On Violations to the Time-of-Flight Assumptions in Atom Probe Tomography

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Atom probe tomography is based on time-of-flight mass spectrometry. In this technique, a trigger pulse strikes the tip of a needle shaped sample and causes the time-correlated evaporation of one or more ions. A DC voltage is applied to the specimen that accelerates the evaporated ions toward a two-dimensional detector where the time and position of each ion hit is recorded relative to the time the trigger pulse was incident on the specimen apex. Under the assumption of instantaneous acceleration of the ion, the mass-to-charge (*m/z*) of the ion(s) can then be calculated using the canonical time-of-flight equation (Figure 1a). For the *m/z* to be well-defined, the accelerating voltage, flight length, time zero, and ion hit time must all be known[1]. Most of the time these inputs are indeed known, however, in our work we have found cases where one or more of these variables is ill-defined. In this presentation we will discuss three cases where calculation of the ion(s) *m/z* is difficult due to poorly defined input variables and how that impacts the resulting data.

In the first case, we were collecting data on SiO_2 specimens and noticed that the mass spectra were of quite poor quality. In some datasets, the mass resolving power was significantly worse than expected and in other datasets we observed peak splitting. After investigation we determined that the voltage at the specimen apex was not solely a function of the standing voltage applied to the base of the electrically insulating SiO_2 specimens[2]. Thus, even after voltage and bowl corrections were applied to the data, the peaks in the time-of-flight history systematically deviated from the mean in a time-dependent manner (Figure 1b). These systematic deviations were ascribed to the poor electrical conductivity of the sample and were responsible for the poor mass resolving power and the presence of additional peaks. An algorithm was developed to track these fluctuations and remove them from the data[3].

In the second case, we were interested in understanding the DC correlated evaporation events that can be a significant source of background/noise/missing ions when operating under high electric field conditions. Specifically, correlated DC evaporation shows up in a time correlation histogram as linear features with a slope of one (Figure 1c). Since these ions show up in the background of a one-dimensional histogram, they are typically not ranged and counted in compositional analyses. But given that these events have structure in two-dimensional histograms, there have been efforts to use delta time-of-flight histograms to range these counts[4]. In our work, we observed that the delta time-of-flight histograms have sharp peaks for small average flight times, but these peaks broaden significantly at longer average flight times (Figure 1c). An analysis of this phenomenon revealed that voltage and bowl correction cannot be naively applied to DC evaporation events because the time zero needed to compute the *m/z* is unknown. An approximation to this time zero was derived that significantly improves the mass resolving power of these delta time-of-flight spectra and thus may improve the ability to range these ions.

In the third case, we were studying Ga_2O_3 specimens and noted strange ‘blobs’ in the one-dimensional mass spectra that shifted around in the mass spectrum as a function of the standing voltage. In some cases, these blobs obscured dopant species that we were attempting to measure and so we desired

to understand and mitigate them. A careful analysis of these data showed that these blobs arise from a non-intuitive intensity distribution along dissociation tracks in the correlation histograms (Figure 1d)[5]. This led our group to explore how dissociation events (where *m/z*, V_{DC}, and time zero are all poorly defined) are evidenced in the one- and two-dimensional mass spectrum for a range of detector geometries and ion lifetimes. The understanding gained from these studies permits an appreciation for where and when these 'blob' features may show up and how to range and/or mitigate their impact in the mass spectrum.

