Quantitative Time-of-flight Mass Spectrometry of Aerosols Using a Digitally Thresholded Analog-to-Digital Converter

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Overview

The Aerodyne Aerosol Mass Spectrometer (AMS) has recently transitioned from a quadrupole to a time-of-flight (ToF) detector. Quantitative procedures are well established for the quadrupole instrument. Cornerstones of these methods are knowledge of the instrument response to single ions and ensured linearity in detector response across broad dynamic range.

In the ToF-AMS, the continuous output of the multichannel plate detector (MCP) is digitized using an analog-to-digital converter (ADC) with adjustable digital threshold for the rejection of low intensity noise signals.

Maximizing sensitivity and dynamic range requires that MCP gain is set low enough to avoid saturation of the ADC yet high enough to allow thresholding of electronic noise without the rejection of ion signal. This work describes methods for (1) determining the average image (shape and area) of the digitized MCP response to single ion arrivals in a ToF-AMS and (2) measuring degradation of that image as a result of thresholding.

Additionally, a configuration is presented where data is simultaneously acquired on two channels of the ADC, which are offset to detect different voltage ranges of the signal waveform. This pushes the effective saturation limit of the ADC to higher MCP gains, and hence allows operation at increased threshold settings without rejection of small ion signals.

Methods and conclusions can be extended to other MCP-based ToF mass spectrometers using ADCs to quantify high ion current signals across broad dynamic range.

Time-of-flight Aerosol Mass Spectrometer

The Aerodyne Time-of-flight Aerosol Mass Spectrometer (ToF-AMS) is a portable instrument (450 lb, 700W), which is primarily used in field studies and aircraft-based campaigns. Typical data sets track ambient loadings of 35 nm to 1.2 um, non-refractory aerosols across periods of hours, days, or months. Data are acquired with temporal resolutions as high as 1-sec. Detection limits for chemical constituents of interest range between 1 and 20 ng m^{-3}.

