reactions.

A conventional three-dimensional (3D) Paul trap[4,5] was composed of a hyperbolic ring electrode and two hyperboloidal end-cap electrodes. A linear quadruple ion trap[6–8] can be composed of four hyperbolical or cylindrical rod electrodes.[6] The conventional ion trap has some disadvantages in terms of its requirement of very high mechanical accuracy and being relatively expensive. There are many reasons for improving the current technology and developing some new ion trap technology including to simplify the machining and assembling process, decrease the expense, and increase the ion trapping capacity and efficiency. The cylindrical ion trap[9–12] (CIT) has much simpler geometries than the hyperbolic Paul trap, so it is easy to be fabricated and has been developed as miniature mass analyzers.[9,10] However, all 3D ion traps, including the CITs, have the disadvantages of low ion trapping capacity and low trapping efficiency for externally injected ions. Linear ion traps have higher trapping capacity and higher trapping efficiency for externally injecting ions than 3D ion traps due to their larger trapping volume.[8] The rectilinear ion trap (RIT) combines the advantages of the geometrical simplicity of the CIT

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and the greater ion trapping capacity of linear ion trap.[13,14] Because of the superiority of RIT, it has been miniaturized and used to build the hand-held mass spectrometers.[15,16] Other ion traps with different geometries such as toroidal[17,18] and halo[19] were also built for the purpose of higher ion trapping capacity and efficiency.

Ion traps have also contributed to high-throughput mass analysis, which is potentially valuable in many scientific fields. Fully multiplexed ion trap mass spectrometers for high-throughput mass analysis were reported including CIT and RIT mass analyzers.[20−25] In the multiplexed CIT mass spectrometer, four identical CIT mass analyzers were housed in a single vacuum manifold and each was coupled to an electron ionization/chemical ionization (EI/CI) source and a detector.[23] All CITs were driven by a single set of control electronics. The mass spectra of four separate samples were recorded simultaneously using a multi-channel data acquisition system. An array of CITs was also coupled to a multichannel electrospray ionization source for the analysis of larger molecules. In the system, two fully multiplexed channels were capable of analyzing different samples simultaneously.[21]

The multiplexed RIT mass spectrometers show better performance than multiplexed CIT mass spectrometers, which is principally due to the inherent larger ion capacity and better analytical performance of the RIT mass analyzer. The first version of a multiplexed RIT instrument consists of four parallel EI sources/RIT mass analyzers/detection channels, each housed in one quadrant of a specialized vacuum manifold.[22] Multichannel experiments of simultaneous, high-throughput mass analysis of four different analytes were performed in parallel, and good results were achieved. However, the instrument has a relatively large size because of the specially designed vacuum manifold. If more analysis channels are needed, the vacuum manifold should be redesigned to fit new applications. Recently, a new version of a multiplexed four-channel RIT mass spectrometer coupled with four parallel atmospheric pressure ion sources was built.[25] The complete instrument was housed in a single vacuum manifold, and so it has relatively small size.

In this paper, we report a new ion trap mass analyzer: the ion trap array (ITA) mass analyzer. An ITA mass analyzer could contain multiple ion trapping and analyzing channels. The electric field distribution in each channel is similar to that in conventional linear ion traps. So an ITA can be used as multiple ion trap mass analyzers, and multiple sample ions can be trapped and analyzed simultaneously with one ITA. Since an ITA was built with only several simple planar electrodes, it has a very simple structure and is easy to fabricate and operate. The preliminary test was performed using one ion trap region in an ITA with four ion trapping and mass analysis channels. The electric field in each channel was also simulated using computer software.

## EXPERIMENTAL SECTION

**Design and Structure of the ITA.** Several factors should be taken into account when we design the ITA. First, it should contain multiple ion trapping and mass analysis channels in a single ITA mass analyzer. And every channel should have a large ion trapping capacity. Second, for ease of fabrication and miniaturization, the structure of the ITA should be as simple as possible.

A conventional quadrupole linear ion trap usually consists of three sections: two end electrode sections and one central ion trap region. Each section is constructed with hyperbolical or cylindrical rod electrodes. Three dc voltages are applied to the separate sections of each rod to produce an axial ion trapping potential well, and an rf voltage is applied to each quadrupole rod set to produce a radial quadrupole trapping field. In the way, ions are trapped in the central section through the combination of the trapping field in all three directions. The RIT simplified the structure of the quadrupole linear ion trap and was built with two pairs of rectangular electrodes supplied with rf potentials and a pair of two end-cap electrodes supplied only with dc voltages. Furthermore, an RIT can also work with only one pair of rectangular electrodes supplied with an rf potential while another pair is applied with a supplementary ac waveform.

