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Printed Circuit Board Ion Trap Mass Analyzer: Its Structure and Performance

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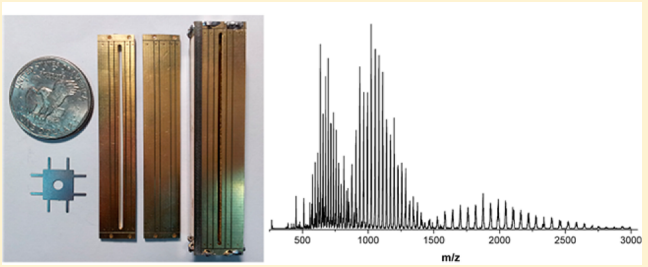
Supporting Information

ABSTRACT: An ion trap (IT) mass analyzer can be simply built with low cost material—the printed circuit board (PCB). A printed circuit board ion trap (PCBIT) can perform ion trapping, mass analysis, and tandem mass spectrometry as a conventional ion trap mass analyzer. In a PCBIT, each PCB electrode was fabricated to specially designed patterns with several separate electric strips. The strips' electrodes were insulated from each other and applied with different voltages during the experiment. Therefore, the electric field distribution inside the ion trap region may be adjusted and optimized by simply adjusting the voltage on each strip. The performance of the PCBIT can also be optimized since the property of an ion trap is strongly dependent on the field distribution. The fabrication, operation, and performance of the PCBIT are described and characterized in this paper. A prototype PCBIT was built with two pairs of 64 mm × 12 mm PCB rectangular plates and one pair of 10 mm × 10 mm stainless steel square plates. A mass analysis with a resolving power of over 1500 and a mass range of around 3000 Th was observed. The mass-selected isolation and collision-induced dissociation (CID) of ions were also tested using the homemade PCBIT system. The adjustable electric field distribution, simple structure, and low cost of PCBIT make it certainly suitable for the further miniaturization of the portable mass spectrometer.



Mass spectrometry, one of the most popular analytical techniques in modern science, provides high specificity, high sensitivity, and high resolving power for analyte identification. It has been extended to many fields[1−7] such as chemistry, astronomy, pharmacy, life science, food safety, homeland security, and environmental protection. Among all types of mass analyzers, the ion trap mass analyzer has the advantages of a simple structure, compact size, high working pressure, and tandem mass analysis capability using only one single ion trap. However, the geometry of the traditional three-dimensional ion trap[8−10] with high accurate hypobolic electrodes is hard to fabricate and assemble. Meanwhile, it suffers drawbacks of low trapping capacity and low trapping efficiency for externally injecting ions.[11]

Several new ion traps, such as cylindrical ion traps (CITs)[12−15] and linear ion traps (LITs),[16−18] were developed in past decades. CIT has simpler geometry which is easier to fabricate,[19,20] but the trapping capacity and trapping efficiency are still low.[11] LIT can greatly improve the trapping efficiency and increase ion capacity,[16,17,21] but it requires high mechanical accuracy in fabrication and assembly.

Rectilinear ion trap (RIT), which increased trapping capacity compared with CIT and significantly simplified the geometry compared with LIT, was first invented in 2004 by Cook's group[22,23] as a combining version of CIT and LIT. The mass resolution, mass range, and tandem mass spectrometry (MS^n) capabilities can be improved by optimizing the experiment conditions. RIT has made a great contribution to the miniaturization of the hand-held mass spectrometer.[24−26] One of the major characteristics of RIT is its simple geometry, which is constructed of rectangular plates, and it makes RIT much easier to fabricate. However, the rectangular shape of the electrodes also results in aberration of the internal electric field distribution, and some unnecessary multipolar electric fields would exist in the ion trap region besides the quadrupole field.[27,28] As is well-known, the properties of ion traps largely depend on the electric field distribution. So it means the geometric structure of RIT, including the geometry of the electrodes, fabrication imperfections, and the apertures and slots in the electrodes, will affect the electric field distribution and the performance of the ion trap.[22] In order to optimize the ion trap property, several studies have been published recently,[25,26,29−38] such as the study on the effect of different trap geometries, electrode materials, and different assembly methods. Obviously, most methods of performance optimization need hardware modification, which will definitely require longer time and a higher cost.

