Digital Thresholding, MCP Gain, etc

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1. Time-to-digital and Analog-to-digital converters (TDC and ADC)
2. Dynamic Range
   i. Digital Thresholding – Small signals
   ii. ADC Saturation – Large signals
   iii. Balance of MCP Gain and Threshold Setting
3. Threshold and m/z Ratio windows
4. Using Two Channels of the ADC

![MCP Diagram](image-url)
Time-to-Digital Converter (TDC)

A TDC converts a signal of sporadic pulses into a digital representation of their time indices.
Neither the height nor the area of the pulse is recorded.
Most often used in applications where measurement events happen infrequently.

Analog-to-Digital Converter (ADC)

• An analog-to-digital converter is an electronic circuit that converts continuous signals to discrete digital numbers.
• Records time and amplitude of waveform events.
• Characterized by:
  Sampling rate
  Resolution

Demo from Learning by Simulation. By Hans Lohninger (http://www.vias.org/simulations/simusoft_adconversion.html)
Cornerstone of AMS quantitative strategy is ability to determine # of ions detected.

The smallest signal to be measured will always be a single ion.

The magnitude of the largest signal depend on the size and composition of particles present. But, the ToF-AMS inherently records ions originating from particles in short bursts.

For example, during the 50 µsec following ionization the m/z corresponding to the most abundant species in a 350 um inorganic particle (e.g., m/z 30 in Ammonium Nitrate), will have a count rate of approximately $7 \times 10^9$ Hz, or, in the ToF-AMS, 20 ions/extraction for 3 extractions.

These rates, which grow as the cube of the particle diameter, makes ion counting with a typical time-to-digital converter (TDC) inappropriate, particularly for larger particle.

Quantification from total waveform depends on:

1. The detector having a response that is proportional to the number of incident ions (See Figure)

2. The ADC recording signal waveforms with fidelity
   - Small signals not threshold rejected
   - Large signals not clipped by ADC saturation

3. Knowledge of the relative detector response in order to calculate the ion count rate.
   - “Single Ion Area”

Data show total integrated signal at m/z 30 and 46 for single ammonium nitrate particle detection events. Total signal grows as cube of diameter, indicating that recorded intensity is proportional to the number of ions.
Fidelity – Thresholded Rejection

The 8-bit ADC of the ToF-AMS offers thresholding capabilities.

Noise in the ToF-AMS has electronic and chemical components.

Chemical noise originates from scattered ions, and thus has an intensity equivalent to real, low-intensity signals.

Choosing the ADC threshold setting is a balance of SNR and dynamic range.

The threshold is ideally set at a value where electronic noise is rejected and all ion signal intensity is recorded.

SI Arrival Event Image

As a first step toward quantification of detector response, the image (shape + area) of the average single ion detection event must be determined.

This image represents the smallest signal that the instrument must measure.

To maintain quantitative linearity for small signals, MS acquisition must completely record this image.

Thus, to properly set the threshold, we must determine the effect of threshold on the average detected image of the single ion arrival shape.
Threshold Effects

Discard noise, maintain signal

Threshold Analysis Window is an automated routine that:

1. Determines the % of electronic baseline noise that is discarded as a function of ADC threshold
2. Measures the average image (voltage waveform) of the detector response to single ion arrival events
3. Calculates the degradative effects of threshold setting on this image

SI Image / Threshold Setting Determination Routine

The Threshold Analysis Window is an automated routine that:

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Single Extraction, Unaveraged ToF-AMS data are filtered to isolate ion peaks.

Within these, single ion arrival events are identified based on probabilistic considerations and the average shape and area of these events are calculated from the raw data.

Software then thresholds the data in a manner identical to the processing of the ADC. The single ion arrival events are re-analyzed within the thresholded data in order to quantify thresholding effects.
(1) Acquire Raw Baseline Matrix – software thresholds to produce baseline statistics == red line plot 1.