An ITA also applied a simple structure as the previous arts. It is constructed with six planar electrodes, as shown in Figure 1a: two end-cap electrodes for applying dc voltages, two boundary electrodes were grounded during experiments, and two central ion trap electrodes for applying the rf voltage. The central electrodes were fabricated to several identical rectangular electric strips, and there was a gap between any two adjacent rectangular electric strips. The two central ion trap electrodes were placed symmetrically to those on the opposite plate. When an ITA was built as shown in Figure 1b, the six planar electrodes were perpendicularly mounted together and form a closed space. Figure 2a shows a cross section of an ITA with four ion trap channels. There is no electrode between any two adjacent strips as shown in Figure 2a.

In the experiments, two up-and-down corresponding strips were connected together and applied with an rf potential, and the polarity of the rf potential applied to the adjacent two strips is opposite, but their absolute voltage value is the same. It means that all of the ion trap channels were driven by one rf power supply. While two boundary electrodes were grounded, the electric potential between two adjacent strips is zero because of the symmetry of the electrodes and the opposite rf voltages applied on them. So it seems like there was a grounded plane between any two adjacent strips. And then electric fields could be produced in every space which formed by the two up-and-down electric

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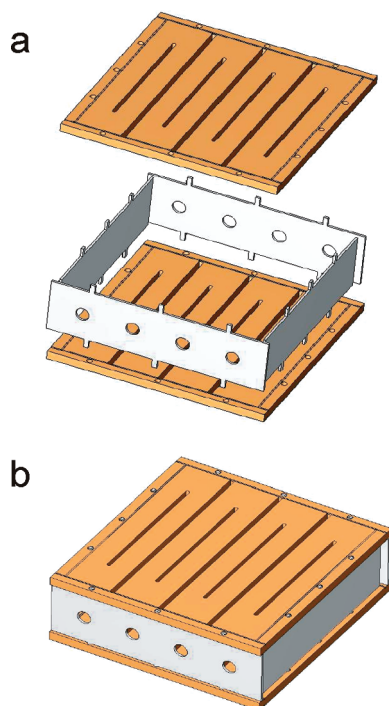
**Figure 1.** ITA mass analyzer. (a) It consists of a pair of printed circuit board plates, a pair of end-cap electrodes, and a pair of boundary electrodes. Both the end-cap electrodes and the boundary electrodes are made of stainless steel. (b) An ITA mass analyzer with four channels was assembled using the three pairs of electrodes.
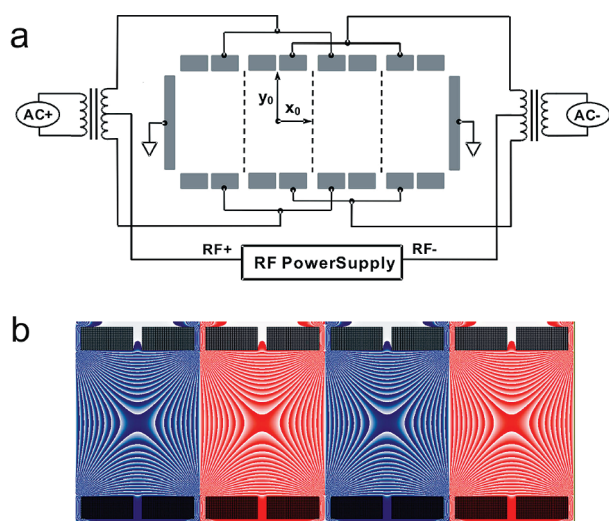


**Figure 2.** ITA operation. (a) Connection of power supply: signals applied to the adjacent electrodes have the same potential but opposite polarity. The ac waveforms were coupled to the rf signal or digital trapping waveform by transformers. All the dashed lines in the figure are not grids but fields that keep constant while operating that separate each ITA channel. All the voltages are applied to the whole rectangular electric strips. (b) Electric fields in each channel of the ITA with dimensions $x_0 = 5.5$ mm and $y_0 = 6.25$ mm.

strips, two end-cap electrodes, and the two grounded planes. The method of dc and rf power supply applications and the produced trapping electric fields are shown in Figures 2a and 2b, respectively.

