

# Influence of Detector Pulse Height Distribution on Abundance Accuracy in TOP-MS

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Ion signals from a Time-Of-Flight mass analyzer are normally detected by an electron multiplier, either a large-area single point electron multiplier or a microchannel plate (MCP). All such ion detection devices produce a pulse of electrons in response to an input ion event. These output pulses do not have a fixed height, but follow a distribution of pulse heights.

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The object of this study is to determine the influence of this distribution of pulse heights on the accuracy of the measured abundance of the ion signal.

A computer simulation model of a TOF-mass spectrometer has been developed which includes the following key elements:

- ion source
- ion transport to the detector
- ion-to-electron conversion
- response of the detector
- operation of the detection electronics

This model has been applied to determine the influence of the output pulse height distribution of the uncertainty in a measurement of ion signals containing from one to ten ions. Detectors with output pulse height distributions ranging from 70% to 310% FWHM have been modelled.

## TOF-MS SIMULATION MODE

Detection systems for TOF mass spectrometers generally make use of an electron multiplier detector to convert the ion signal into electrons and then to multiply the electron current. This signal is then fed into an Analog - to - Digital - Converter (ADC) to give a digitalized form of the signal.

It is highly advantageous to use Monte-Carlo methods to simulate the operation of a TOF mass spectrometer.

Monte Carlo methods use probability distributions and random number generators to simulate the statistical nature of the physical processes involved.

The following aspects are particularly well suited to being modelled by Monte-Carlo methods:

- The number of ions generated by the ion source that reach the multiplier for each observation of the signal.
- The conversion of ions to electrons by the first dynode of the multiplier.
- The size of the electron pulse generated by the multiplier.

For this analysis the pulse height distributions were calculated using Monte - Carlo methods with Poisson statistics describing the variations in the gain at each dynode of a 20 stage multiplier.

The resulting output pulse height distributions are shown in figure 1. This spans the range from 58% FWHM to 310% FWHM.

## MEASUREMENT PROCEDURE

The ion source algorithm is set to a selected average number of ions. For each observation the number of ions arriving at the detector and its response to those ions is determined.

The electron pulse output from the detector is then digitized by an ADC.

It is common practice to sum many repeated measurements of the signal into a buffer before extracting the final measurement. In this study each measurement of the ion signal is the result of 1000 separate observations summed together.

In order to obtain statistical information the procedure was repeated 5000 times.

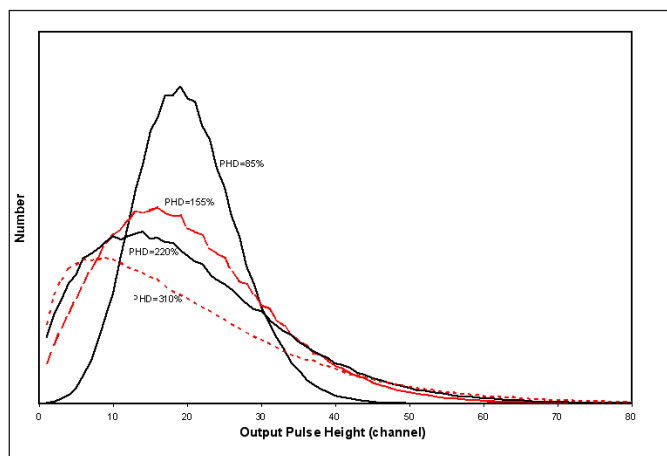


Figure 1. In total four different output pulse height distribution from the electron multiplier were considered. These four distribution have a FWHM\* of: i) 85%; ii) 155%; iii) 220% and iv) 310%

\*FWHM is the distribution width at half maximum height and expressed as a percentage of the peak position of the distribution.

The measurement of ion signals in this simulation model follows these criteria.:

- The number of ions reaching the multiplier for each observation of a signal includes statistical intensity variations according to Poisson statistics
- The threshold of the 1st bit of the ADC is set so that it corresponds to 50% of the mean pulse height. The thresholds of each bit of the ADC are equispaced
- To determine the mean and standard deviation information on each measurement point the experiment was repeated 5000 times

The simulation model was set to measure the intensity of ion signals ranging over >6 orders of magnitude.

The ion signals range between an average of 0.001 and 200 ions per observation.

The averaging 1000 observations of the ion signal for each measurement point, the total measured ion signal ranges between 1 and 200,000 ions per measurement.

