

## One hundred anode microchannel plate ion detector

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A one-hundred-anode microchannel plate detector is constructed on a 10 cm × 15 cm printed circuit board and attached to a homebuilt matrix assisted laser desorption ionization (MALDI) time-of-flight mass spectrometer. Ringing and cross talk between anodes have been successfully eliminated and preliminary mass spectra of peptide ions recorded. With one hundred anodes on the printed circuit board, spatial information about the ion beam can also be readily determined with this detector. During operation, the detector anode assembly loses sensitivity after ions strike it for a considerable period of time due to charging of the non-conductive regions between anodes. However, this effect can be minimized by deflecting matrix ions away from the detector. © 2011 American Institute of Physics. [doi:10.1063/1.3622506]

### I. INTRODUCTION

Time-of-flight (TOF) mass spectrometers have become a powerful tool for identification and structure elucidation of complex organic and biological compounds.<sup>1,2</sup> Well-known advantages of TOF include its unlimited mass range, the acquisition of a complete mass spectrum for each pulsed ion extraction event, its relatively high resolution, and mass accuracy. Two types of data acquisition systems are used in TOF mass spectrometers – transient recorders and time-to-digital converters (TDCs). Transient recorders digitize the ion current from the output of a microchannel plate (MCP) or dynode electron multiplier detector, and are mainly used in MALDI-TOF instruments because of their wide dynamic range. TDCs register the arrival of individual ions (relative to the TOF ion extraction pulse), and store the arrival time in memory. Each TOF acceleration pulse can result in one or more arrival times, and these individual events are summed in memory over the course of the acquisition period, forming a mass spectrum that is a histogram of several thousand events. A problem with this method is that the electronics cannot distinguish two or more particles that arrive simultaneously at the detector, making it impossible to detect more than one particle for each mass in one cycle. One solution to this problem is the use of multiple anodes. In this case, ions that arrive at the detector at the same time but at different locations lead to electron cascades that impinge on different anodes. If each anode is connected to a different data acquisition channel, dead time on one channel does not affect another, thereby improving the dynamic range of the detection system. Previously, Russell and co-workers built a four-anode detector in an ESI-TOF instrument that improved the counting efficiency of a TDC data acquisition system by a factor of 2.5.<sup>3</sup>

A multi-anode MCP-based detector with completely independent anodes would also be a powerful tool for measuring the spatial distribution of a large number of incident particles striking the detector on a nanosecond time scale.<sup>4</sup> This could be useful in a distance-of-flight mass spectrometer (DOF-MS).<sup>5</sup> In this type of instrument, ions leave the source with  $m/z$ -dependent velocities. At some specific time, their mass-dependent locations are determined. An array of ion de-

tectors is needed in DOF-MS and the multi-anode MCP detector described in this work could serve in this capacity. Several types of MCP signal readout schemes have been used such as resistive anodes or strip anodes.<sup>3,4</sup> The design and technology to build the anodes are particularly critical in order to obtain good spatial resolution and accurate timing. So far, a multiplex acquisition system in a MALDI-TOF biological mass spectrometer has not been reported.

A multi-anode detector was constructed and mounted onto a homebuilt MALDI time-of-flight instrument in our laboratory. This detector is made of dual rectangular microchannel plates backed by 100 individual anodes, each connected to an independent TDC channel. (While in principle a transient digitizer could be connected to each anode, in practice this would be cost-prohibitive). In this paper, we describe the multiplex acquisition system and the design of the detector. We successfully solved the problem of cross talk between the anodes and preliminary data involving peptide ion spatial distributions were obtained. An anode charging problem was encountered, but by deflecting matrix ions from the detection region, it was minimized.

### II. EXPERIMENTAL

#### A. Material

$\alpha$ -cyano-4-hydroxycinnamic acid, anhydrous methanol, and acetonitrile were obtained from Aldrich Chemicals (Milwaukee, WI, USA). Formic acid and trifluoroacetic acid were purchased from Mallinckrodt Baker (Phillipsburg, NJ, USA). Angiotensin II (DRVYIHPF) and fibrinopeptide A (ADSGEGDFLAEGGGVR) were purchased from Sigma (St. Louis, MO, USA).