The electric fields in every channel of the ITA are dominantly quadrupolar fields while other high-order fields are also involved, which is caused by many factors such as the

**Table 1. Electric Field Distribution for Each Ion Trap Channel in an ITA Mass Analyzer**

| geometry | | quadrupolar | octapolar | | dodecapolar | |
|---|---|---|---|---|---|---|
| $y_0$ | $y_0/x_0$ | $A_2$ | $A_4$ | $A_4/A_2$ (%) | $A_6$ | $A_6/A_2$ (%) |
| 6.25 mm | 1.136 | 0.604 | 0.056 | 9.27 | $-0.072$ | $-11.9$ |

rectangular geometry of the electrodes, the slits on the electrodes, and fabrication imperfections such as mechanical errors and misalignment. The high-order fields generally degrade the analytical performance of the ion trap, but with appropriate combination of these electric fields, their effects can be mutually compensated to minimize the performance loss or even they can be used to improve the analytical performance.[12,13,26,27] The appropriate distribution of the high-order fields was obtained by optimizing the geometric parameters in RIT and CIT.[12,13] The geometric parameters of the ITA mass analyzer used in this paper were selected based on the simulation and experimental results of the RIT and CIT. In the ITA, the electric field distribution is the same in every ion trap channel as listed in Table 1. The electric fields were calculated using a computer program based on Simion 7.

**Fabrication of the ITA.** The simplicity of the structure of the ITA makes it possible to be built using the printed circuit board (PCB) fabrication technology, which is used extensively throughout the electronic manufacturing industry. In this study, an ITA consists of two identical PCB plates, and each PCB plate was imprinted with simple but specially designed patterns as shown in Figure 3a. Each PCB was fabricated to four parallel rectangular electric strips and then was coated with gold. Every electric strip has the same dimension of 10 mm width by 46 mm length. A 1 mm gap was fabricated between any two adjacent electric strips. There are 30 mm long and 0.8 mm wide slits centrally located on the middle of each rectangular electrode for ion ejection. The slits were also coated with gold. In the process of mass analysis, the trapped ions can be ejected from these slits and detected by ion detectors which are placed near these slits. A channeltron-type CEM was used as ion detectors in our experiments.

The positioning holes on the edge of each PCB were used to assemble the ITA. The process of assembling the ITA is shown in Figure 1a. A pair of end-cap electrodes, a pair of boundary electrodes, and the two identical PCBs were assembled together to form an ITA. The end-cap and boundary electrodes were made of stainless steel and were all 1 mm in thickness and 12.5 mm in width. There are four apertures (3 mm in diameter) in each end-cap electrode, and these apertures confront with the center of each rectangular electrode on the PCBs. Ions are injected into the ITA through them. Figure 3b shows a picture of the ITA that used in this work.

Theoretically speaking, the channels on the sides and middle are identical on the condition that the distance between the outside grounded electrode and the nearby rectangular electric strip is half of two adjacent rectangular electric strips. In that case all the channels are surrounded by two rectangular electric strips and

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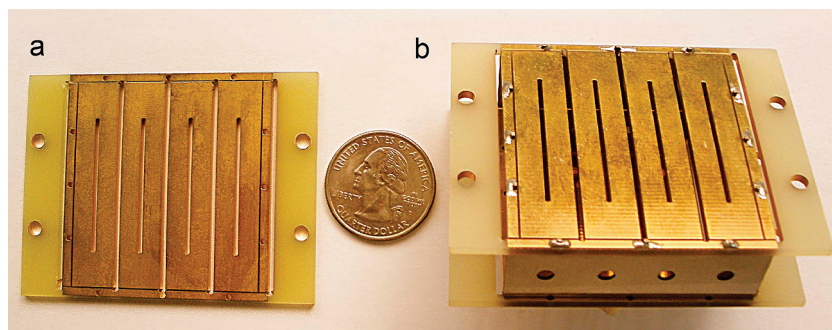
**Figure 3.** Picture of the ITA: (a) top view of a PCB plate with four parallel rectangular electrodes; (b) picture of the ITA mass analyzer which used in the experiments.
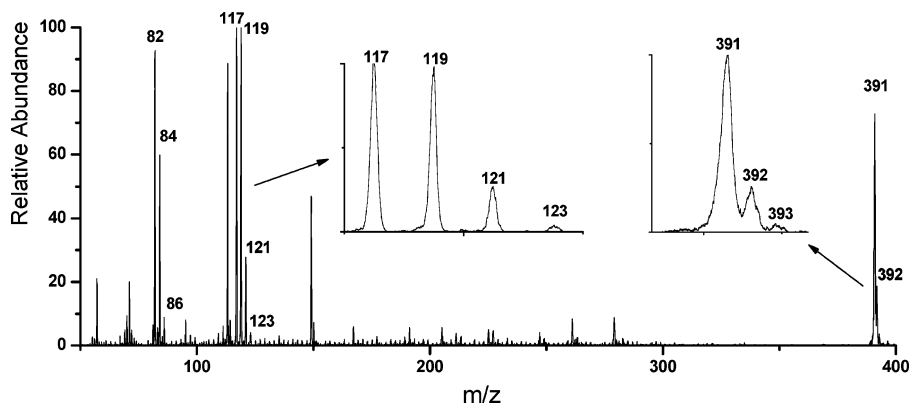