In this study, a new kind of ion trap mass analyzer, printed circuit board ion trap (PCBIT), is reported. A prototype PCBIT was built with two pairs of PCB rectangular plates and

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one pair of stainless steel square plates. Each PCB plate was fabricated to specially designed patterns with several separate electric strips, and the strips were insulated from each other and applied with different voltages. Therefore, the internal electric field distribution can be adjusted and the performance of the PCBIT can be optimized during the experiment by simply changing the voltage application on each strip. The demonstrated capabilities of the PCBIT include a mass resolution in excess of 1500, a mass-to-charge range of 3000 Th, and tandem mass analysis. In addition, PCB fabrication technology can greatly simplify the fabrication of the electrode[32,37] and PCBIT. PCBIT, which has the advantage of an adjustable electric field distribution and excellent performance, simple structure, and low cost, is certainly suitable for miniaturization of the portable ion trap mass spectrometer.

EXPERIMENTAL SECTION

Structure and Assembly of PCBIT. A prototype PCBIT was made with four identical 64 mm ×12 mm PCB plates. The geometry of the cross section and its electrodes are shown in Figure 1. Each PCB plate was fabricated to five parallel

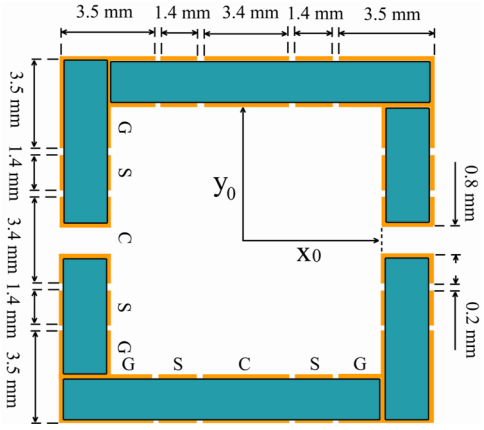

Figure 1. The geometry of the cross section of a PCBIT and its electrodes. Each electrode was fabricated to five parallel rectangular strips: the central strips C (3.4 mm strip), the two side strips S (two 1.4 mm strips), and the two corner strips G (1.5 mm strip, 3.5 mm strip). A 0.2 mm insulate gap was fabricated between two adjacent strips. A slot with a 0.8 mm width was fabricated on the central strip C of the X-direction electrode. The conductive surfaces of four PCB plates and slots were all coated with gold.

rectangular strips, and the widths of the five strips are (from end to end): 1.5 mm, 1.4 mm, 3.4 mm, 1.4 mm, and 3.5 mm. There was a 0.2 mm insulate gap between two adjacent strips for the electric isolation. For each electrode, the five electric strips could be divided into three groups: the central strips C, the two side strips S, and the two corner strips G. A 58 mm × 0.8 mm slot was fabricated on the center of the 3.4 mm central strip C on each of the two X-direction electrodes. The other two plates, with no slots, were used as Y-direction electrodes. In the process of mass analysis, the trapped ions can be ejected from the slots and detected by ion detectors nearby. The conductive surfaces of four PCB plates and slots were all coated with gold for better electric conductance.

The assembly method is shown in Figure 2. The two ends of each PCB electrode were soldered onto two 10.0 mm × 10.0 mm square shape 304-stainless steel (SS) plates as end-cap

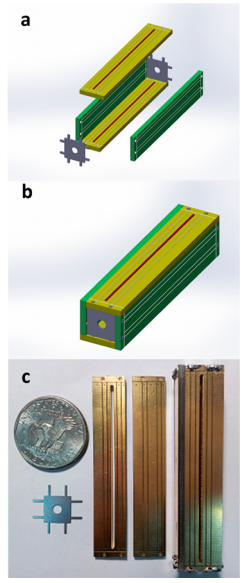

Figure 2. PCBIT mass analyzer. (a). It consists of two pairs of 64 mm × 12 mm PCB plates and a pair of 10 mm × 10 mm SS end-cap electrodes with 3.0 mm apertures in the center. (b). An assembled prototype PCBIT mass analyzer: an aperture on each SS end electrode for ion injection and a slot on each X-direction electrode for ion ejection. (c). Picture of PCBIT: top view of SS plate, PCB plate with slot on, PCB plate with no slot on, and PCBIT used in the experiment(from left to right).

electrodes. Then, a 10.0 mm × 10.0 mm rectangular prism was formed with four PCB electrodes and two SS plates. A 3.0 mm diameter aperture was fabricated in the center of each SS electrode, so the ions from an ion source and quadrupole ion guide could be introduced into the ion trap region through the aperture.