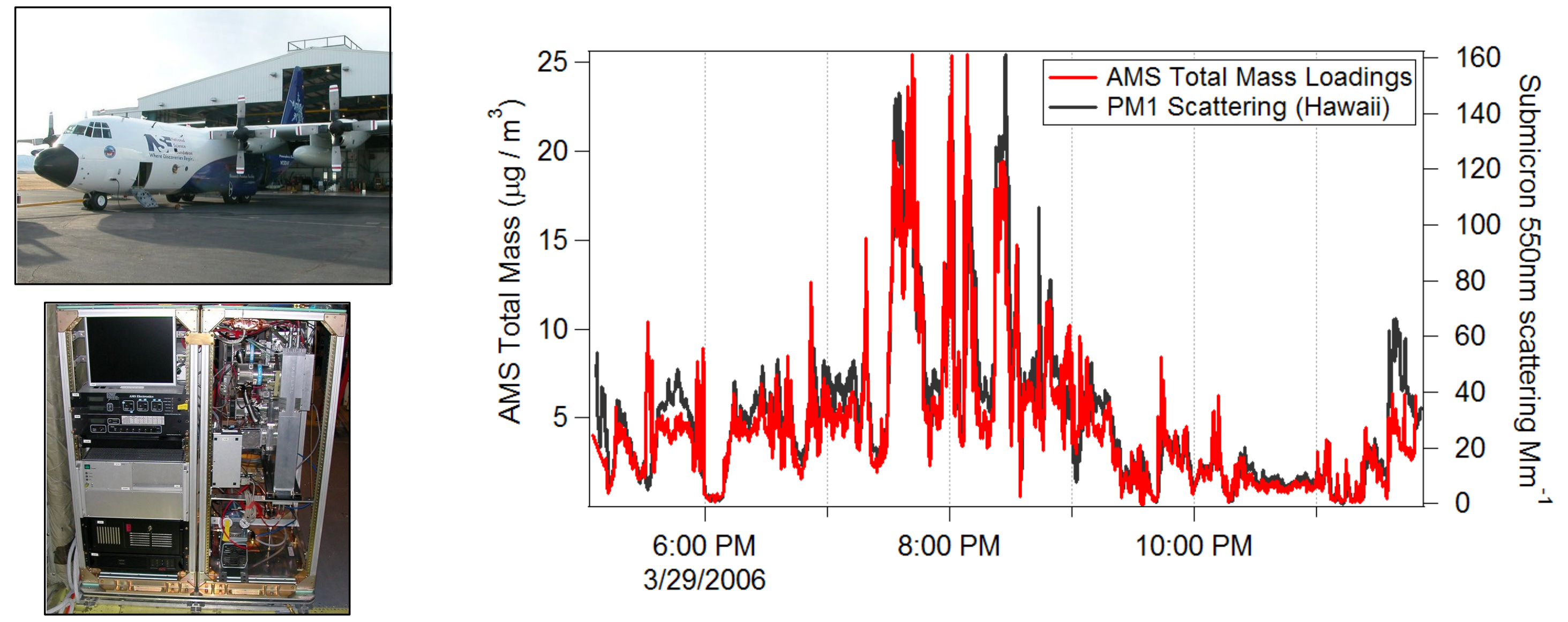


Figure 1. Preliminary data from Research Flight #12 of the MIRAGE Field Campaign. This experiment was studied the outflow of pollution from Mexico City. Left Top: NCAR C-130 aircraft where ToF-AMS was installed. Left Bottom: ToF-AMS inside the C-130. Right: Time series of ToF-AMS total mass concentration compared to total PM_1 light scattering (scattering data from A. Clarke et al., Univ. Hawaii)

In the ToF-AMS sampled aerosols are focused into a narrow beam by an aerodynamic lens. The beam exits the lens into vacuum, where aerodynamic particle size is determined via particle time-of-flight measurements. A rotating mechanical chopper modulates the particle beam in order to define the beginning of drift.
At the end of the drift region, particles impact a heated surface (~600 C) that causes flash vaporization of non-refractory species. The resultant plume of vapor is ionized by electron impact, and ions are transferred to a time-of-flight mass spectrometer.