#### B. Instrument design

Experiments were performed on a homebuilt MALDI time-of-flight instrument, shown schematically in Fig. 1(a). MALDI ions are generated in the source by irradiating the sample spot with 337 nm light from a nitrogen laser (VSL-337ND-S, Spectra-Physics) at a repetition rate of 30 Hz. Our

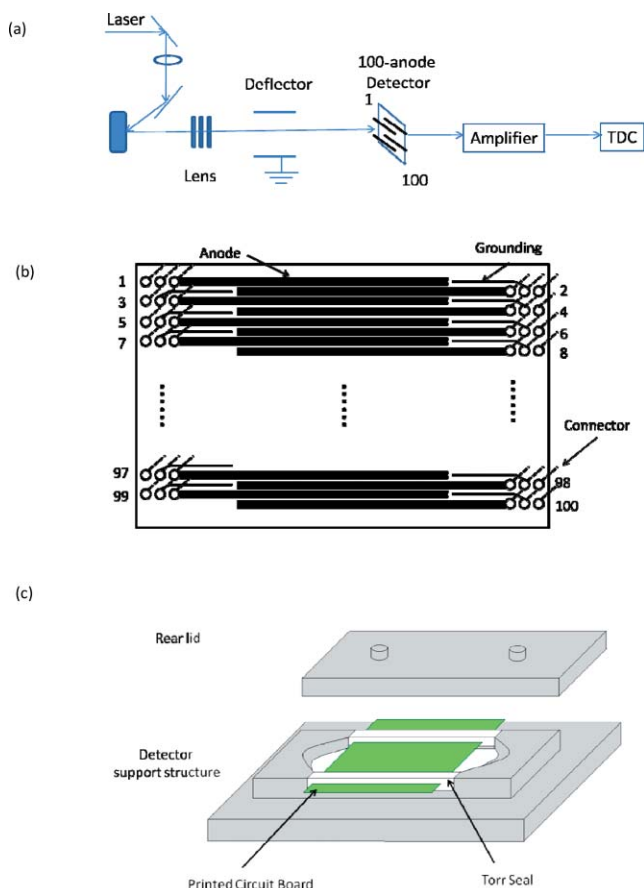


FIG. 1. (Color online) (a) The time-of-flight apparatus, (b) the printed circuit board, and (c) the back flange.

linear time-of-flight instrument is operated using pulsed ion extraction with ion drift energies of 20 keV. The extraction delay is 120 ns after the laser pulse and the draw out voltage pulse is 3 kV. Peptide ions are then separated in a 110 cm horizontal linear flight tube and finally detected by the microchannel plate detector. Ions pass through a two-plate deflector that is used to steer them to different regions on the detector.

### C. Detector

The design of a 100-anode detector presents two primary challenges. The first is to design the optimum width and shape of this large number of anodes and construct them to cover a small region of space. The anode spacing must enable useful spatial resolution. At the same time, it should be compatible with standard electronics components. We chose to construct the multi-channel detector from a printed circuit board. Conductive traces are the anodes and the non-conductive regions serve as insulators. The width of the anodes is also crucial in this experiment. If they are too narrow, then electrons can accumulate on the non-conductive regions between traces. In this case, the surface of the printed circuit board can charge up and sensitivity is lost. In contrast, if they are too wide, the gaps between traces are smaller and cross talk between anodes increases.

The second challenge is to transfer fast signals from so many anodes to the data acquisition electronics without distortion. Standard printed circuit board connectors and twisted pair ribbon cables were used to connect the multiple anodes to data acquisition electronics.

In the final design (Fig. 1(b)), the 100 anodes on the printed circuit board are spaced 1 mm center to center. Each anode is a conductive trace  $\sim 0.85$  mm wide and the spacing between traces is about 0.15 mm. The channels are numbered from 1–100 from top to bottom. The printed circuit board was mounted on a support flange such that only the left and right ends shown in Fig. 1(b) protruded outside of the vacuum system. Varian Torr-Seal epoxy was applied to seal both ends of the board to the flange. The epoxied area was then milled flush with the adjacent surface shown in Fig. 1(c). A rear lid was sealed to the support flange using an o-ring and machine screws. The whole assembly was mounted onto the MALDI-TOF instrument. Because the region behind the printed circuit board is evacuated, there is no pressure causing it to bend. The mass spectrometer is evacuated to  $2 \times 10^{-7}$  Torr. Outside the vacuum chamber, standard printed circuit board connectors were mounted to the two exposed ends of the circuit board. Preamplifiers described below were plugged onto both connectors.

