TECHNICAL ARTICLE

ACHIEVING LINEAR DETECTOR RESPONSE in TOF-MS

ETP Electron Multipliers

Dick Stresau and Kevin Hunter, ETP, Sydney, Australia
John Gray, ETP Scientific, Inc., Auburn, Ma., USA

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Rapid development of Time-Of-Flight mass spectrometry is placing increased demands on detectors. This challenge has been met using discrete-dynode electron multipliers designed specifically for TOF applications. Our work has shown that three different issues are involved in achieving linear response in TOF detectors:

1) linearity with large average output currents;
2) linearity for large peaks;
3) gain recovery after a large peak.

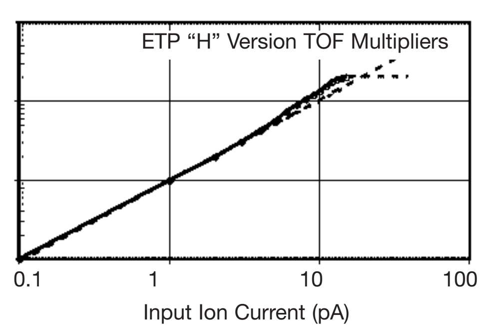
The flexibility of discrete-dynode technology allows us to achieve exceptional performance in each of these areas by optimizing the ion and electron optics, individual dynode shapes, dynode voltage distribution, and inter-dynode capacitance. The result is a multiplier specifically tailored for TOF-MS applications. We have been able to achieve exceptional performance in each of these three key areas because of our flexible discrete dynode technology.

The 14860 TOF multiplier includes:

- a 10kV conversion dynode
- a 20mm X 25mm input aperture
- fast pulse recovery
- large current and pulse dynamic range
- and a snap-in replaceable multiplier section

Linearity with large average output currents: Linear response for large output currents is similar to the considerations required in conventional mass spectrometry where one must be careful not to go beyond the linear limit for output current drawn from the multiplier.

Figure 1



Linear detector response means that its output signal is proportional to the input ion current. On **Figure 1**, the straight, dashed line shows linear response and the solid line shows response of an ETP TOF multiplier. Notice that it is linear right out to 30 µA. Beyond this point the multiplier over-responds until it reaches about one third of its bias current.

Figure 2

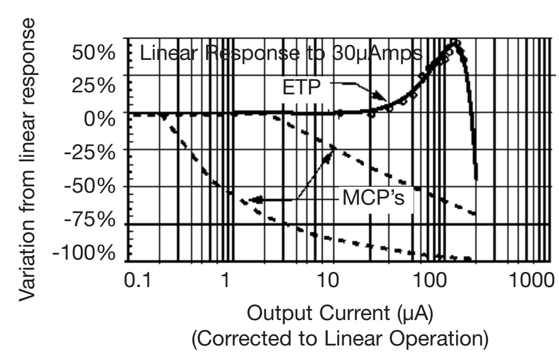


Figure 2 uses the same data but is plotted as a percentage variation from linear response against the output current expected for linear response. Notice that the discrete-dynode multiplier is linear out to 30µA. It is interesting to compare this to MCP performance. Even high current MCPs have only one tenth the current capacity of the new discrete-dynode TOF multipliers. Exceeding the linear limit will result in a loss of abundance calibration for the entire spectrum. A multiplier can be driven to very high output currents by operating at high gain with a high input ion current from samples with high abundance.

Figure 3

Excessive Output Current Changes Calibration for all Peaks in TOF Spectra

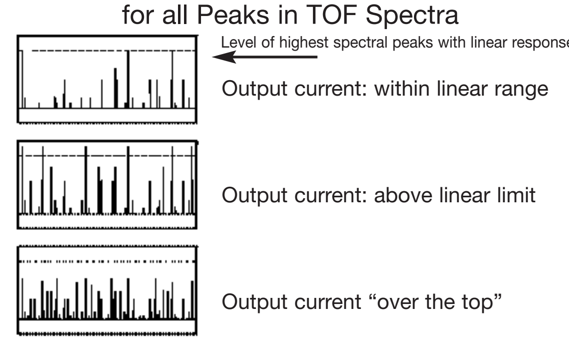
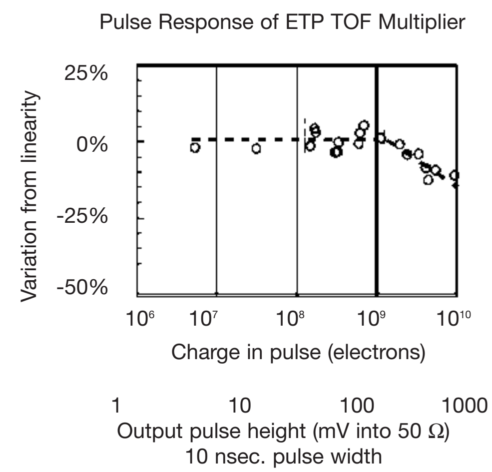


Figure 3 shows how excessive output current influences TOF spectra. When increasing the output current of an ETP multiplier beyond its linear limit it will initially over-respond and indicate higher than actual abundance's for all peaks. Further increase of output current will result in under-response indicating lower than actual abundances for all peaks. In each case the result will be a loss of abundance calibration for the entire spectrum.