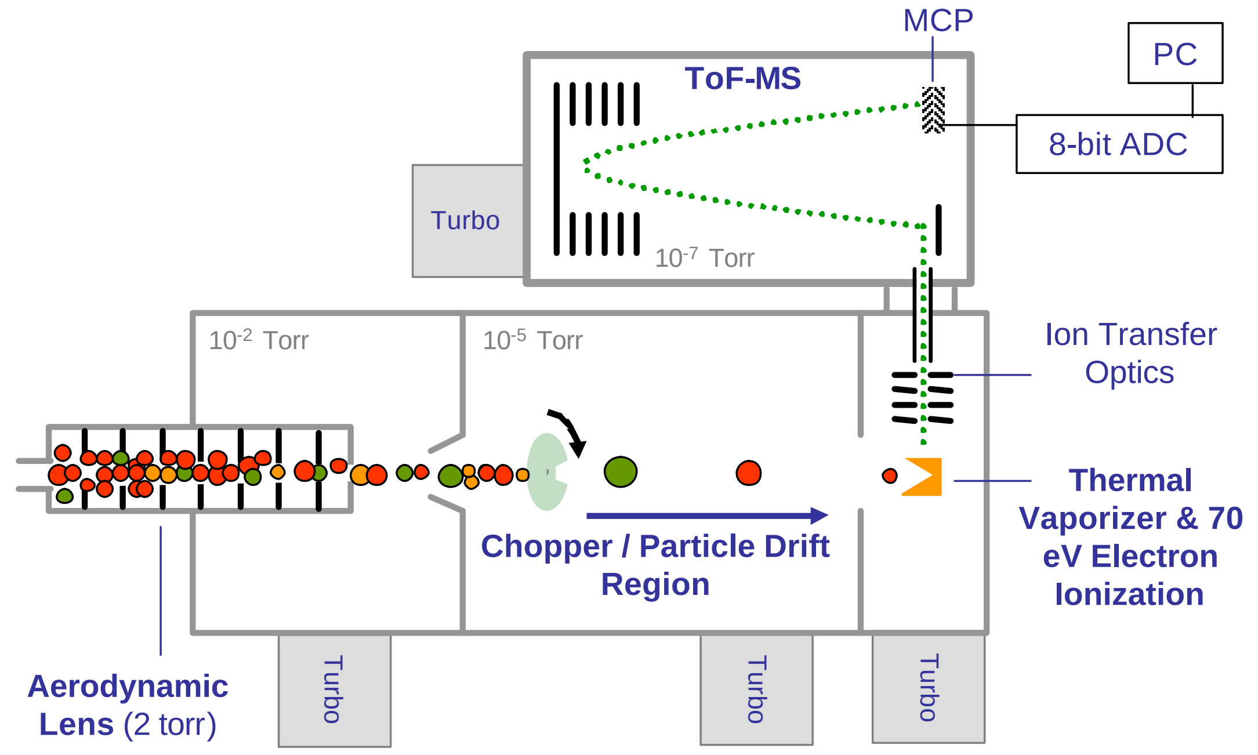
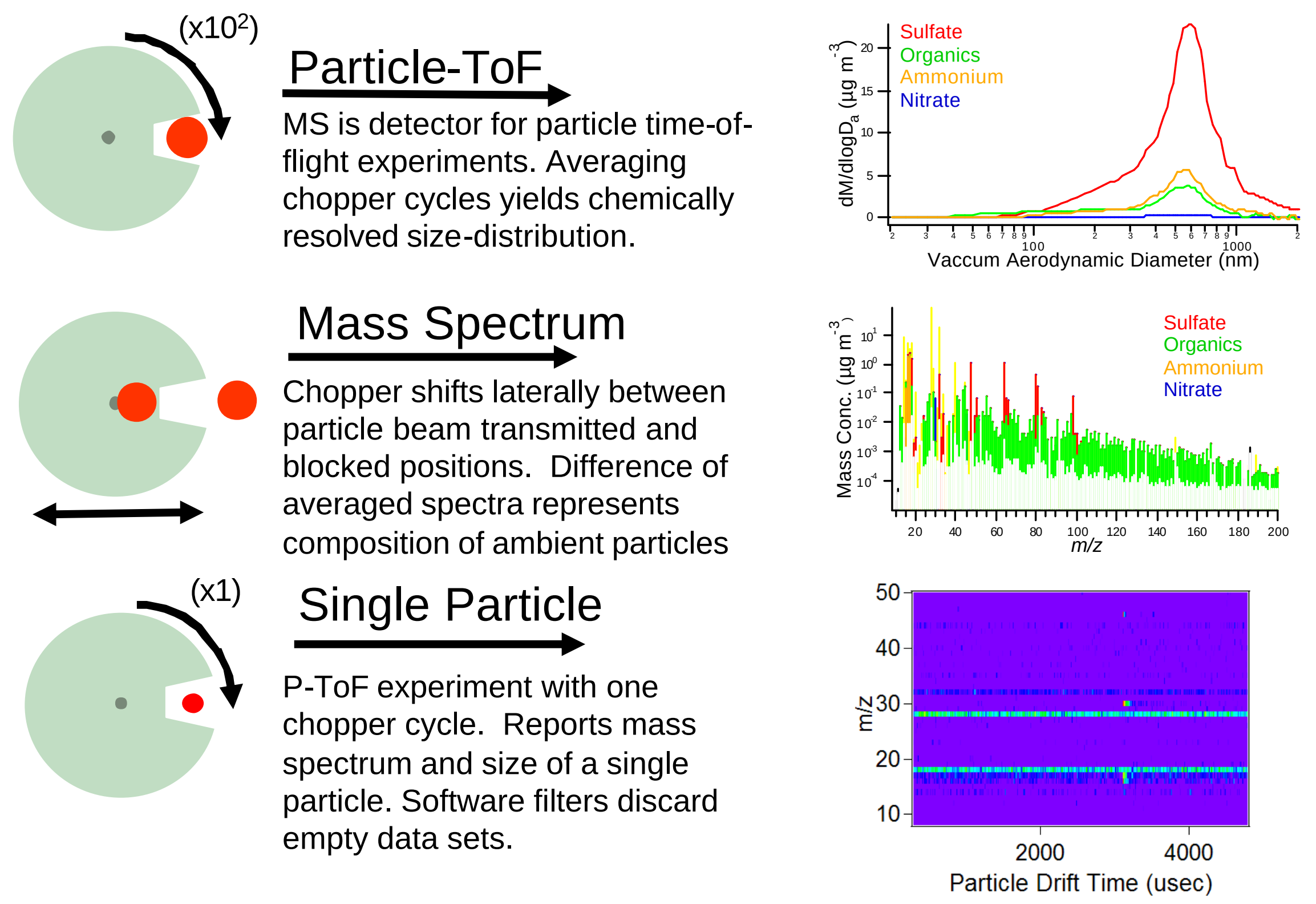


Figure 2. The quadrupole detector of the AMS has been replaced with a Tofwerk compact- (c-) or v/w-ToF-MS. The c-ToF-MS is smaller and lighter and offers higher sensitivity. The v/w-ToF-MS offers higher resolution, and can be run in a reflectron (v-) or multi-pass (w-) mode. All data presented here were collected with a c-ToF-MS.

Particle drift times are on the order of 3 msec, while the ToF-MS is pulsed with a period of approximately 15 μsec. Hence, the ToF-AMS is able to record particle drift times with high resolution and provide *m/z* data for all detected particles.

Lateral movement of the mechanical chopper in the ToF-AMS facilitates three distinct acquisition modes, as described in Figure 3.

Figure 3. ToF-AMS modes of acquisition.



Particle-ToF

MS is detector for particle time-of-flight experiments. Averaging chopper cycles yields chemically resolved size-distribution.

Mass Spectrum

Chopper shifts laterally between particle beam transmitted and blocked positions. Difference of averaged spectra represents composition of ambient particles

Single Particle

P-ToF experiment with one chopper cycle. Reports mass spectrum and size of a single particle. Software filters discard empty data sets.

