Diving Deep into Single-Ion Counting with *FASTFLIGHT™*

According to common knowledge in time-of-flight mass spectrometry, the correlated noise in a digital signal averager sets the detection limits for peaks exhibiting exceptionally-low ion rates. Normally, that would cause one to choose a time digitizer to optimize detection limits at low ion rates. However, a trivial adjustment of the Vertical Offset allows ***FASTFLIGHT*** to duplicate the detection limits of a time digitizer at low ion rates.

The Problem

When time-of flight mass spectrometers are operated at high ion rates, each acceleration pulse usually generates multiple ions in a peak at a specific mass. Time digitizers cannot operate at such high ion rates, because they can only record one ion in a specific peak for each acceleration pulse. This limits time digitizers to operating at ion rates where the probability of more than one ion in a peak is negligible for each accelerating pulse. Digital signal averagers, on the other hand, thrive on multiple ions in a pulse, because they can record a signal that is proportional to the number of ions in a pulse.

Under normal operating conditions, the noise correlated with the trigger and clock in a digital signal averager limits the ability to detect ions at extremely low rates. For example, suppose the amplitude of the pulse from a single ion is 50 mV at the input to the digital signal averager. If the probability of detecting a single ion event in a specific peak is 0.004 for each acceleration pulse, then the average amplitude for the peak after averaging a large number of records will be 50 mV x 0.004 = 0.2 mV. But, the correlated noise for the ***FASTFLIGHT*** is 0.2 mV rms. Consequently, the averaged signal will be obscured by the correlated noise.

The Solution

A time digitizer avoids the correlated noise problem by setting a discriminator threshold above the noise level. Thus, noise is not detected and averaged. Only single-ion pulses are counted. This methodology can be adapted to a digital signal averager to reap the same benefits. Essentially, the dc offset at the input to the digital signal averager is adjusted so that the noise is shifted off scale, but the single-ion pulses are still on scale. If a single-ion pulse is detected, its amplitude will be added to the sum of the amplitudes of the previously detected single-ion pulses for that peak. If a single-ion pulse is absent for that peak in a specific record, the number “zero” will be added to the peak in the averager memory. Consequently, the noise is suppressed, whereas the single-ion pulses are summed. In this mode, the digital signal averager behaves like a time digitizer, but with one additional benefit: If two or more ions arrive simultaneously, the digital signal averager will record an amplitude that is approximately proportional to the number of ions, whereas the time digitizer will record only one ion. Thus the digital signal analyzer can accommodate peaks with both high and low ion rates in the same spectrum. The time digitizer cannot.

Specifics

Here is the specific recipe for implementing the above method with the ***FASTFLIGHT*** Digital Signal Averager:

1. Adjust the gain of the ion detector and/or preamplifier so that the pulse amplitude at the ***FASTFLIGHT*** input is at least 50 mV for single-ion pulses.
2. To achieve a sharp threshold at the bottom of the scale, turn the Precision Enhancer OFF. This eliminates the ±32-mV baseline meander contributed by the Precision Enhancer.
3. Turn off the source of ions and record a spectrum containing a few thousand records using a Vertical Offset of –0.1 V. Observe the maximum amplitude of the noise on the recorded baseline. Estimate the new value of the Vertical Offset that would shift the maximum of the noise just below zero on the amplitude scale.
4. Using the newly estimated value of the Vertical Offset repeat Step 3, until the noise just disappears below zero on the amplitude scale. Under this condition the baseline will be identically zero throughout the entire spectrum. The Vertical Offset value needed to achieve this condition should be in the range of +5 to +15 mV, depending on residual dc offsets.
5. Turn on the source of ions and acquire a spectrum composed of a large number of records. Verify that the single-ion amplitudes are still large enough to be recorded given the threshold introduced by the Vertical Offset selected in Step 4.
6. Because low ion rates do not produce high data rates, one usually can turn off data compression. However, adjustments of the Auto Noise Threshold and the Minimum Threshold may be needed to get the desired response for the Total Ion Count.
7. With the above settings, spectra with low ion rates can be acquired for long periods of time without being limited by the correlated noise.

Specifications subject to change
051705

ORTEC®
www.ortec-online.com
Tel. (865) 482-4411 • Fax (865) 483-0396 • info@ortec-online.com
801 South Illinois Ave., Oak Ridge, TN 37831-0895 U.S.A.
For International Office Locations, Visit Our Website

AMETEK®
ADVANCED MEASUREMENT TECHNOLOGY