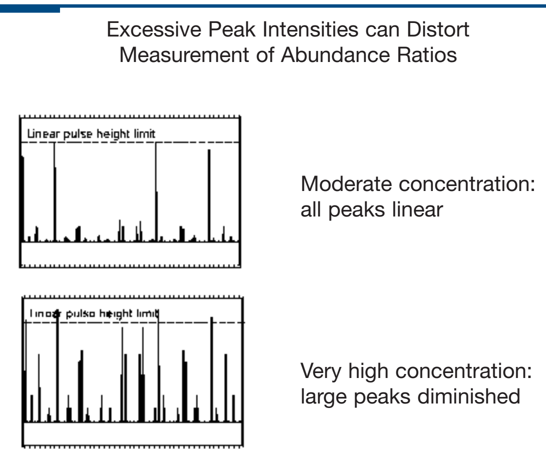
Linearity for large peaks: The linear limit for an individual peak in a TOF spectrum is several orders of magnitude greater than the average current limit.

Figure 4



Our new discrete dynode TOF multipliers operate linearly with very large output pulses: up to 10^9 electrons or 500 mV (into 50 ohms, 10 nsec. wide). Beyond this point space charge effects inhibit the flow of electrons between dynodes.

Figure 5



Whereas excessive average-output-current affects the height of all peaks in a spectrum, an individual peak that exceeds the linear limit will be diminished without influencing the level of the smaller peaks. This results in distorted abundance ratio measurements.

Figure 6

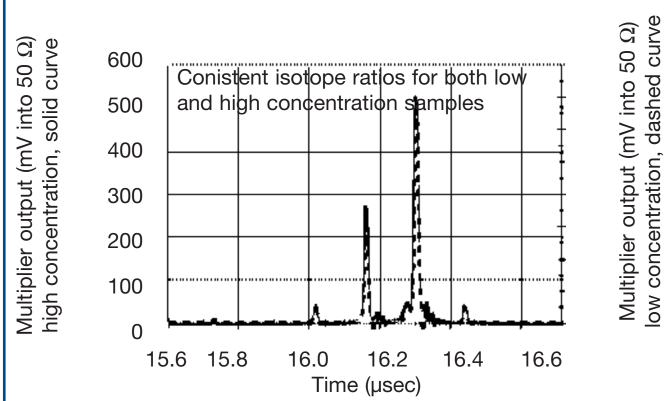


Figure 6 shows two spectra superimposed. The solid curve was taken with a very high concentration sample (left scale). The dashed curve is of the same compound but with 1/30th the concentration (right scale). The second spectrum is used as a "standard," as its low peak sizes give an undistorted measure of abundance ratios. The two spectra are virtually identical. The dicrete-dynode multiplier shows no sign of non-linearity even with a 500 mV pulse!

The actual dynamic range of a TOF system depends on its electronics as well as the detector performance. Carefully engineered electronics will enable operation with low multiplier gain and directly increase the system's upper limit in number of ions in a single pulse as shown in **Table 1**.

Table 1

Low Gain Operation can Provide Increased Dynamic Range

$$I_{max} = \frac{Q_{max}}{G}$$

I_{max} = Maximum number of ions in peak
Q_{max} = Maximum linear output pulse (electrons)
G = Multiplier Gain

I_{max}	Gain	Q_{max} (14860 TOF Multiplier)
100	10^7	10^9
1000	10^6	10^9
10,000	10^5	10^9

Gain Recovery after a large peak:
Achieving good linearity in a single pulse will have little advantage if the multiplier becomes saturated and effectively non-functional following the pulse. Therefore it is important for a TOF ion detector to have very fast recovery time after a large signal pulse.

Figure 8

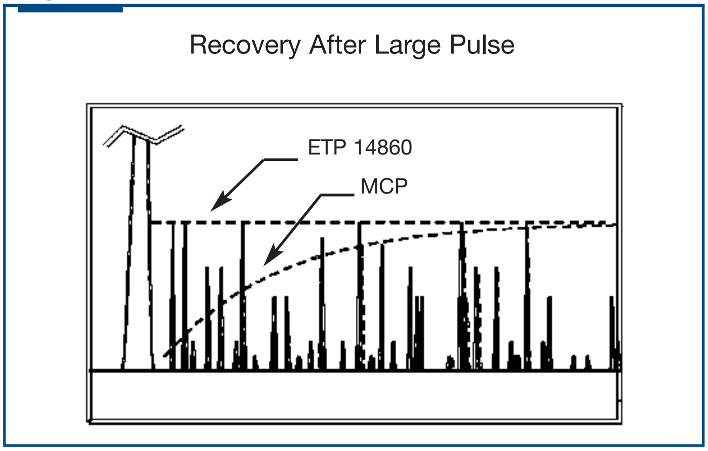


Figure 8 shows how slow gain recovery after large pulse can affect TOF data. If not well designed, a multiplier can have its electrical charge depleted by large pulses causing a reduction in gain until the bias current recharges its internal capacitance. MCP's may take several milliseconds to recover. Careful use of distributed capacitance has virtually eliminated this effect from the latest ETP TOF multipliers.