Ion Rates Require Analog-to-Digital Converter

A single aerosol can produce ions at hundreds of *m/z* values, including parent and fragment ions. 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 x 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.

Rather than count peaks, as is done with TDCs, the ToF-MS must record the total signal waveforms.

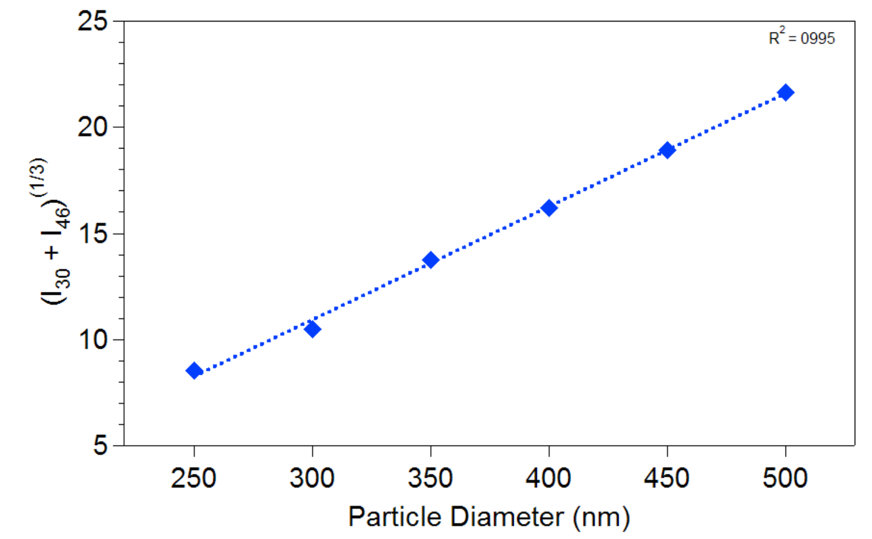


Figure 4. Total integrated signal at *m/z* 30 and 46 for single ammonium nitrate particle detection events. Total recorded signal grows as cube of diameter, indicating that recorded intensity is proportional to the number of ions.

Quantification then relies on:

1. **The detector having a response that is proportional to the number of incident ions (See Figure 4)**
2. **The ADC recording the signal waveform with fidelity**
3. **Knowledge of the relative detector response in order to calculate the ion count rate.**

Thresholding

The 8-bit ADC of the ToF-AMS includes the option of noise rejection threholding.
Any portions of the signal waveform with amplitude greater than a user-defined threshold are recorded; all portions with amplitude below user defined amplitude discarded .
As demonstrated in Figure 5, use of this threshold can increase signal-to-noise ratios (SNR) by orders of magnitude.
Noise in the ToF-AMS has electronic and chemical components. The latter originates from scattered ions, and has an intensity equivalent to real, low-intensity signals. Thus, not all noise can be rejected while simultaneously maintaining maximum dynamic range.
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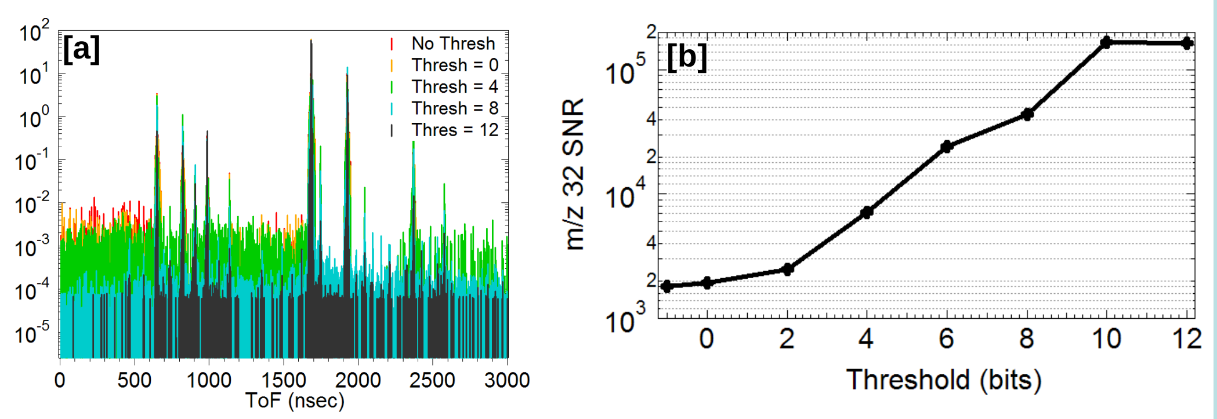


Figure 5. [a] Averaged ToF mass spectra of filtered air with varied ADC threshold applied, and **[b]** calculated SNR for *m/z* 32. Across the range of settings NoThreshold to 12-bit threshold, rejection of noise increases the SNR by two orders of magnitude.