Dual rectangular microchannel plates were mounted in a chevron configuration in front of the printed circuit board anode. They each have  $25 \mu\text{m}$  pores with a bias angle of  $8.0^\circ$ . The gain of each MCP is about 400 at 1000 V and 10 000 at 1200 V. The voltage across the two MCPs was adjusted between 1600 V to 2000 V for different experiments.

### D. Electronic parts and acquisition system

A  $3 \text{ cm} \times 3 \text{ cm}$  preamplifier was linked to each anode channel at one of the printed circuit board connectors. Preamplifiers consisted of a  $5 \times$  gain stage and a high speed comparator with an adjustable threshold. An auto-zero circuit compensates for the offset of the amplifier and comparator. For each end of the printed circuit board, differential outputs from 50 preamplifiers were gathered on a collection board. In supplementary material Fig. 1(a), six of the 50 preamplifier printed circuit boards are shown bridging the anode printed circuit board and one collection board.<sup>6</sup> Mounted on each collection board is a connector that is compatible with regular ribbon cables as shown in supplementary material Fig. 1(b). Two ribbon cables connected each collection board to a single 128 channel multi-hit TDC (V1190A, CAEN Technologies, Inc.). The TDC, whose double-hit resolution is 5 ns, is located in an extended Versa Module Eurocard (VME) crate for time measurements. Time encoding was achieved in a time bin of 100 ps for one single anode experiments and 800 ps for 100 anodes experiment. The full event built in the VME processor was then buffered and sent to the acquisition computer. The data were collected and monitored by using software READOUT (Michigan State University) and SPECTCL (version 3.2-pre4, Michigan State University) software. Two sets of

