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On the Voltage and Bowl Correction of Trigger-Uncorrelated Multihit Events

Benjamin Caplins[1], Ann Chiaramonti[2], Luis Miaja-Avila[1] and Norman Sanford[1]

[1]NIST, United States, [2]NIST, Boulder, Colorado, United States

Modern atom probe tomography is based on time-of-flight (ToF) mass spectrometry. In this method, the detector precisely measures the time difference between when an ion evaporates and the time it strikes a detector located a known distance away. Combining this ToF measurement with knowledge of the detector geometry and the electric fields applied to the sample the mass-to-charge ratio (*m/z)* of the ion can be determined accurately. Ideally for any such measurement scheme there is a well-defined trigger pulse (voltage or light) that causes field ion evaporation, and evaporation does not occur in the absence of a trigger pulse. Realistically however, this is not the case -- field evaporation occurs in the absence of the trigger pulse and contributes to the background signal. For the case of ion evaporation events that are truly random (i.e. uncorrelated with respect to the trigger pulse and the other ions), there is no current method to extract accurate *m/z* information and if these ions originated from the sample then information is permanently lost. For a `singles' event where only one ion strikes the detector following a trigger pulse there are two pathways shown in Figure 1a. The pathway denoted `i' shows the ideal behavior -- a single ion leaves the sample coincident with the trigger pulse and thus the recorded time duration between trigger and detection is the actual ToF for the ion. In contrast, the pathway denoted `ii' shows the background signal -- here a single ion leaves the tip uncorrelated with the trigger pulse and so the recorded ToF differs from the actual ToF and renders the ion's measured *m/z* incorrect. Because signal is lost in pathway `ii' events, experimental conditions are chosen to minimize this behavior (e.g. increasing the pulse fraction, reducing the temperature, minimizing the standing DC field).

An analysis of single hit events makes it appear that ions are either correlated to the trigger pulse or not, and that fact uniquely determines whether they are counted accurately in peaks or lost as background. In reality however, higher order correlations for multihit events can complicate matters. Figure 1a shows the different pathways possible for `doubles' events. Pathways `iii', `v' and `vi' are superpositions of the `singles' event pathways, however, in pathway `iv' the ions are uncorrelated with the laser pulse but correlated to each other; the fact that these ions are mutually correlated means that the time difference between their measured stop times can, in principle, be used to identify both ions recovering information that would have been lost. This information may be particularly important for measurements performed at relatively high fields which are known to have a propensity to undergo correlated evaporation (such as measurement performed on III-V semiconductors). The idea to plot a delta time spectrum for multihit events to recover ion identity information from `background' hits was first described by Saxey [1] and has been further explored by others [2-5].

These previous studies have been hampered, however, by a problem not yet described in the literature -- namely that the standard bowl (geometric) and voltage corrections that are applied to the timing data prior to generating a delta time histogram are not valid for these trigger uncorrelated ions. Briefly, this is because the standard voltage and bowl corrections assume that the ion's observed ToF is accurate, however for ions of pathway `iv' there is an unknown offset added to the ToF. The practical effect of this incorrect voltage and bowl correction is that the delta time spectra taken at different slices through a time correlation histogram show significant broadening as the average observed flight time increases away from the real values as shown in Figure 2a and

Figure 2b. In order to accurately analyze a delta time histogram over the full range of time delays this peak broadening must be corrected. Notably, if the delta time histogram was only accumulated for small average flight times, the peaks would be narrow, but most of the ions would be excluded.

In this presentation we will discuss the problem of voltage and bowl correcting mutually correlated multihit events, outlining the exact reason for the observed peak broadening. Additionally, we will discuss in detail a parameter-free algorithm that we have developed that is capable of dramatically reducing the peak broadening in the delta time histogram (Figure 2c). In some cases, peak heights increased (peak widths decreased) by nearly an order of magnitude and should lead to improved quantification of these previously `lost’ ions. This will be of particular interest for materials such as III-V nitrides which are known to evaporate in a correlated manner and have significant compositional biases.