Determining Single Ion Response and Effects of Thresholding

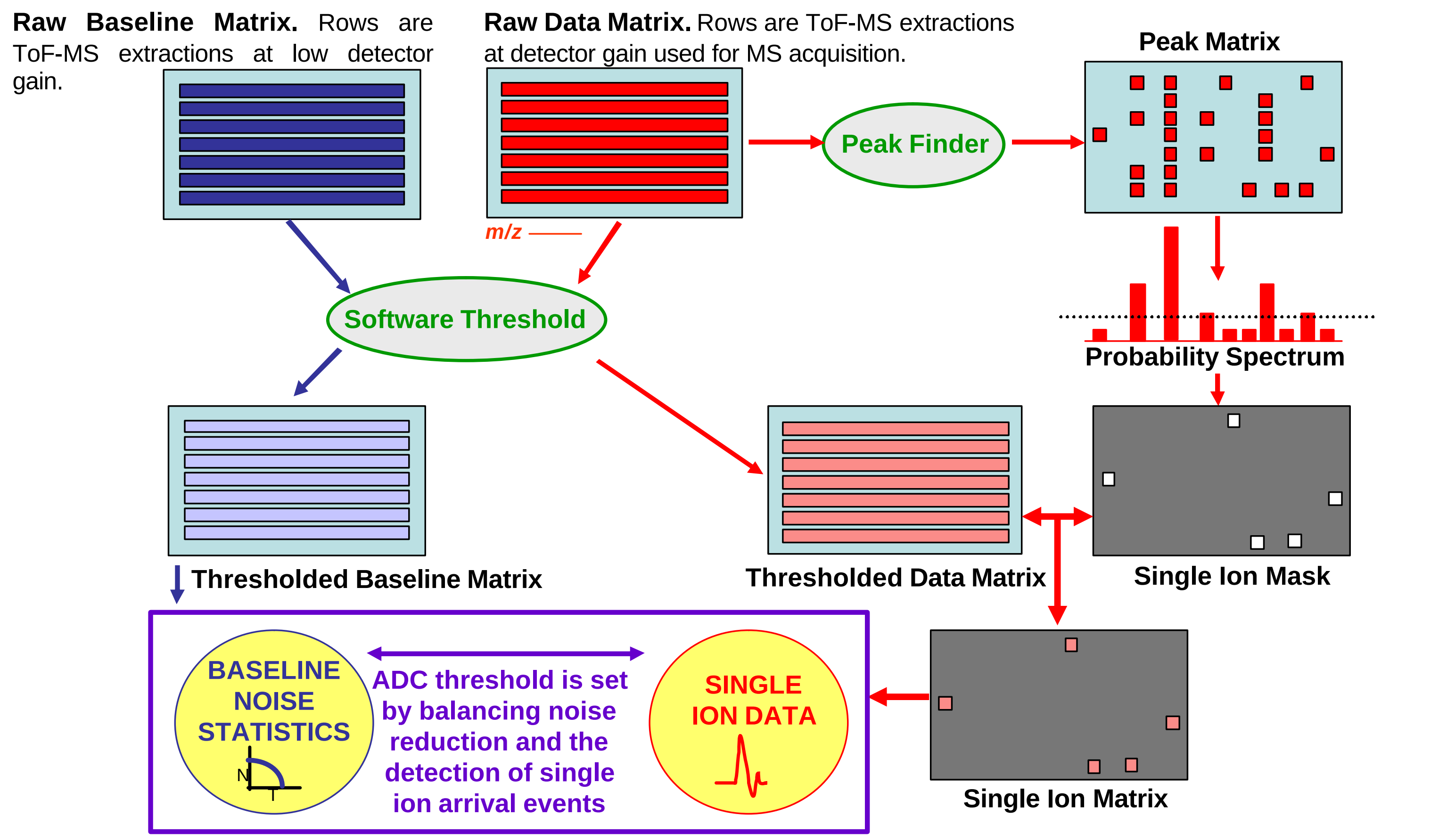
As a first step toward quantification of detector response, the image (shape + area) of the average single ion detection event must be determined.

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.

The ToF-AMS Acquisition Software includes an automated routine that:

1. Determines the fraction 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

Figure 6. Automated SI Image / Threshold Effect Determination. 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. To determine threshold effects on electronic noise, software filters are used to process a data matrix acquired with no MCP gain.



Raw Baseline Matrix. Rows are ToF-MS extractions at low detector gain.

Raw Data Matrix. Rows are ToF-MS extractions at detector gain used for MS acquisition.

