Improving Quantification in Time of Flight (TOF) Mass Spectrometers by Optimizing Detector Response

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Overview:

Purpose:

To improve quantification of ion abundance in a time of flight mass spectrometer by adjusting the operating parameters of the ion detector.

Methods:

The pulse amplitude distribution for a finite number of samples of a multi-ion peak with internal variation is measured for three different gain-balance settings of a hybrid ion detector. Peaks representing two isotopes that occur in a known ratio are used to simultaneously check detector linearity.

Results:

Increasing the MCP gain in a hybrid detector can improve signal to noise ratio while maintaining linear response.

Introduction:

Pulse Height Distributions:

The electron emission process that all electron multipliers rely on is a random process that is typically described with Poisson statistics. The output of electron multipliers is based on repeated electron emission events that occur on many discrete dynodes or along a continuous dynode structure. Calculating the pulse height distribution (the probability of measuring a pulse of a particular height for a single input event) from secondary electron yield data is difficult[1,2], but properties of pulse height have been calculated and are summarized by the curves shown in Figure 1.

Figure 1. Pulse height distributions.

Generally, mean ion-induced electron yields in the keV energy range are proportional to the primary ion velocity which, in a TOF mass spectrometer, varies across the mass range by design. In general, however, for singly charged ions in the mass range 100-3000 with energies <10 keV, the mean ion-induced electron yield is low. This makes the TOF abundance measurement inherently very noisy. Even with excellent multiplier performance, the resulting pulse height distributions will not allow real ion counting, but instead ion abundance must be inferred from averaging many waveforms assuming that the many samples of the pulse height distribution will converge to the mean (which is the average gain).

Introduction (continued):

Orthogonal TOF Ion Source:

Even if electron multipliers produced the exact same output with every ion arrival, practical orthogonal TOF ion sources do not deliver the same number of ions to the detector with each pulser push. As an example, in the single-push waveform shown in Figure 2, the main ion peak (which on average should be approximately 14 times more abundant than the second peak) is completely absent, while the isotopic peak is a waveform that is likely the result of multiple ions hits. This variation is an additional noise source in abundance measurements.

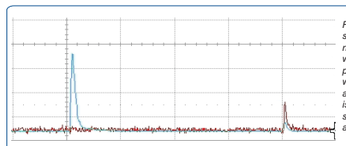

Figure 2. The orthogonal TOF ion source does not deliver the same number of ions to the ion detector with every ion push. In this ion push, the isotope peak is present while the main peak (which is on average ~14 times more abundant) is not. The averaged signal (blue) shows a waveform with the proper abundance ratio.

BiPolar Ion Detector:

Because of the importance of "first-strike" ion-induced electron emission, ions are typically accelerated to keV energies to impact the detector input surface. These potentials are much higher than the multiplier bias voltages and differ in polarity when both positive and negative ions are to be evaluated.

The bipolar detector used in this study (Figure 3) is a hybrid detector that uses a single microchannel plate operated far from saturation to produce an output electron pulse in response to incoming ions. A scintillator is used to convert the output electron cloud to a pulse of light. A fast photomultiplier tube (PMT) module (Figure 4) is used to measure the resulting light pulse. This allows the output signal to be measured at the same ground reference anode regardless of the DC bias on the MCP input. The use of a PMT also allows for very high output currents as well as exceptional detector lifetime, since the dynode surfaces are protected from the environment that typically degrades detector gain[3]. The use of these three sources of gain (MCP, scintillator, and PMT) allows for gain balancing in the detector.

Figure 3. Ultra-Fast BiPolar TOF detectors.

Figure 4. Photomultiplier Tube (PMT) module with integrated power supply.

Introduction (continued):

Microchannel Plates:

The microchannel plate (Figure 5) is a parallel array of independent electron multipliers. When operated with large localized input signals or at very high gain, the high charge density at the output end of one of the 2-5 micron diameter pores of the MCP can reduce the voltage gradient formed on the channel wall and produce an output that is no longer linearly related to its input.

Figure 5. Microchannel Plate.

The saturation behavior of MCP pores is highly localized when a single MCP is used, and less so when two MCPs are used in series[4,5]. In general, operating the MCP at low voltage/low gain can give exceptional dynamic range, because the limitation is on extracted charge. The channel density of small pore MCPs is 3-20 million per cm^2, so this saturation behavior can be further minimized by using large areas.

Isotopic Ratios:

A method for determining detector linearity relies on comparing magnitude of two peaks which occur in a known ratio. The method relies on the taller peak saturating first, driving the abundance ratio artificially high while the smaller peak is still measured properly. This is a first-order determination of linearity as there are multiple factors that can affect this ratio.

Methods:

An ESI source was used with a calibrant sample including a high concentration of purine to generate ion packets in an orthogonal TOF ion source at a rate of 10 kHz. The accepted isotope ratio of the 122 peak predicts an abundance peak that is 6.93% of that of the 121 peak.

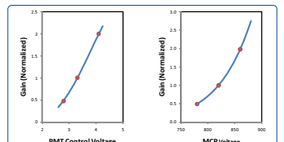

Figure 6. PMT and MCP gain as a function of applied voltage.

A LeCroy 7300A Oscilloscope with 3 GHz Analog bandwidth was triggered off the pulse induced on the system ground by the high voltage pusher pulse. Waveform data was collected at a 20 Giga-samples/second rate for a 200 ns time interval around the 121 mass peak flight time (~20 µs.)

Data was collected for a fixed number (5000) of ion pushes. The amplitude of the primary and isotope ion peaks were measured by restricting the analysis to two 20 ns time windows centered on the two peaks. Isotopic ratios were measured by comparing amplitudes of averaged waveforms and the ratio of amplitude distribution means. This process was repeated for three combinations of MCP and PMT gain (Figure 6) keeping the overall gain of the detector constant at ~6 million at mass 121.

Results:

The ion source used for these measurements produced a significant number of individual-push waveforms with no ions of the target mass 121 as well a significant number with what appeared to be low populations. The distribution of resulting pulse amplitudes is the thus the convolution of the detector response and the characteristics of the source. A typical distribution is shown in Figure 7.

Amplitude distributions like those in Figure 7 were fitted as the sum of a decaying exponential and a Gaussian peak. The width of the Gaussian, which represents the multi-ion peak, broadened as the MCP gain was decreased and the PMT gain was increased as is shown in Figure 8.

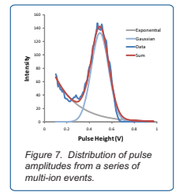

Figure 7. Distribution of pulse amplitudes from a series of multi-ion events.

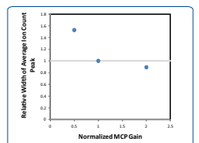

Figure 8. Multi-ion peak width as a function of relative MCP gain.

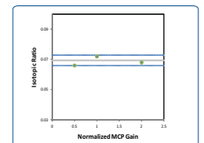

Figure 9. Isotopic ratios over the range tested.

Isotopic ratios remained constant within 5% of their expected value (Figure 9) which, given the limited number of pushes being sampled, is reasonable agreement.

Conclusions:

- Increasing the gain contribution of the MCP at the front of the hybrid detector improves signal to noise;
- Over the range tested here the improvement in signal to noise provided by the MCP does not compromise the linear response of the detector.

References:

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