(2) Acquire Data Matrix.
   i. Software isolates peak events and standard single ions.
   ii. Apply software thresholds (0 to 15) to determine degradative effects.
• Key values from the threshold window:
  – SI Area: INDEPENDENT OF THRESHOLD

• NOTE:
  – You CANNOT yet set your threshold
  – YOU CANNOT yet know that your MCP voltage is okay

• Proper threshold setting is determined by comparing threshold window data to m/z Ratio Window Data – where the effect on small signals is measured.

• Proper MCP setting determined based on ADC saturation.
Threshold window looks at effects on single extraction single ion events, this window looks at how these effects manifest in averaged data.

m/z Ratio Window measures effect of thresholding on small mass spectral peaks AND detects ADC saturation by large signal.

Routine acquires MS without threshold and at 15 threshold values and plots ratios 40/28 and 32/28 as function of threshold.

The thresholded rejection of real ion intensity manifests as a non-linear response to small signals. In particular, the area of m/z peaks originating from single ion arrival events is deflated, while larger peaks are unaffected.

As a diagnostic for this effect, we track the ratio of ambient Ar⁺ (m/z = 40) and N₂⁺ (m/z=28). Ar is prototypical “small signal,” dominated by SI arrivals.

The rise at low thresholds results from the rejection of negative noise (random and/or ringing) without rejection of positive noise or signal intensity.

Significant portions of the signal origination from m/z 40 ions are lost at higher thresholds, although increasing the MCP gain somewhat combats this effect.
The fact that the degradation of m/z 40 is less drastic as MCP gain is increased suggests that the instrument should be run with maximum gain. But, one must be careful to avoid saturation of the ADC, as this will limit linearity in the instrument’s response to large signals.

To detect ADC saturation, the signal of ambient O$_2^+$ (m/z 32) is compared to the signal of ambient N$_2^+$ (m/z 28) in unthresholded ToF aerosol mass spectra. Neither is affected by typical ADC threshold values. N$_2^+$ signal will saturate at far lower MCP gain than O$_2^+$. Across the range of gains where no saturation occurs, the ratio (m/z 32 / m/z 28) will be constant. Beyond the N$_2$ saturation limit, the N$_2^+$ will not longer increase and the ratio (m/z 32 / m/z 28) will grow.

In these data we see saturation beginning around 2200 V.

Rules of thumb
The ADC of the ToF-AMS is equipped with two input channels. These channels must be run with identical timing (triggering, sampling frequency, averaging time ...), but their voltage full scales and offsets may be adjusted independently.

In an attempt to extend the saturation limit of the ADC and to facilitate acquisition with higher MCP gains, the second channel of the ADC has been offset such that it only records those portions of signal waveforms that exceed the channel 1 full scale (i.e., voltage equivalent to 256-bits).

Summing two channels assumes identical digitization of waveforms by the two channels.

To demonstrate that this is true, the two channels were fed a split signal and set to identical full scale and offset. 300 MS with no averaging were simultaneously saved on both channels.

The blue points in the upper plot compare all acquisition element intensities.

The red points in the lower plot compare the areas of the m/z 28 peak for all acquired mass spectra.
True concern for saturation is large particle. m/z 28 is a surrogate for a roughly 500 nm pure inorganic.

BFSP data acquired on two channels. Signals offscale on CH1 are captured by CH2.
Use of the calculated single ion area for quantification requires that the value is independent of m/z.

Collect a large number of single extraction ToF mass spectra and tracking the integrated values of peaks corresponding to low intensity species.

The histograms show the distribution of areas for all non-zero peaks corresponding to 8 different m/z species.

A fit of the mean peak area values versus m/z shows a slight mass dependence, corresponding to approximately 4.5% across our typical mass range of 300 amu.

By this method, we calculated a single ion response with area 52.8 bit-ns. For the same instrument settings, the automated procedure calculated 49.9 bit-nsec, which is approximately a 5% difference.

C and V, no mass dependence