ADC threshold is set by balancing noise reduction and the detection of single ion arrival events

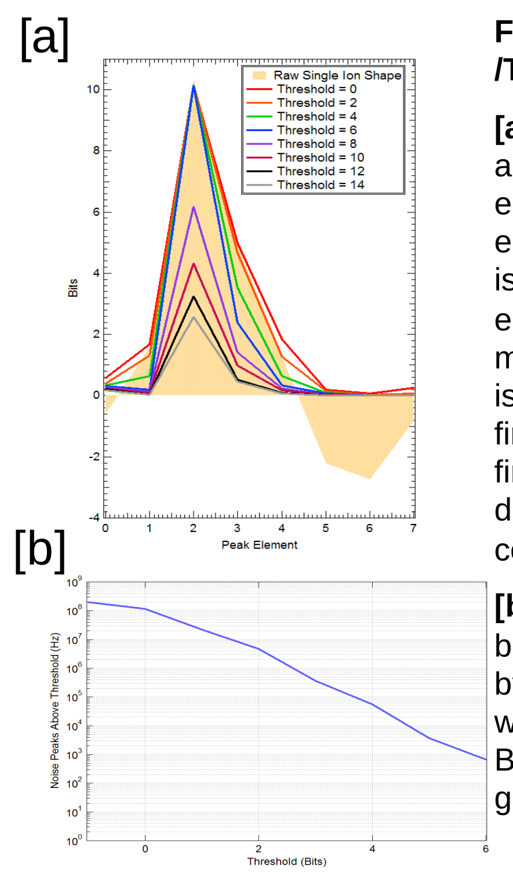


Figure 7. Sample Single Ion /Threshold Routine Data.

[a] Single ion events are analyzed across 8 acquisition elements with the peak always at element 2. Each element value is calculated as the mean of like-elements in all events. The majority of the positive peak area is contained in the peak and the first falling edge (2 and 3). The final elements are generally dominated by the negative component of detector ringing.

[b] The effect of thresholding on background noise is quantified by recording the frequency with which acquisition elements in the Baseline datasets (low detector gain) break threshold.

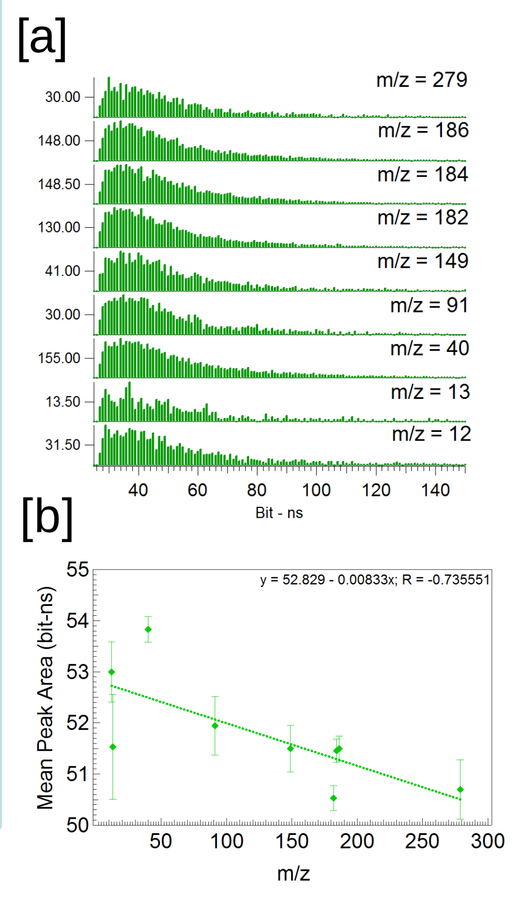


Figure 8. *m/z* Dependence of Single Ion Response.

Use of the calculated single ion area for quantification requires that the value is independent of *m/z*. To detect any such dependence, the integrated values of 8 low-frequency *m/z* peaks were tracked in 150,000 unaveraged mass spectra.

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

[b] A linear fit shows that single ion response decreases by 0.008 bit-nsec / amu, which is acceptable across our 300 amu mass range. (Note also that this mean area is within 5% of the value calculated by the automated routine at these settings.)

m/z Ratios of Dynamic Range Diagnostics.

Within mass spectra, the thresholded rejection of real ion intensity manifests as a non-linear response to small signals. As a diagnostic for this effect, we track the ratio of ambient Ar+ (*m/z* = 40) to N_2^+ (*m/z* = 28).