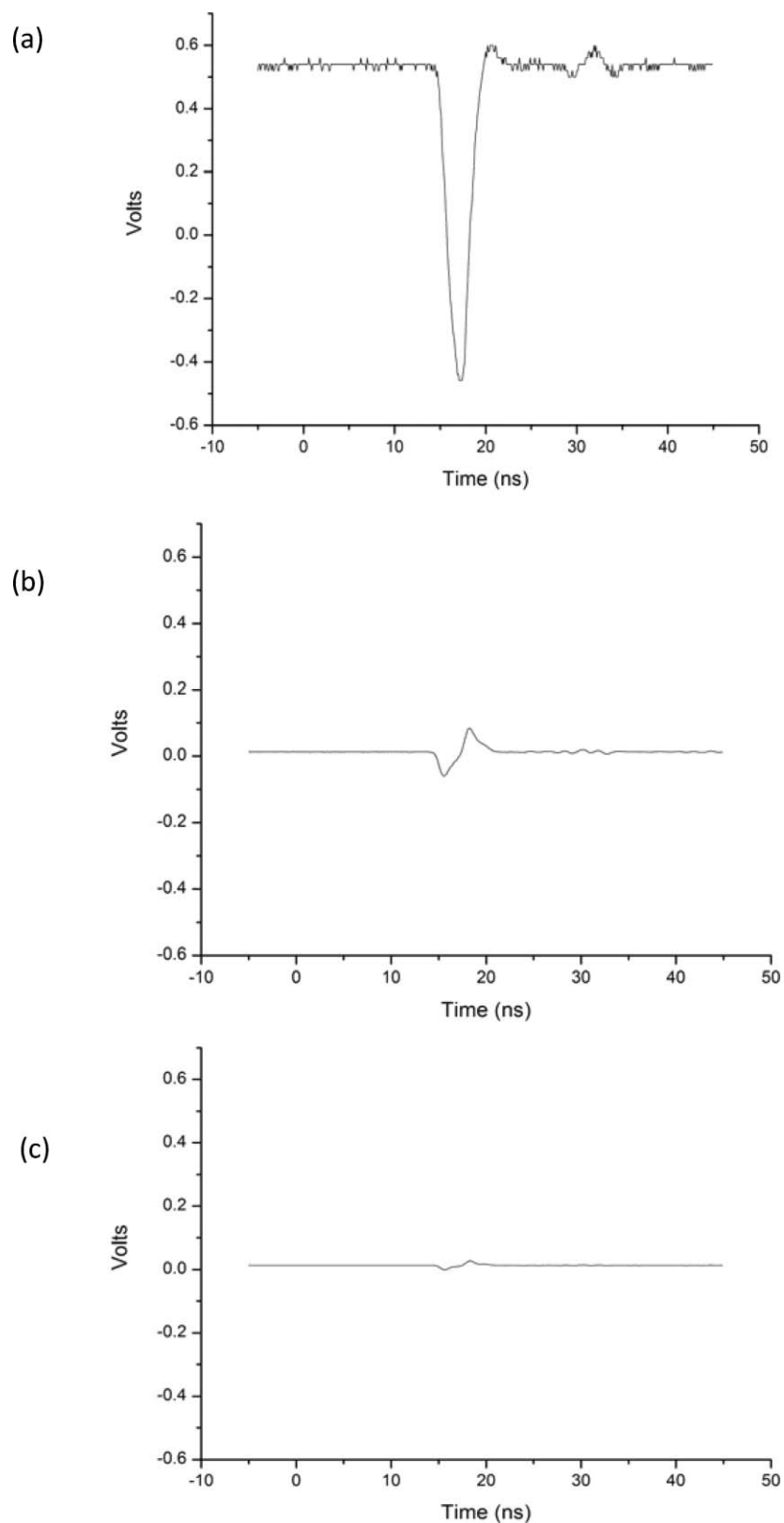


FIG. 2. Following application of a voltage pulse to anode 5, amplified signals detected on (a) anode 5, (b) anode 4, and (c) anode 3.

data from the collection boards were obtained and recombined in ORIGIN 7.0 to generate one and two-dimensional spectra.

### E. Sample preparation

Peptide samples were prepared in  $40 \text{ pmol}/\mu\text{l}$ , and  $0.5 \mu\text{l}$  of this solution was spotted on a stainless steel MALDI plate.

When the spots were dry, 0.5  $\mu\text{l}$  of matrix solution (10 mg/ml  $\alpha$ -cyano-4-hydroxycinnamic acid in 0.1% trifluoroacetic acid in 50:50  $\text{H}_2\text{O}$ :acetonitrile) was applied on top.

### III. RESULTS AND DISCUSSION

#### A. Validation of the printed circuit board

Different printed circuit board designs were built and tested. The shape and length of the anode traces and the spacing between them were all varied. A printed circuit board with 10 cm long parallel traces each  $\sim 0.85$  mm wide and spaced 1 mm center to center was finally constructed. Connectors were then soldered onto the two ends of the circuit board.

To test the design of the printed circuit board, a 3 ns, 200 mV pulse from a commercial pulse generator was applied to the center of anode 5. The signal from this anode was amplified by a factor of five and recorded by a fast waveform digitizer. The result is displayed in Fig. 2(a). It is apparent that the pulse is not distorted by the preamplifier; it is fast and there is little ringing.

To measure the cross talk between anodes, signals on anode 3 and 4 were monitored when the pulse was applied to anode 5. As displayed in Figs. 2(b) and 2(c), a small amount of cross talk is observed between the adjacent odd and even trace. However, the level of the cross talk is sufficiently low that it does not trigger the comparator on the preamplifier. In an attempt to reduce it further, thin metal traces held at ground potential were added between anodes as shown in Fig. 1(b), but no obvious improvement was found.

#### B. Comparison with a conventional MCP detector

Signal from all anodes of the multi-channel detector can be monitored simultaneously. A single channel yields spectra that are similar to those generated from a conventional MCP detector. When the data from multiple anodes are combined, three-dimensional information, with anode number as the third dimension, can be recorded.

A conventional single-anode round MCP detector was mounted on the MALDI-TOF instrument for a performance comparison. The spectrum obtained with angiotensin II is displayed in Fig. 3(a). The FWHM of the monoisotopic peak is about 10 ns. Under the experimental conditions employed, the linear TOF instrument did not completely resolve isotopic structure.