The PCB plates, five strips, the slots, SS electrodes, and apertures were precisely fabricated with less than 0.02 mm mechanical tolerance.

Voltage Application and Adjustment of the PCBIT. The five strips were applied with different voltages during the experiment, and the voltages were adjusted until the optimized results were obtained. A digital trapping waveform power supply[37,39] was used to drive the PCBIT in this work. The method of the power connection is shown in Figure S-1a, Supporting Information. All of the corner strips G were grounded, while the central strips C and the side strips S were applied with the trapping voltages having a certain ratio by using a voltage divider. For example, the central strips C_x (3.4 mm strip with slot on) on X-direction electrodes were applied with V_{x1} and V_{x2} ($V_{x1} - V_{x2}$ = dipole voltage, as explained later), and the two side strips S_x (1.4 mm strip) were applied with αV_{x1} or αV_{x2} accordingly ($\alpha < 1$). Similarly, the central strips C_y (3.4 mm strip with no slot on) on Y-direction electrodes were applied with V_y, while the two side strips S_y (1.4 mm strip) were applied with αV_y. The details of the voltage divider is shown in Figure S-1b, Supporting Information. The X-direction electrodes were applied with an adjustable trapping waveform coupled with an excitation waveform, and the Y-direction electrodes were applied with the trapping waveform of the same amplitude as the X-direction electrodes applied, but with 180° out of phase. The trapping waveform coupled with the excitation waveform could eject ions from the PCBIT during mass analysis. α, which stands for

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the voltage ratio, was kept the same on both X-direction and Y-direction electrodes in the experiment. It can be adjusted by changing the value of variable resistors and capacitors in the voltage divider to get different voltages on strips C and S.

Simulation of Electric Field Distribution. For better understanding the properties of the PCBIT, a computer program based on Simion 7 was used to simulate the electric field distribution inside the ion trap region. Figure 3a shows the

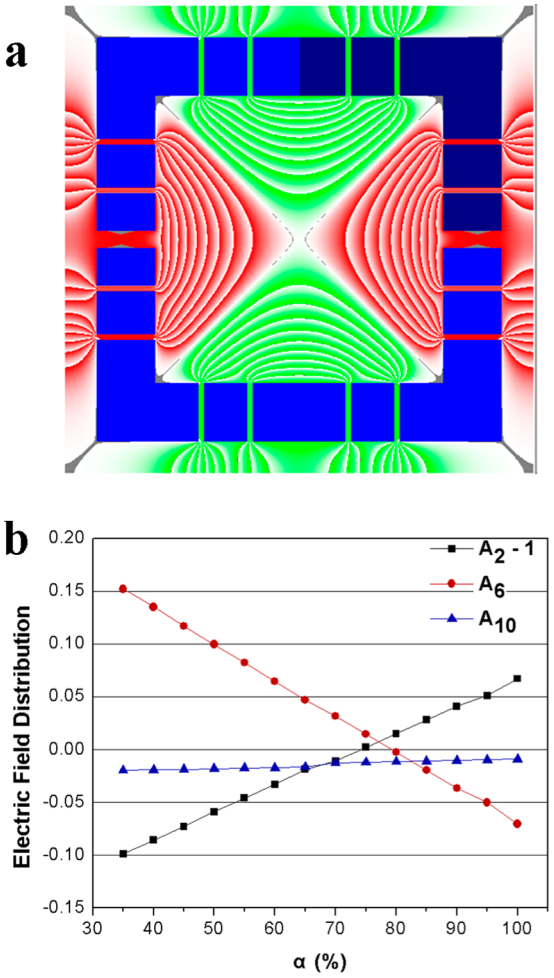

Figure 3. The electric field distribution of the prototype PCBIT. (a) Electric field distribution diagram inside the PCBIT when $x_0 = y_0 = 5$ mm. (b) The simulation results of the major electric field components with different α values.