**Figure 4.** Mass spectrum of unpurified carbon tetrachloride. The ITA was operated in "digital ion trap mode". The amplitude of the digital trapping waveform is 280 V (zero-to-peak), and the scan rate is 1433 Th/s. The amplitude of the supplementary ac is 0.98 V, and its frequency is one-third of the frequency of digital trapping waveform.

two zero-potential planes. Therefore, they are identical. However, there could be some mechanical errors on the outside ground electrodes and make the side channels different from the middle channels. To overcome this, more channels could be built and by using the middle channels only.

**Experimental Setup.** The experiment was performed using a homemade two-stage vacuum system which was pumped by two diffusion pump systems. An electron impact (EI) ion source was used to produce sample ions. The produced ions were introduced into one of the ion trap channels of the ITA through an aperture on the front end-cap electrode. The vacuum in the EI source chamber was about $2 \times 10^{-3}$ Pa. The background pressure in the ITA chamber is about $2 \times 10^{-4}$ Pa. Helium buffer gas was admitted into the ITA area to kinetically cool down the trapped ions during the experiments.

The ITA can be operated as conventional 3D ion traps or other linear ion traps using the technique of mass-selective instability scan and resonance ejection. There are mainly two methods to a perform mass-selective instability scan in a quadrupole ion trap mass analysis. One utilizes a highly tuned rf resonator to generate a fixed-frequency sinusoidal trapping waveform. A linear scan of the amplitude of the rf trapping waveform corresponds to "q-scanning" in the Mathieu stability region, and mass spectra are achieved during the scan. In addition, a supplementary ac signal is coupled to the rf trapping waveform to achieve resonance ejection during the rf scan to improve the efficiency of ejecting ions and mass resolution. This well-established method has been commonly used in the commercialized ion trap mass spectrometer, and in this paper we call it "conventional rf mode". Another

method, called "digital ion trap", was invented by Ding and co-workers[28–30] and first applied to a "nonstretched" 3D ion trap. Instead of using sinusoidal waveform, a "digital trapping waveform", generated by the rapid switching between discrete dc high-voltage levels, was applied to the ring electrode of the ion trap. Mass analysis was performed by implementing a frequency scan of the digital trapping waveform, and resonance ejection was also used during the scan. Many advantages, such as improvement of mass range and mass resolution and ease of performing electron capture dissociation, have been found using the digital trapping waveform in an ion trap.[29]

In this work, the ITA mass analyzer was operated in both "conventional rf mode" and "digital ion trap mode" to test its performance. The method of how the trapping waveform and supplementary ac waveform are applied to the ITA is illustrated in Figure 2a. The "rf power supply" in the figure refers to either a conventional sinusoidal trapping waveform or digital trapping waveform. In both modes, dc voltages are applied to the pair of end-cap electrodes to generate a dc trapping potential well. And the dc voltage on the front end-cap electrode can be pulled up or down, so it acts as an ion gate. The electronic systems including the trapping waveform generator and control circuitry are different when a different operation mode is used. Descriptions of the electronic systems in both modes are given as follows.