With the multi-anode detector mounted in the same location, the mass spectrum shown in Fig. 3(b) was obtained. As seen in this single anode spectrum, the isotopic distribution is not resolved and the FWHM of the angiotensin II peak is about 35 ns. The spectrum looks rough compared to the previous one. This is probably due to higher jitter associated with triggering the multi-anode data acquisition system compared to the waveform digitizer. Figure 3(c) is a typical three-dimensional spectrum generated by the multi-anode detector where one axis displays the anode number from 1–100 and the other axis specifies the time bin number (Each bin corresponds to 800 ps). For the anode that displays the maximum signal, 5009 total counts spread over 140 bins. The bin with

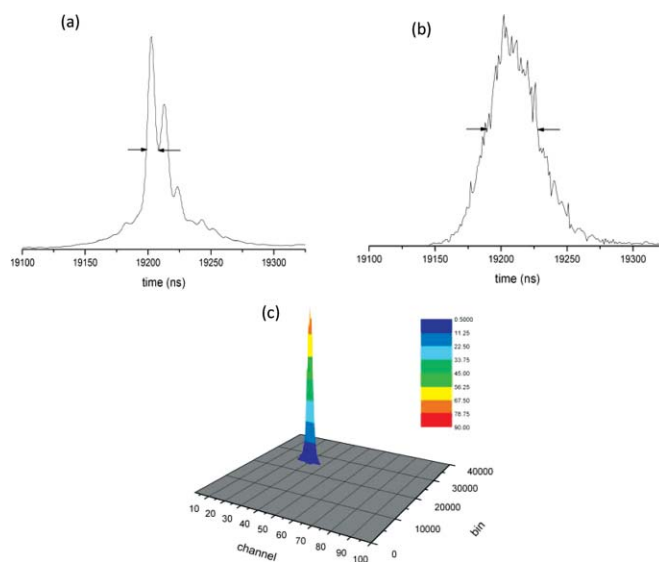


FIG. 3. (Color online) MALDI-TOF spectra of the singly charged peptide angiotensin II (DRVYIHPF) obtained with (a) a conventional round detector, (b) one anode on the multi-anode detector, and (c) all the anodes on the multi-anode detector.

the most signal has 82 counts. The ion beam profile extends over anodes 23–38 corresponding to a distance of  $\sim 16$  mm, and it peaks near anode 30. Approximately 80% of the ions strike the detector in a 5 mm wide region.

As an example of the simultaneous spatial and temporal resolution of the detector, two peptides (angiotensin II,  $m/z$  1046.5 Da and fibrinopeptide A 1536.5 Da) were loaded onto the sample plate and MALDI ions were detected. Figure 4 displays the resulting spectrum. Both peaks are centered at anode 32. angiotensin II reaches the detector in 19.2  $\mu\text{s}$  and fibrinopeptide A arrives 23.3  $\mu\text{s}$  after the extraction pulse.

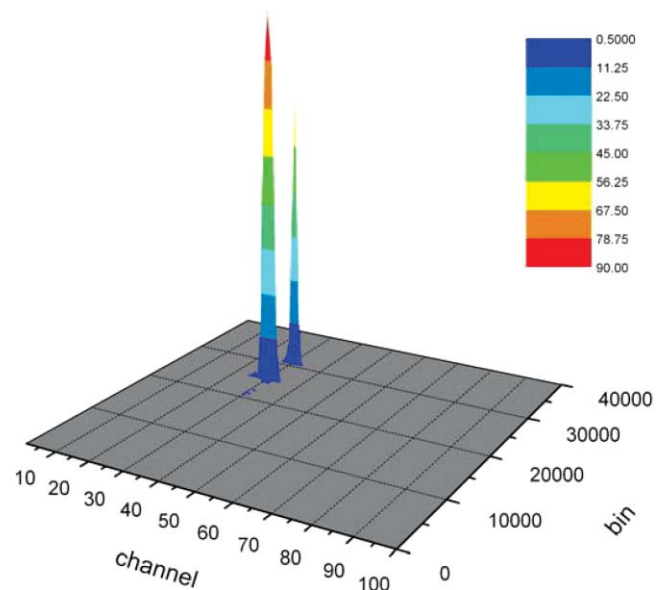


FIG. 4. (Color online) MALDI-TOF spectrum of the singly charged peptide angiotensin II (DRVYIHPF) and fibrinopeptide A (ADSGEGDFLAEGGGVR) obtained with the multi-anode detector.