electric field distribution diagram inside the PCBIT when $x_0 = y_0 = 5$ mm. The simulation results with different voltage ratios are shown in Figure 3b, which strongly proved that the electric field distribution inside the PCBIT can be easily adjusted by simply adjusting the applied voltages. During the experiment, 67% was finally selected as the voltage ratio for this work according to the optimized experimental results. And under this condition, the major electric field components include $A_2 = 0.981$, $A_6 = 0.0333$, $A_{10} = -0.0151$, and some very few A_4, A_8, and so on.

Experimental Setup. All experiments were performed on a homemade three-stage vacuum system as previously described.[37,40] The schematic diagram of the PCBIT system can be seen in Figure 4. An electrospray ionization source (ESI), coupled with an atmospheric pressure interface, was used to

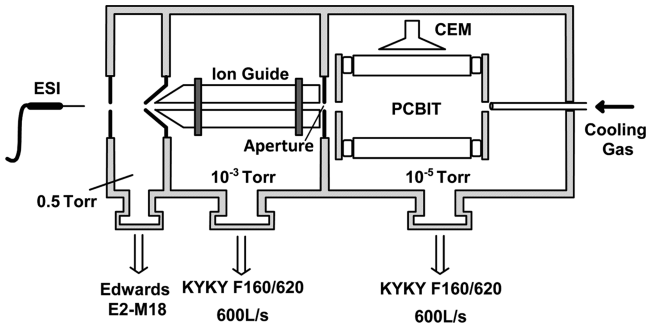

Figure 4. Schematic diagram of the homemade three-stage vacuum system for the PCBIT experiment.

produce sample ions. The sample solutions were pumped into the capillary at a flow rate of 1 μL/min. During the experiment, a high voltage of ESI was applied typically at 4000 V, and the voltage of the orifice and skimmer was set at 150 and 30 V, respectively. The electrospray ions directly went into the orifice without a curtain gas. Ions were transmitted via a quadrupole ion guide and imported into the PCBIT through the aperture on the front end-cap electrode. Helium buffer gas was introduced into the PCBIT region to kinetically cool down the trapped ions. The pressure of the buffer gas was kept at about $(1-2) \times 10^{-5}$ Torr for a normal mass scan and $(5-8) \times 10^{-5}$ Torr for the tandem mass spectrometry (MS/MS) experiment. A channeltron electron multiplier (CEM 4879, Burle/Photonis) was used as the ion detector, which was placed near the slot in the horizontal direction.

The "digital ion trap" method[32,39,40] was used in this experiment. The theory and the technology were described clearly by Ding et al.[40−43] The scheme of time sequence in freq/period sweep mode can be seen in Figure 5. An advanced

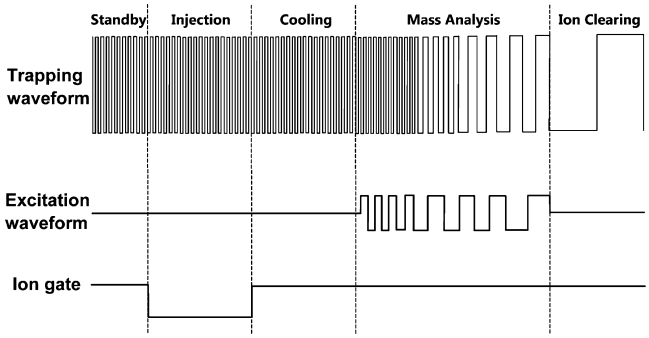

Figure 5. Scheme of the experimental time sequence in freq/period sweep mode.