To demonstrate large pulse recovery speed, we used a double gating pulse on an orthogonal gate TOF system. This produced two overlapping spectra in the same TOF scan. The time between the two gate pulses was adjusted, allowing adjustment between the mass 28 peak from one pulse and the mass 32 peak of the other. Note how the height of the mass 32 peak remains unchanged as the time between peaks is decreased. The large pulse recovery time is less than 30 nanoseconds!

Figure 9a

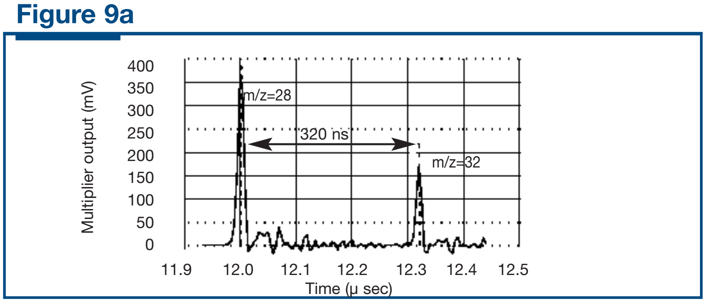


Figure 9b

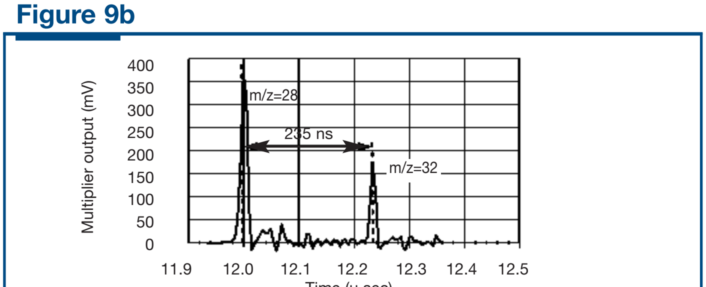


Figure 9c

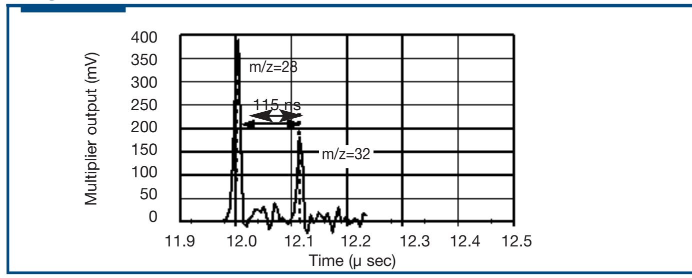


Figure 9d

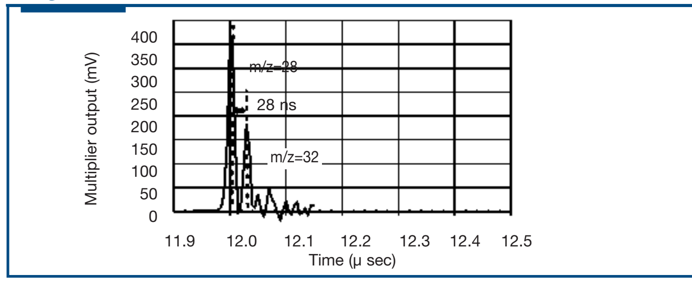
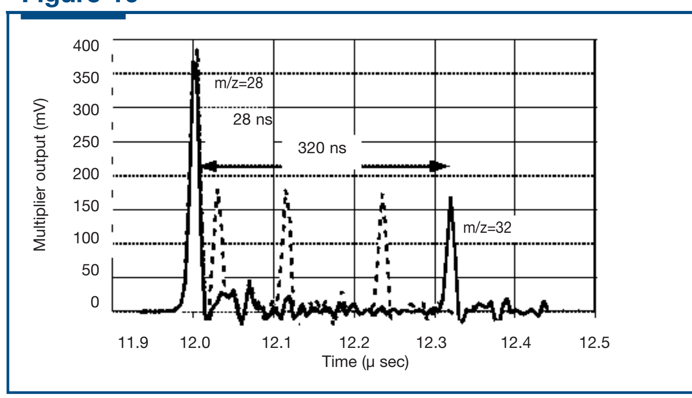


Figure 10 shows the four measurements superimposed so that the pulse height consistency is easily seen.

Figure 10



Conclusion: The newly developed multipliers excel in all of the areas which are important for achieving large dynamic range in TOF systems:

linear output currents up to 30mA,

linear response for pulses up to 500 mV,

recovery time after large pulse of less than 30 nsec.

All of ETP's latest TOF multipliers incorporate these features for a large dynamic range. They have been tailored to suit a diverse range of TOF-MS applications, and represent the latest development in TOF-MS ion detection.