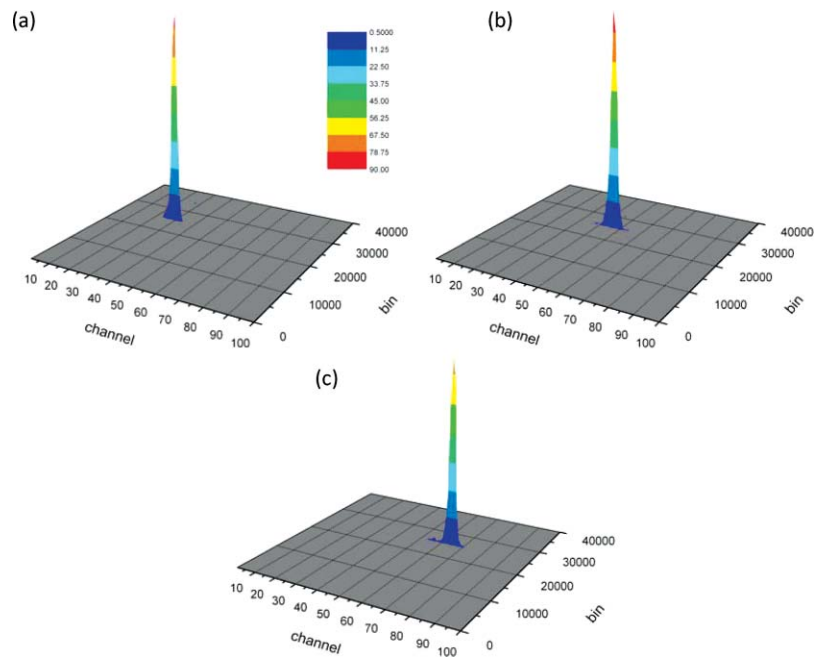


FIG. 5. (Color online) MALDI-TOF spectra of the singly charged peptide angiotensin II (DRVYIHPF) recorded with the multi-anode detector with dc voltage on the deflector of (a) 0 V, (b) 500 V, and (c) 1000 V.

### C. Ion position change on the multi-anode detector

The position of the ion beam could be moved by changing the ion deflector voltage. With angiotensin II ( $m/z$  1046.5 Da) loaded onto the sample plate, and no deflector electric

field, the ions arrived at anodes 25–35 and the center of the packet was at anode 31 (Fig. 5(a)). When 500 V was applied to the deflector, the center of the ion packet shifted to anode 47 (Fig. 5(b)). Similarly, it moved to anode 66 when the voltage