RISC machines (ARM) based microcomputer was used to control the timing sequences. During the period of "injection," the DC potential of the front end-cap electrode and back end-cap electrode were set at −45 and 60 V, the voltage of the ion guide was set at 9 V, and the voltage of the aperture was set at 5 V to guide sample ions into the PCBIT. The front end-cap electrode was used as an ion gate. The frequency of the tapping waveform was kept at 1 MHz (the period of the waveform is 1 μs). During the period of "cooling," the DC potential of the front end-cap electrode was adjusted to 60 V to trap ions in the direction of the Z axis. The voltage of the ion guide and aperture were also adjusted to 5 and 4 V. The accumulated ions in the PCBIT would be collided with helium buffer gas and

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gradually lose their kinetic energy. During the period of "mass analysis," the frequency of the trapping waveform was scanned from 1 to 0.33 MHz (the period of the waveform changes from 1 to 3 μs), so ions with different mass-to-charge ratios would be ejected sequentially from the PCBIT. The frequency of the excitation waveform was derived digitally by dividing the frequency of the trapping waveform signal, and a division rate of 1/3 was employed in the experiment. During the period of "ion clearing," the excitation waveform was turned off, and the trapping waveform potential was adjusted to 5 μs to force the residual ions in the trap to leave.

Materials. The arginine (Aladdin-Reagent Ltd. Shanghai, China) solution was prepared with 50:50 methanol/water and 0.5% acetic acid and diluted to 5×10^{-5} M.

The reserpine (Aladdin-Reagent Ltd. Shanghai, China) solutions were prepared with 50:50 methanol/water and 0.5% acetic acid and diluted to 5×10^{-5} M.

The PPG standard solution was purchased from the mSPEC Group.

RESULTS AND DISCUSSION

Mass Resolution. A prototype PCBIT with a geometry of $x_0 = y_0 = 5$ mm was first operated in "digital ion trap mode" to record mass spectra of arginine and reserpine. The amplitude of the trapping waveform, the amplitude of excitation waveform, and the scan rate were adjusted to optimize experimental results.

The mass spectrum of arginine, with a mass resolution around 500, is shown in Figure 6a, obtained when the amplitude of the trapping waveform was fixed at 420 V_{p-p}, the amplitude of AC was fixed at 0.8 V_{0-p}, and the scan rate was fixed at 398 Th/s. The mass spectrum of reserpine, with a mass resolution in excess of 1500, is shown in Figure 6b, obtained when the amplitude of the trapping waveform was fixed at 585 V_{p-p}, the amplitude of the excitation waveform was fixed at 0.9 V_{0-p}, and the scan rate was fixed at 199 Th/s, correspondingly.

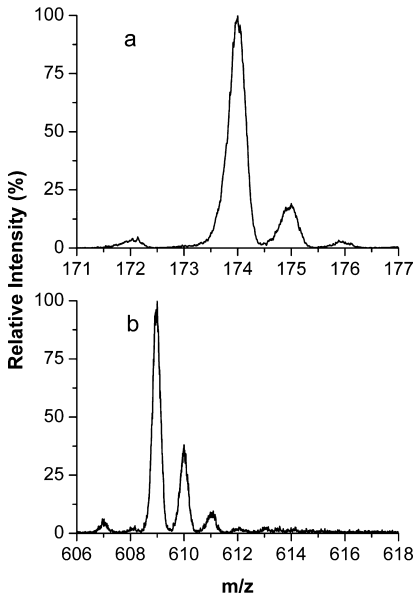

Figure 6. Mass spectra of arginine and reserpine with best mass resolution (samples were both tested in "digital ion trap mode"). (a) Mass resolution of arginine: mass resolution around 500. The amplitude of the trapping waveform was fixed at 420 V_{p-p}, the amplitude of AC was fixed at 0.8 V_{0-p}, and the scan rate was fixed at 398 Th/s. (b) Mass resolution of reserpine: mass resolution in excess of 1500. The amplitude of the trapping waveform was fixed at 585 V_{p-p}, the amplitude of the excitation waveform was fixed at 0.9 V_{0-p}, and the scan rate was fixed at 199 Th/s.