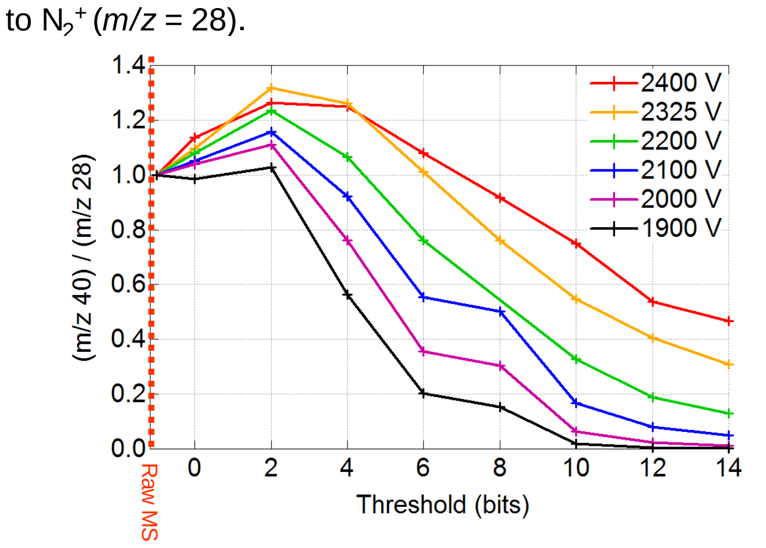


Figure 9. 40/28 ratio vs threshold vs MCP Gain. Data points are normalized to the value of the ratio in the raw, un-thresholded data. The rise at low thresholds results from the rejection of negative noise (random and/or ringing) without rejection of positive noise or signal intensity. Significant portions of the signal origination from *m/z* 40 ions are lost at higher thresholds, although increasing the MCP gain somewhat combats this effect.

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.

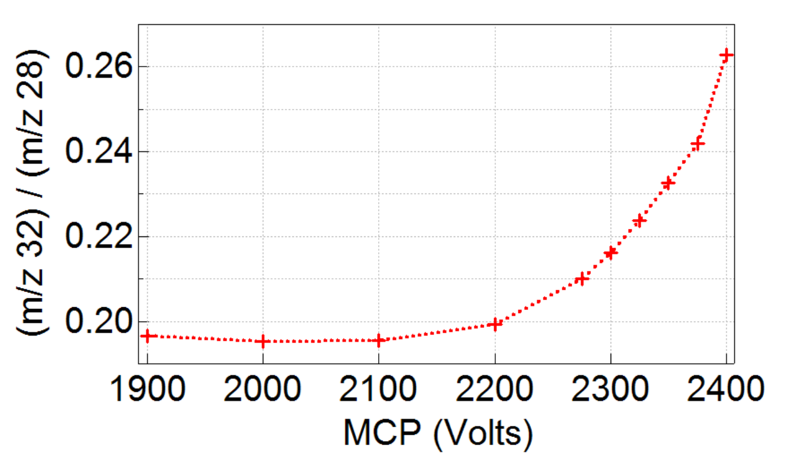


Figure 10. 32/28 ratio vs MCP Gain. Both signals are large, but the N_2^+ signal will saturate at far lower MCP gain than O_2^+. Across the range of gains where no saturation occurs, the ratio (*m/z* 32 / *m/z* 28) is essentially constant. The increase in the ratio (*m/z* 32 / *m/z* 28) above 2200V suggests that the N_2^+ is saturating the ADC.

Two-ADC-Channel Recording.

The ADC of the ToF-AMS is equipped with two input channels. These channels must be run with identical timing, but their voltage full scales and offsets may be adjusted independently.

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 of 256-bits). Figure 12 demonstrates how this methods effectively captures large signals (e.g., *m/z* 28 at high MCP gain).

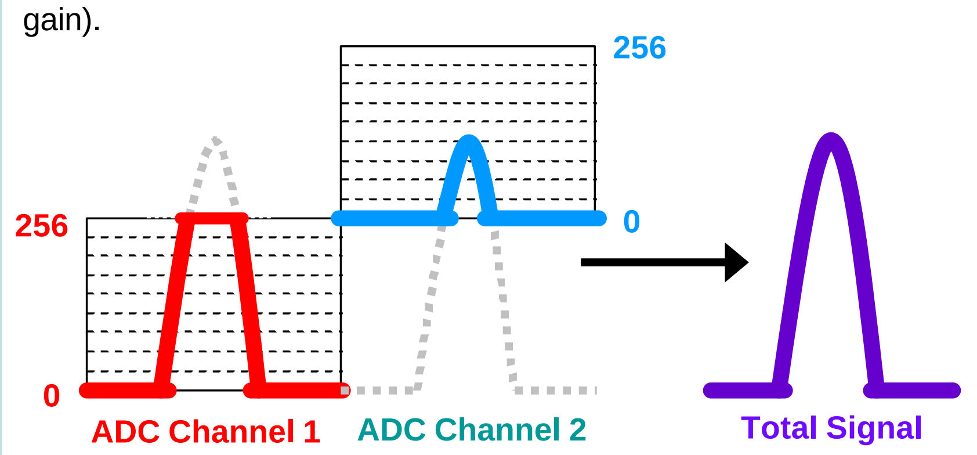


Figure 11. Schematic of Two-Channel Accquisition.