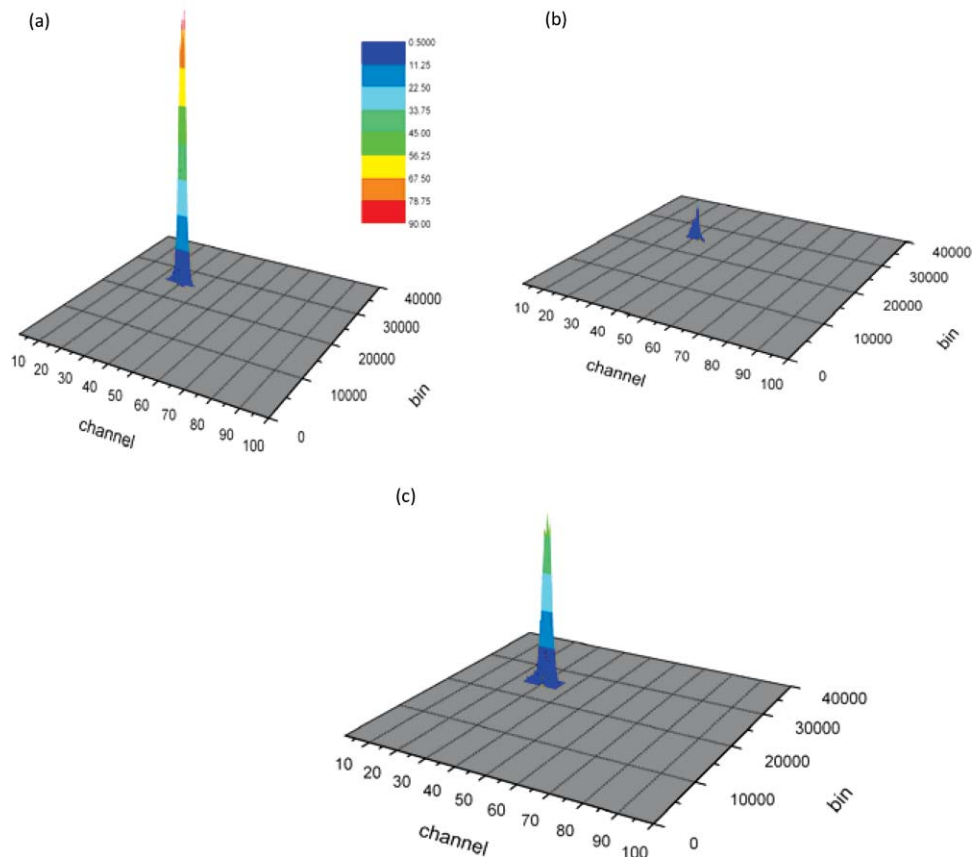


FIG. 6. (Color online) MALDI-TOF spectra of the singly charged peptide angiotensin II (DRVYIHPF) obtained from the multi-anode detector (a) at the start of data acquisition, (b) after the detector had been exposed to matrix and peptide ions, and (c) after deflecting matrix ions off the detector.



was increased to 1000 V (Fig. 5(c)). In general, the ion beam can be steered toward any anode on the multi-anode detector by changing the voltage on the deflector. In this instrument design, for every 500 V, the beam of peptide ions moved up or down about 18 anodes or 1.8 cm.

Since we can easily monitor the lateral position and the breadth of an ion beam, this multi-anode detector can be a useful tool for optimizing instrument performance. Furthermore, since there are essentially 100 independent detectors, spatially resolved and high throughput experiments are quite feasible.

#### D. Detector charging

One concern about this detector design involves surface charging caused by electrons striking the non-conductive regions between the anodes. This could cause a loss in sensitivity. In our experiments, we noticed a temporary reduction in sensitivity after intense ion signals were detected over a period of time. For example, Fig. 6(a) is the spectrum generated at the beginning of one experiment. Figure 6(b) is the spectrum obtained on a new MALDI spot from the instrument after 3 h of data acquisition. In these experiments the matrix was not deflected from the detector. It is obvious that the detection sensitivity decreased. Typically, the detector regains its sensitivity after about 8–10 h of isolation.

Approximately 99% of the molecules on a MALDI spot are matrix, so matrix ions and their clusters are dominant ion signals. By deflecting these ions, we expected to reduce or eliminate the process of detector charging. To test this, 2000 V dc was applied across the deflector plates, causing matrix ions to be pushed downward by about 7.2 cm, which is off the detector. Then, 2.1  $\mu$ s after the ion extraction pulse the deflector voltage was dropped to ground allowing peptide ions to

pass through. Figure 6(c) is the spectrum obtained after 6 h of continuous MALDI ion production with the matrix ions deflected. It is clear that the charging effect is considerably reduced by deflecting most of the matrix ions off the detector. This multi-anode detector still maintains sensitivity after 6 h, which is suitable for daily routine analysis.

#### IV. SUMMARY

A multiplex acquisition system was constructed with a 100-anode detector and a multi-channel TDC. Each of the 100 individual anodes was connected to an independent TDC channel. Cross talk between the anodes was small and preliminary mass spectra of peptide ions were recorded. Spatial information about the ion beam can also be derived with this detector. The detector anode displays a tendency to charge up after ions strike it for a considerable period of time causing some loss in sensitivity. However, this can be reduced by limiting the detector's exposure to matrix ions.

#### ACKNOWLEDGMENTS

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<sup>6</sup>See supplementary material at <http://dx.doi.org/10.1063/1.3622506> for photographs displaying the anode printed circuit board, preamplifiers, and collection board.

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