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**Electronics for Conventional rf Mode.** The rf power supply (rf module 009701, Sciex, Toronto, Canada) provides rf voltages with a fixed frequency of 768 kHz to drive the ITA. The positive and negative outputs of the rf power supply were highly balanced, which means the two outputs have the same potential value but with 180° out of phase. A homemade electronic control system was designed base on ARM and FPGA to provide various functions that were desired for mass analysis. First, it provides a control signal to perform the linear scan of the amplitude of the rf trapping waveform. Second, it controls the process of the ion storage and mass analysis, which consists of periods for ionization, cooling, mass analysis, and ion clearing. Third, the control system contains an arbitrary waveform generator to produce supplementary ac waveforms. Signals with designed frequencies and arbitrary waveforms with peak-to-peak amplitude up to 15 V were generated to perform the resonance ion ejection, ion isolation, mass-selected ion ejection, etc. The supplementary ac waveforms were coupled to the rf signal by two homemade transformers and then applied to the electrodes of the ITA, which is shown in Figure 2a. A preamplifier and data acquisition board was connected to the control system to record mass spectra. And the control system was connected to a computer through Ethernet, so it can transfer the data to computer for data processing.

**Electronics for Digital Ion Trap Mode.** The electronic system used in "digital ion trap mode" was totally different from that used in the "conventional rf mode". The system mainly consists of two parts: the switches and the digital waveform generator. The switches used for creating the high-voltage digital trapping waveform were constructed with power MOSFETs. The upper and lower dc levels, which were provided by two high-accuracy dc power supplies (DCS600-1.7E, Sorensen power supplies, Elgar Electronics Corporation), can be adjusted freely between ±500 V. The digital waveform generator was specially designed based on direct digital synthesizing (DDS) technology. It provides precise control of the waveform period at a resolution of 50 ps, and it also provides pulsed dipole excitation and ejection waveforms. Similar to that in the "conventional rf mode", the excitation and ejection waveforms were also coupled to the digital trapping waveform using transformers. A data acquisition system was also used to get mass spectra in this mode.

Since the voltage of the digital trapping waveform is fixed, a linear scan of the frequency does not provide a linear mass scale, so the digital waveform generator was operated at a special way to provide a scan of period of the digital trapping waveform. This is obtained as below: starting at an initial waveform period, $T_{start}$, the scan proceeds by incrementing the period by a fixed value $T_{step}$ after generating a certain number of waveforms. The content way of generating the trapping waveform was described clearly by Ding et al.[29]

## RESULTS AND DISCUSSION

**Mass Resolution.** A prototype ITA with geometry of $x_0 = 5.5$ mm and $y_0 = 6.25$ mm was first operated in "digital ion trap mode" to record mass spectra of unpurified carbon tetrachloride ($CCl_4$). The mass spectrum is shown in Figure 4. In the experiment, the process of mass analysis can be divided into four phases: ionization, cooling, mass analysis, and ion clearing. In the phase of ionization, the dc voltage applied on the front end-cap electrode was pulled down to 10 V, so ions could be injected into
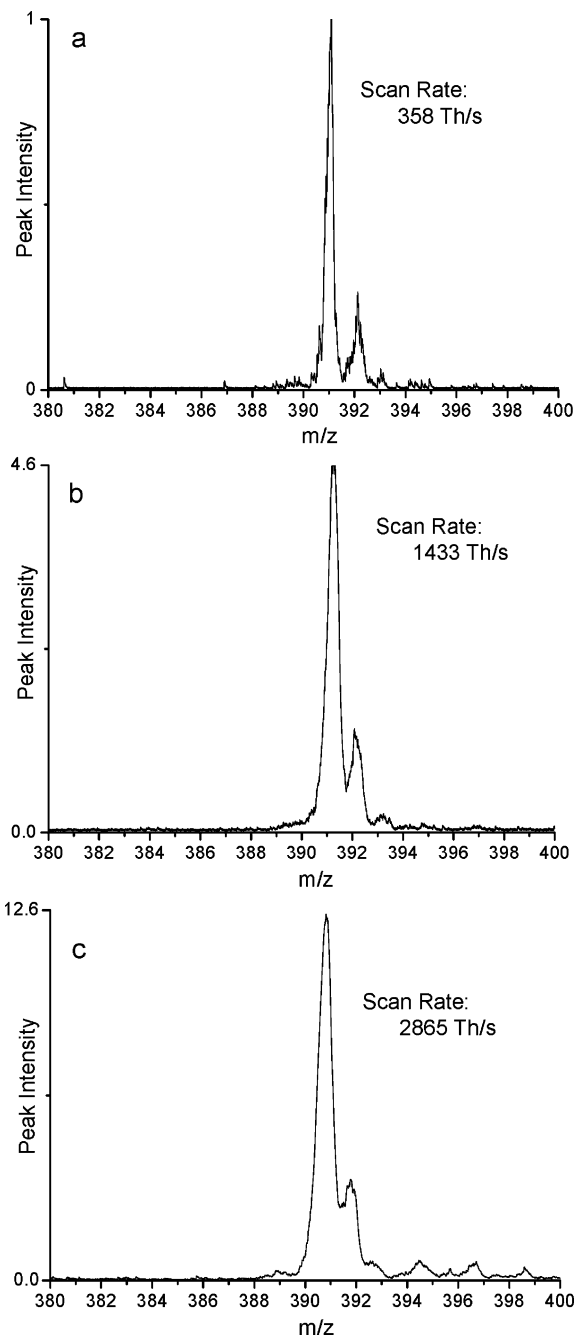