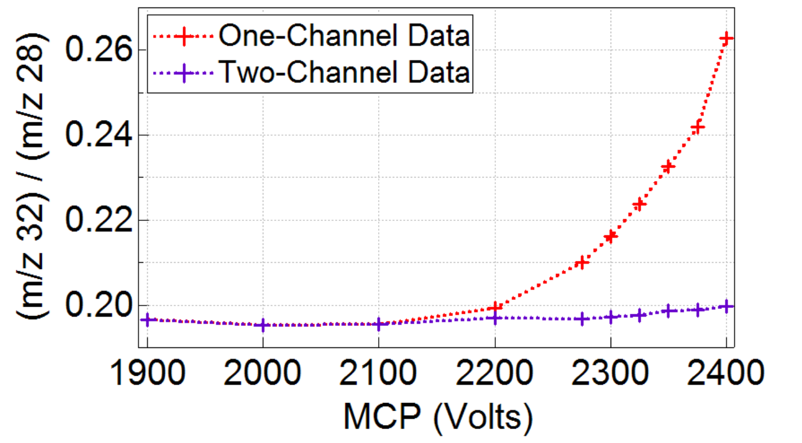
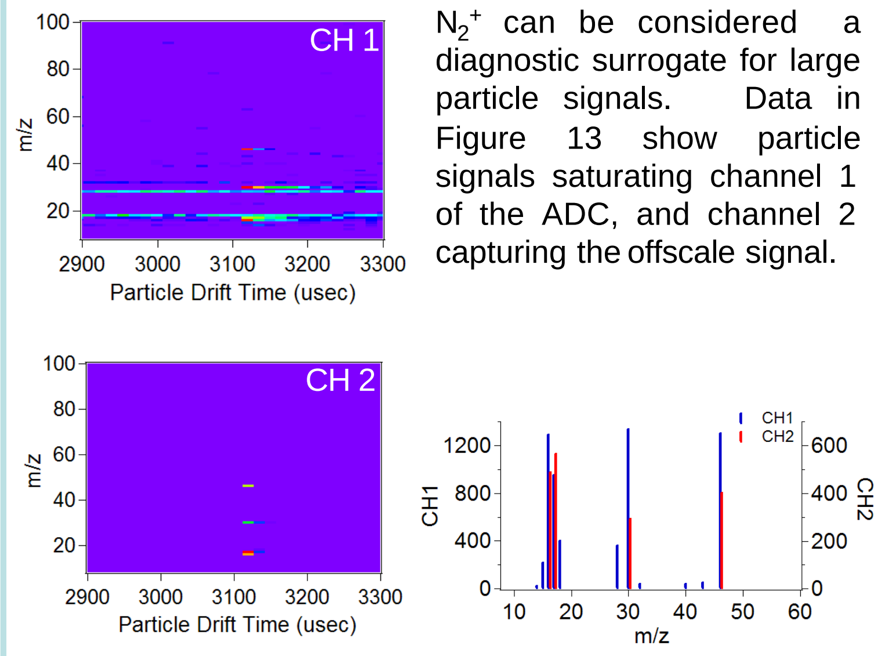


Figure 12. 32/28 Ratio vs MCP with Two-Channel Acquisition. Summing data allows high gain acquisition without loss of signal.



N_2^+ can be considered a diagnostic surrogate for large particle signals. Data in Figure 13 show particle signals saturating channel 1 of the ADC, and channel 2 capturing the offscale signal.

Figure 13. Two-Channel Single Particle Acquisition. PTOF spectrum 500 nm, ammonium nitrate particle with MCP at 2400V and threshold = 6 (see Figure 9). Particle arrival event visible on both channels just after 3100 μsec drift time. Mass spectrum shown is the start of the particle arrival event.

Conclusions.

The ToF-AMS offers quantatative analysis of aerosol composition, with SNR greatly improved (x100) by digitally thresholding ADC signals.

To maintain dynamic range, degradation of single ion arrival events by thresholding must be avoided. Thus, setting threshold is a balance of noise rejection and signal acceptance.

With digital thresholding applied, single ion events are better recorded at high detector gain.

Offsetting and summing the two channels of the ADC allows acquisition at increased detector gain, and hence higher threshold settings without degradation of single ion arrival events.

These findings can be extended to other MCP-based ToF mass spectrometers using digitally threshold ADCs.

Acknowledgements.

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