We also studied the scan rate effect on mass resolution when the amplitude of the trapping waveform was fixed at 510 V_{p-p}, and the amplitude of the excitation waveform was fixed at 0.4 V_{0-p}, correspondingly. A series of different scan rates were tested, and the results are shown in Figure 7. It shows the same trend as other types of ion trap mass analyzers that a lower scan rate leads to a higher mass resolution. When the scan rate is 199 Th/s, the fwhm is the smallest. However, while the scan rate decreased too much, the sensitivity would be sacrificed too

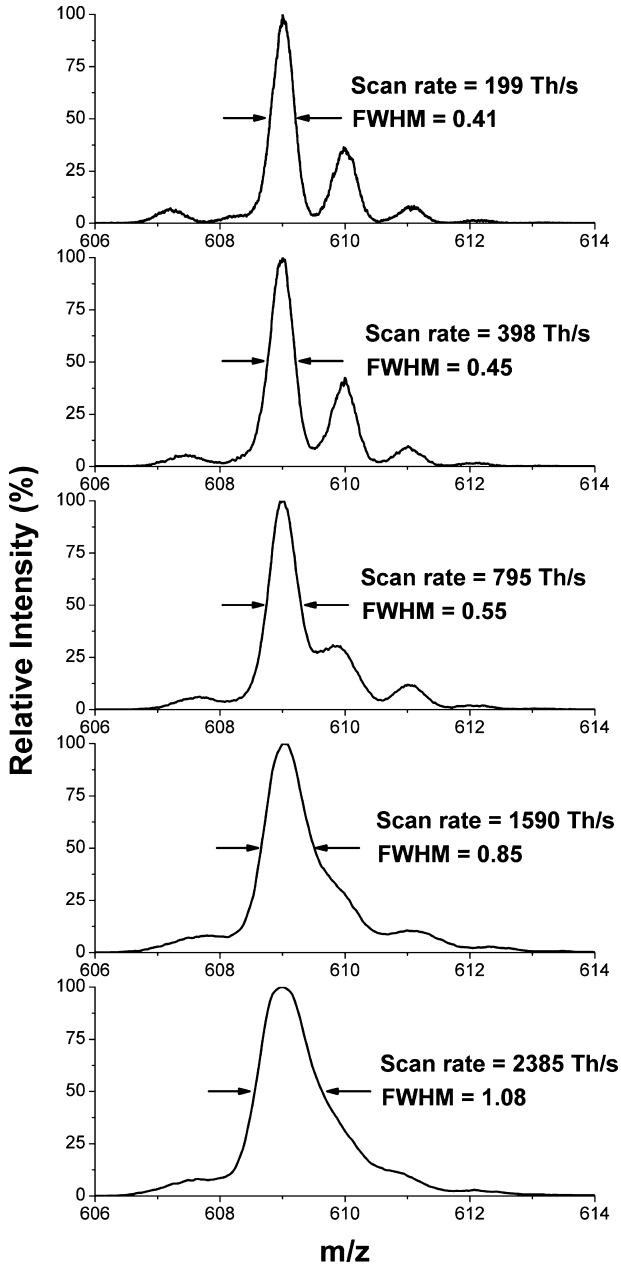

Figure 7. Mass resolution at different scan rates. The highest resolution was observed at a scan rate of 199 Th/s. The amplitude of the trapping waveform was fixed at 510 V_{p-p}, and the amplitude of the excitation waveform was fixed at 0.4 V_{0-p}. The scan rate was set from 199 Th/s to 2385 Th/s.

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much also, which means we need to choose a compromising scan rate in different experiments to keep both the mass resolution and sensitivity acceptable.

Mass Range. During the experiment of mass range, the PPG sample was tested in "digital ion trap mode." The amplitude of the trapping waveform was fixed at 475 V_{p-p}, the amplitude of the excitation waveform was fixed at 1.0 V_{0-p}, and the scan rate was fixed at 1193 Th/s. The result is shown in Figure 8, which indicates that the mass range of PCBIT can