**Figure 5.** Mass resolution at different scan speeds. The ITA was operated in "digital ion trap mode", and the frequency of the supplementary ac was one-third that of the digital trapping waveform in all experiments. The amplitude of the digital trapping waveform is 280 V (zero-to-peak): (a) mass scan rate 358 Th/s, with applied supplementary ac of 0.65 V; (b) mass scan rate 1433 Th/s, with applied supplementary ac of 0.98 V; (c) mass scan rate 2865 Th/s, with applied supplementary ac of 1.55 V.

one of the ion trapping regions of the ITA. During the period of ionization, the amplitude and frequency of the digital trapping waveform were fixed to 280 V (zero-to-peak) and 1.25 MHz ($T = 800$ ns), correspondingly. After 20 ms of ionization, the dc voltage on the front end-cap electrode was pulled up to 60 V so the ion gate was closed. Then ions were kinetically cooled down with "buffer gas" (helium) for 5 ms. In the process of mass analysis, the period of the digital trapping waveform was scanned in the way described before. A supplementary ac signal was applied
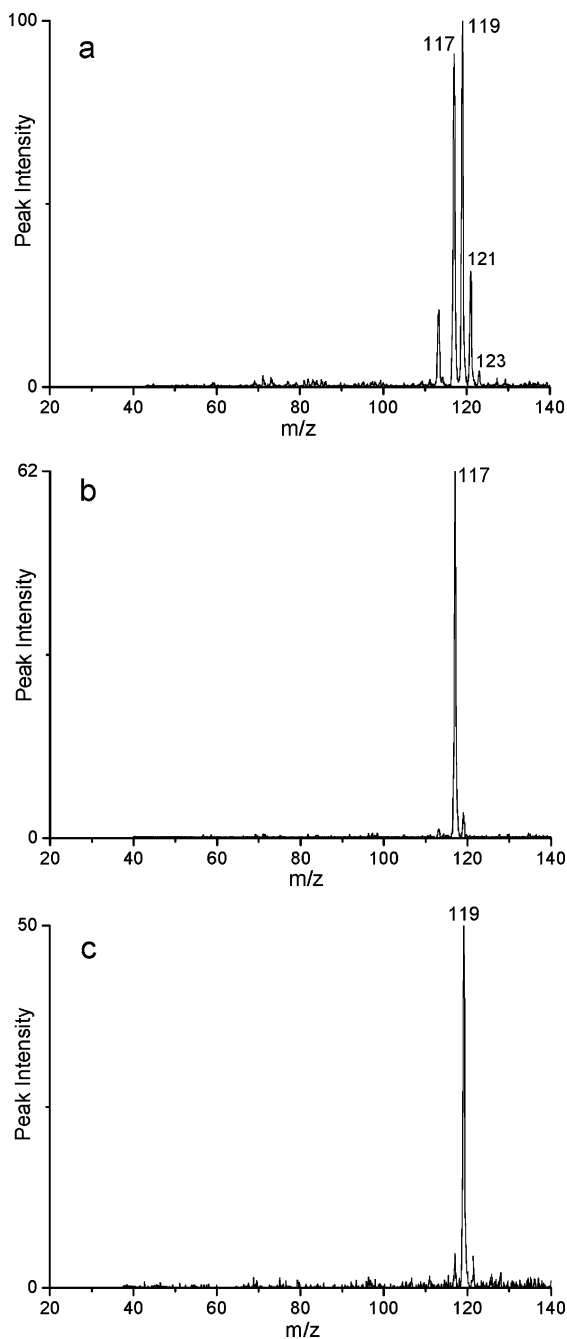
**Figure 6.** Mass-selected ion isolation in the ITA mass analyzer which was operated in "conventional rf mode". The rf trapping voltage was fixed to 175 V (zero-to-peak), and its frequency was 768 kHz: (a) mass spectrum of carbon tetrachloride; (b) isolation of ions $m/z$ 117 using the SWIFT waveform of frequency from 10 to 550 kHz with frequency notches of 131.7−137 kHz and amplitude of 4.5 V; (c) isolation of ions $m/z$ 119 using the SWIFT waveform of frequency from 10 to 550 kHz with frequency notches of 110.5−130 kHz and amplitude of 4.5 V.