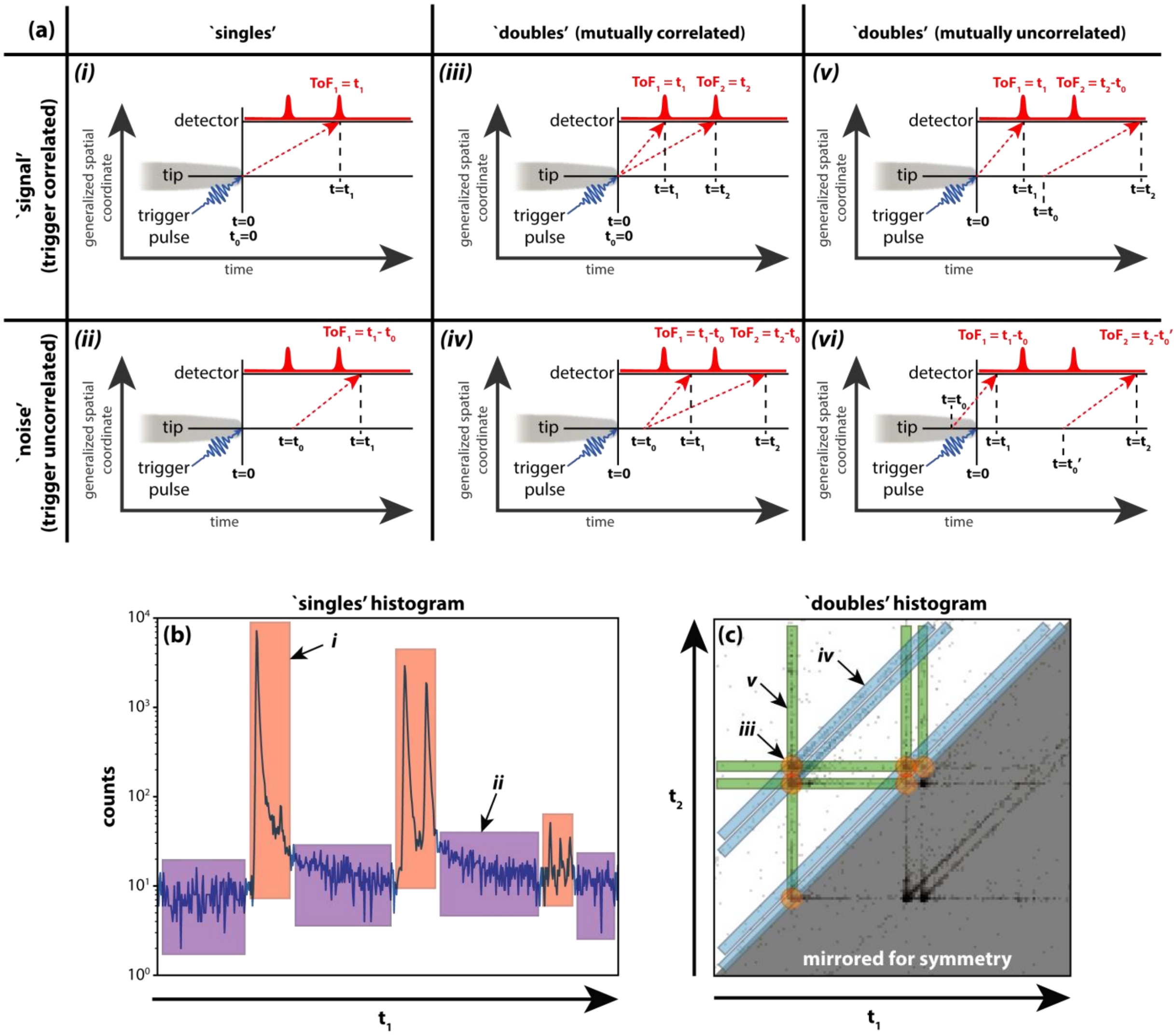

Figure 1. (a) Space-time diagrams showing the different timing pathways that can result from single and double hit events. Some pathways are registered as `signal' and some pathways are registered as `noise' in a 1D histogram. In this contribution we focus on the doubles pathway in subpanel (iv) where the ions are uncorrelated to the trigger pulse, but are mutually correlated with respect to each other. In (b) and (c)

these different pathways are identified in 1D and 2D time histograms. Data in (b) and (c) were collected on a GaN sample at 10 kHz using an EUV trigger pulse and relatively high field conditions.