## RESULTS

The procedure was repeated for each of the four pulse height distributions and the results are shown in figure 2.

The thicker solid line labelled statistical noise represents the situation where the pulse height distribution of the detector has no contribution to the total error on the signal measurement. This corresponds to the physical situation where the multiplier generates a constant output pulse height in response to each input ion (0% FWHM).

$\sigma$ , on the signal equal to:

$$\sigma = \sqrt{N}$$

Where N is the number of ions contained in the measurement.

Note that the typical output pulse height distribution for an ETP TOF multiplier is ~200% FWHM.

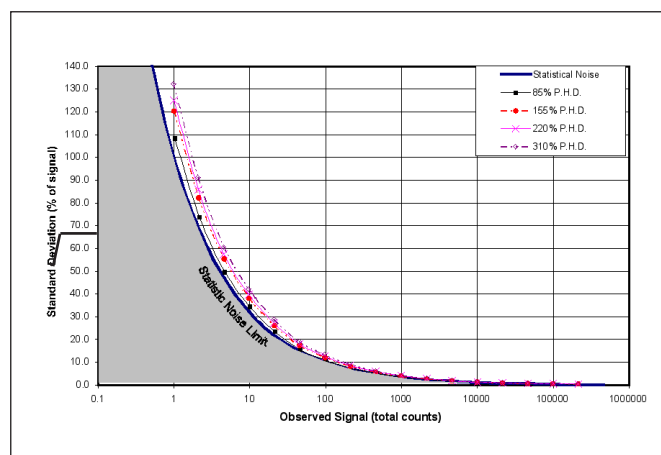


Figure 2. Effect of multiplier Pulse Height Distribution on the Standard Deviation of the measurement. The thicker solid line indicating statistical noise corresponds to the situation where the pulse height distribution of the detector has no contribution to the total noise on the measurement. In this case the multiplier gives a fixed output pulse height in response to every input ion.

From the data shown in Figure 2 it is apparent that by far the largest contribution to the error in the ion signal measurement is that of statistical noise. This type of noise results from the statistics governing fluctuations in the number of information carriers that make up the signal. This represents a fundamental limit on the accuracy of measurement for low abundance ion signals.

As the pulse height distribution of the multiplier increases, the standard deviation associated with the measurement of ion signals also increases. However, this effect is small when compared to the error resulting from statistical noise alone.

Figure 3 shows the increase in standard deviation with increasing detector pulse - height distribution for selected ion signal levels between 1 and 1000 ions per sampling interval.

The data points at 0% FWHM pulse height distribution represent the statistical noise only case (where the multiplier gives a constant output pulse size). A near linear relationship is seen between the pulse height distribution and the standard deviation of the measured ion signal.

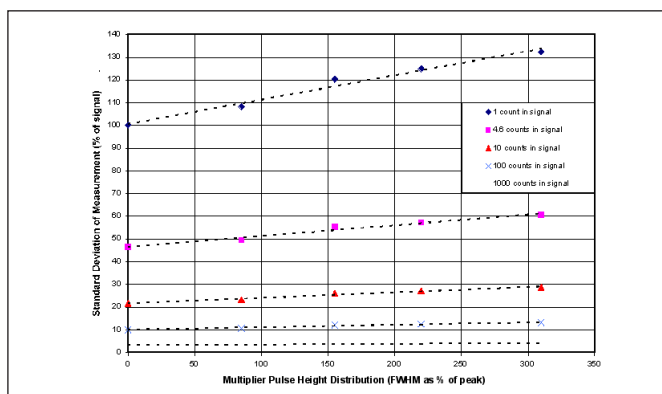


Figure 3. Effect of multiplier Pulse-Height Distribution on the Standard Deviation of the Measurement. In all cases the dominant factor to the standard deviation in the measurement of the ion signal is the statistical noise on the number of ions arriving at the detector.

## CONCLUSIONS

The following conclusions can be made regarding the influence of the distribution of pulse-heights from the detector on the accuracy of abundance measurements on a TOF mass spectrometer:

- Statistical noise related to the number of the ions contained in a measurement is by far the dominant source of error
- Detectors with broader output pulse height distributions have a marginally greater error associated with a given measurement
- There is a very little influence on the accuracy of the measurement of the ion signal by the pulse height distribution of the detector for distributions that span the range normally found in commercial detectors (FWHM 100% to 200%). This is clearly demonstrated in figure 3.

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