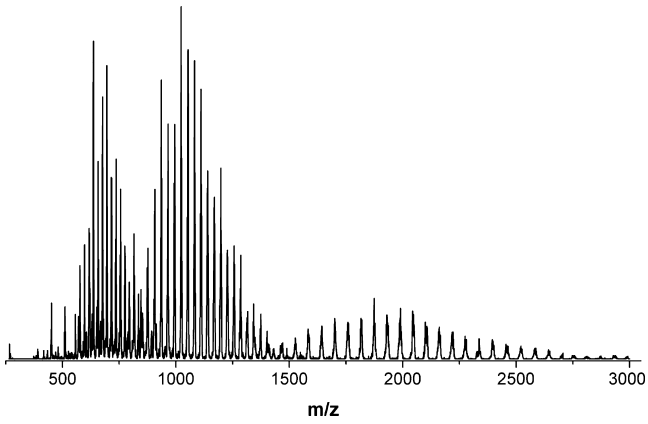

Figure 8. Mass spectrum of PPG. The highest ion peak was observed at m/z = 3000. The amplitude of the trapping waveform was fixed at 475 V_{p-p}, the amplitude of the excitation waveform was fixed at 1.0 V_{0-p}, and the scan rate was fixed at 1193 Th/s.

reach 3000 Th. Obviously, a larger mass range could be obtained if we increased the amplitude of the trapping waveform applied on the PCBIT.

Tandem Mass Spectrometry. Reserpine was used to test the capability of tandem mass spectrometry in our experiments, operated in "digital ion trap mode." The amplitude of the trapping waveform was fixed at 500 V_{p-p}, the amplitude of the excitation waveform was fixed at 1.0 V_{0-p}, and the scan rate was fixed at 2385 Th/s. A mass spectrum of reserpine is shown in Figure 9. The parent ions were isolated by the digital asymmetric waveform isolation (DAWI) method[44] as shown in Figure 9a, while the trapping waveform period was kept at 1.952 μs and its duty cycle was kept at 58%. The digital dipole waveform was used in the collision-induced dissociation.[40] In the experiment, the β value was 0.3478, and the duty cycle of the excitation waveform was 50.27%. Figure 9b shows the fragment ions of CID when the trapping waveform period was set at 1.549 μs.

CONCLUSIONS

In a PCBIT, each PCB electrode was fabricated to specially designed patterns with several separate electric strips, so that PCBIT can optimize the internal electric trapping field distribution and its performance by simply applying different voltages on each strip. A prototype PCBIT was built with two pairs of 64 mm × 12 mm PCB rectangular plates, and one pair of 10 mm × 10 mm stainless steel square plates. The experiments tested with the same voltage ratio here for X-direction electrodes and Y-direction electrodes at 67%. The results show that mass spectra with a mass resolution over 1500 and a mass range up to 3000 Th can be achieved in the experiment. The capability of tandem mass spectrometry was also tested using the PCBIT system. The PCBIT has the

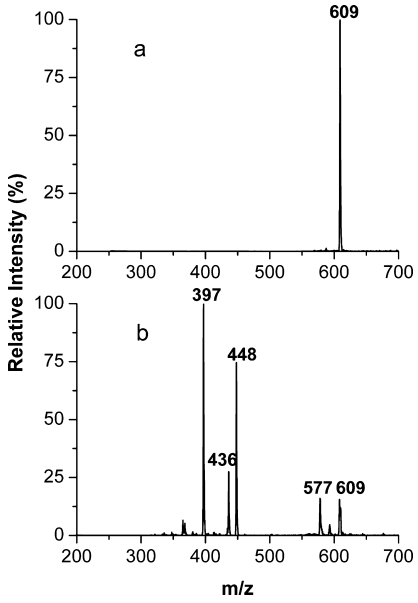

Figure 9. Mass spectrum of reserpine performing tandem mass spectrometry. The amplitude of the trapping waveform was fixed at 500 V_{p-p}, the amplitude of the excitation waveform was fixed at 1.0 V_{0-p}, and the scan rate was fixed at 2385 Th/s. (a) Mass-selected isolation of the reserpine ion, obtained when the trapping waveform period was kept at 1.952 μs and its duty cycle was kept at 58%. (b) CID of the reserpine ion, obtained when β was 0.3478, the trapping waveform period was kept at 1.549 μs, and the duty cycle of the excitation waveform was kept at 50.27%.

unique advantage of an adjustable internal electronic field, as well as the advantages of its simple structure and low cost, and is very suitable for miniaturization of the mass spectormeter. Obviously, the PCBIT technology deserves further research work in many aspects and will be carried on in this laboratory next.

ASSOCIATED CONTENT

Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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