during the period scan of the digital trapping waveform. The frequency of the ac signal was derived digitally by dividing the frequency of the trapping waveform, and a division rate of 3 was employed in the experiment. The amplitude of the supplementary ac signal was optimized to get the best resolution. A typical mass spectrum as shown in Figure 4 was achieved when the amplitude was turned to 0.98 V. After mass analysis, the amplitude of the digital trapping waveform was turned to 0 V to clear all ions in the ITA.
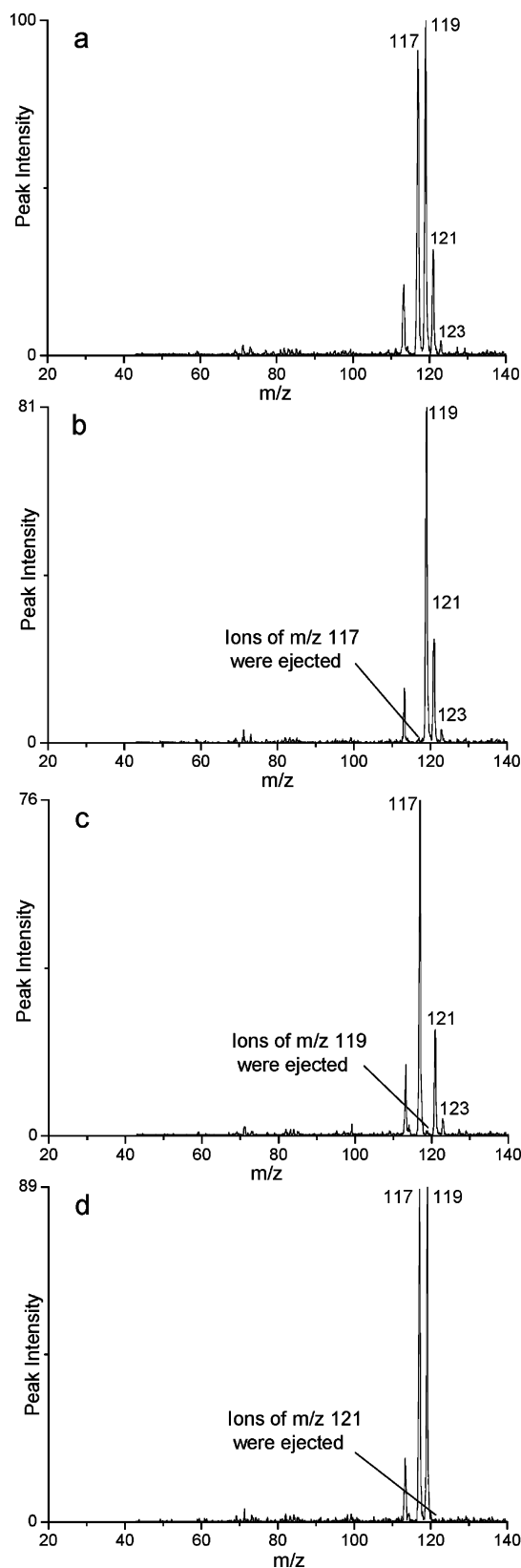


**Figure 7.** Mass-selected ion ejection in the ITA mass analyzer which was operated in "conventional rf mode". The rf trapping voltage is fixed to 175 V (zero-to-peak), and its frequency was 768 kHz: (a) mass spectrum of carbon tetrachloride; (b) mass-selected ejection of ions $m/z$ 117 using an ac waveform of 133 kHz, 0.9 V for 8 ms; (c) mass-selected ejection of ions $m/z$ 119 using an ac waveform of 129.4 kHz, 0.9 V for 8 ms; (d) mass-selected ejection of ions $m/z$ 121 using an ac waveform of 125.8 kHz, 0.9 V for 8 ms.