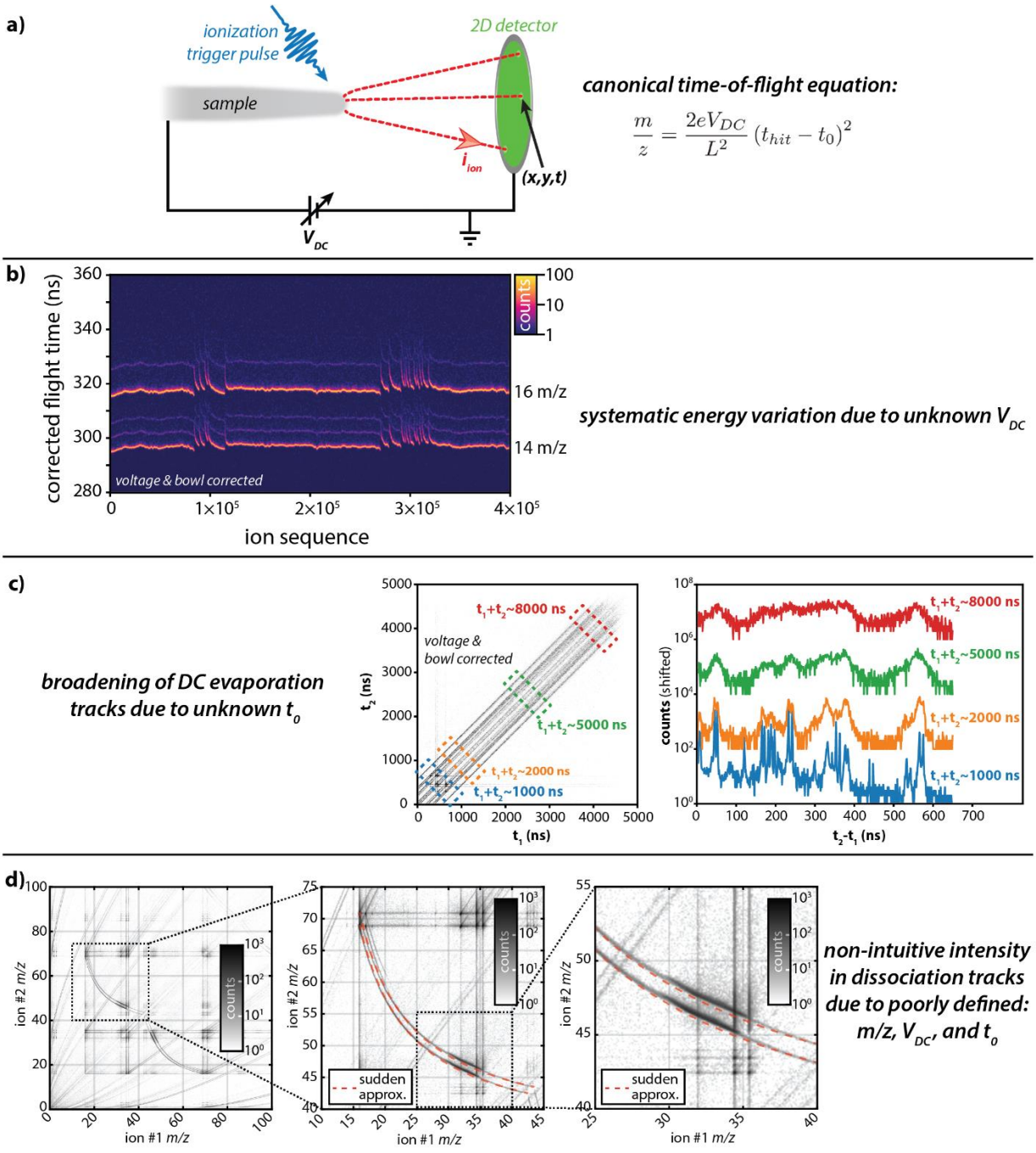

Fig. 1. (a) Schematic of an atom probe tomography experiment and the canonical time-of-flight equation showing how the mass-to-charge of a detected ion is related to the applied voltage, ion path length, and time-of-flight of the event. (b) Systematic energy deficits in SiO_2 due to an unknown voltage drop along the length of specimen tip. (c) DC correlation evaporation tracks are evident in a GaN sample. The delta time-of-flight spectrum for double hits is plotted for different areas of the correlation histogram. Due to the unknown t_0 for DC evaporated ions the voltage and bowl corrections fail to work as intended. (d) A correlation histogram obtained for a Ga_2O_3 specimen. Zooming in on a dissociation track (GaO^{2+} → Ga^{1+} + O^{1+}) shows a very non-intuitive intensity distribution within the track.

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