It is well-known that a slower scan rate will give higher mass resolution of ion trap mass analysis. The scan rate effect on mass resolution was tested in this work. Figure 5a shows a mass spectrum achieved at a scan speed of 358 Th/s, and its mass resolution is greater than 1000 at $m/z$ 391 Th. When the scan speed was increased, the mass resolution decreases as shown in Figure 5, parts b and c. However, the sensitivity was sacrificed when the mass resolution is improved by decreasing the scan speed. It is worthwhile to use a proper scan rate to achieve a good mass resolution as well as high sensitivity.

**Mass-Selected Ion Isolation.** The function of mass-selected ion isolation and mass-selected ejection of ITA was tested in "conventional rf mode". Carbon tetrachloride ($CCl_4$) was used to produce sample ions as well. A mass spectrum of carbon tetrachloride is shown in Figure 6a. To perform mass-selected ion isolation, the rf trapping voltage is fixed to 175 V (zero-to-peak) while the frequency is 768 kHz; a stored waveform inverse Fourier transform (SWIFT) waveform, whose frequency varies from 10 to 550 kHz with frequency notches of 131.7−137 kHz and amplitude of 4.5 V, was coupled to the rf signal and applied to the electrodes of the ITA for 8 ms, and then ions that remained in the ITA were mass-analyzed by ramping the voltage of the rf signal. The result is shown in Figure 6b; it can be seen that all other ions except $m/z = 117$ ions were ejected from the ITA. The mass resolution of the mass-selected ion isolation is about 100 in the current test. At the same time, similar results are also gained on the isolation of ions $m/z = 119$ (Figure 6c).

**Mass-Selected Ion Ejection.** The capability of mass-selected ion ejection using an ac waveform was also tested in the ITA (Figure 7). As mentioned above, the purpose of ion isolation is to save ions with certain $m/z$ inside the ion trap while ejecting others out. And a mass-selected ion ejection is just doing the opposite thing, which is ejecting certain $m/z$ ions out while the others are saved in the ion trap. When the trapping voltage is fixed, there must be a resonant frequency for each type of ion with a particular mass-to-charge ratio. We use different ac waveforms with different frequencies to eject ions of $CCl_3^+$ ($m/z$ 117, 119, and 121). In our experiment, the amplitude of the rf signal was fixed to 175 V (zero-to-peak) and its frequency was also fixed to 768 kHz. Ions of $m/z$ 117 were ejected when a supplementary ac waveform with frequency of 133 kHz and amplitude of 900 mV was applied for 8 ms. Ions of $m/z$ 119 and 121 were ejected in

the same way while using ac waveforms with frequency of 129.4 and 125.8 kHz, respectively.

## CONCLUSIONS

An ITA mass analyzer which contains multiple ion trap channels can be easily built with some planar electrodes. It has a very simple structure and can be built with some very cheap material, such as normal PCB plates. An ITA could perform multiple sample mass spectrometry analysis simultaneously. Although only one ion trap channel in a four-channel ITA was tested in this work, it could be concluded that the ITA could perform mass analysis of multiple samples simultaneously because of their identical geometric structure and electric field distributions.

Since some basic properties of mass spectrometer are very important for the applications of ITA technology, such as the coincidence of mass range, it is worthwhile to test the performance of more ion trap channels in an ITA. Also, since the ITA geometric structure, such as the ratio of its the height to width ($y_0/x_0$ as mentioned before) will affect the electrical distribution inside the ion trapping region and their performance, it is highly necessary to test the structural effect and find the best geometry. Furthermore, instead of the planar electrodes, an ITA can be built with electrodes of other shapes as well, and the study of the electrode shape effect will certainly be very useful.

When an ITA is used for multiple sample mass analysis, it should be equipped with multiple ion sources. How to separate the multiple ion sources and avoid the possible interference of multiple ion sources is another subject of our next research.

Obviously, the ITA technology deserves further research work in many aspects. And the ITA mass spectrometer shows a great promise for many applications in many fields.