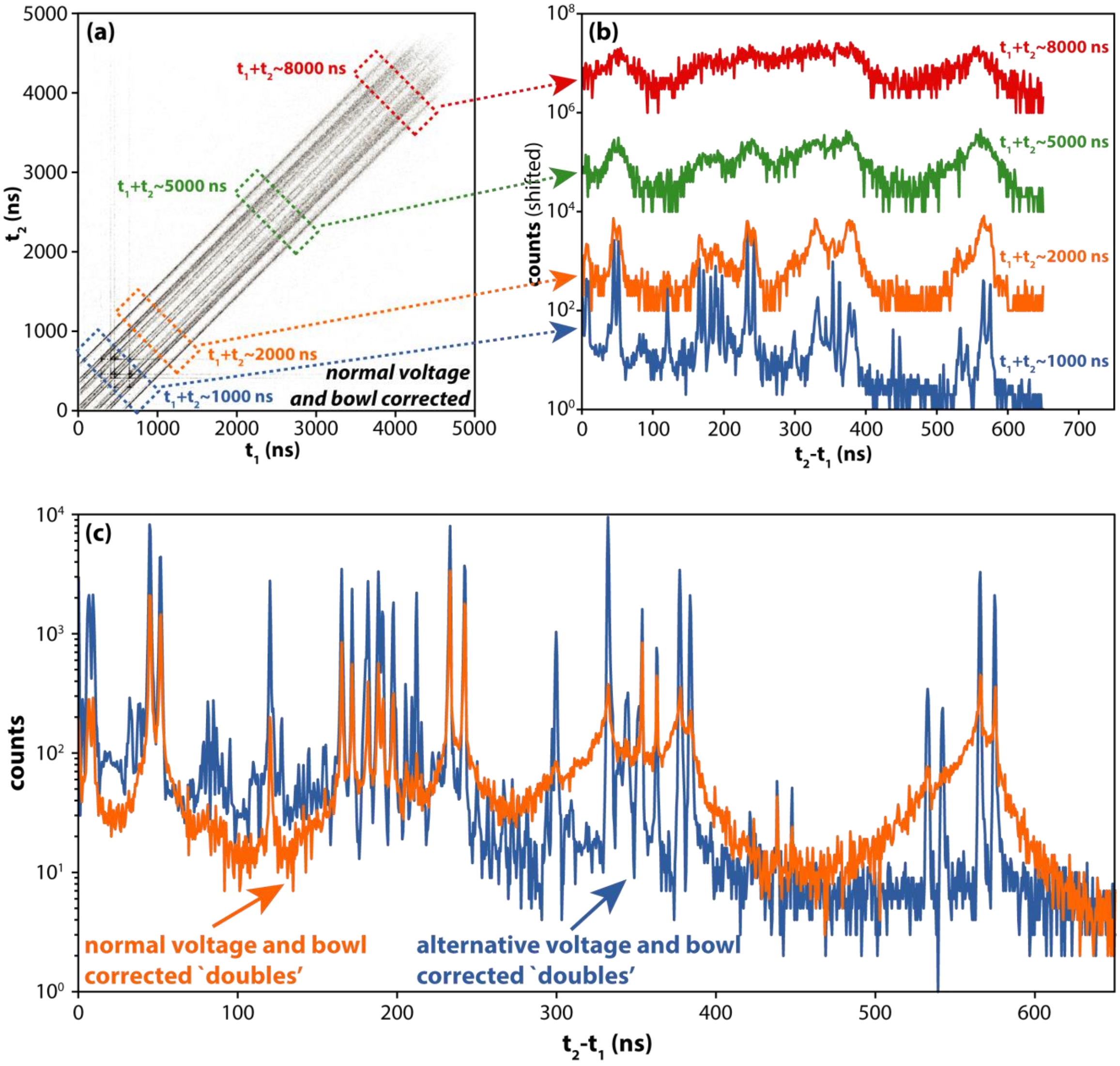

Figure 2. (a) Here is a time correlation histogram for doubles events. A `normal' voltage and bowl correction has been applied to this data. (b) Slices along the antidiagonal are plotted as delta time histograms and exhibit a rapid broadening at higher average times. (c) The delta time histogram of the full doubles dataset is shown using both the normal voltage and bowl correction algorithm and the alternative algorithm developed here. It is seen that the alternative algorithm significantly improves the spectrum and should permit more accurate quantification of these mutually correlated ions. Data were collected on a GaN sample at 10 kHz using an EUV trigger pulse and relatively high field conditions.

References

[1] Saxey, D., (2011). Correlated ion analysis and the interpretation of atom probe mass spectra. *Ultramicroscopy*, 111(6), 474-479. doi:10.1016/j.ultramic.2010.11.021

[2] Kruska, K., & Schreiber, D. (2015). Background Recovery through the Quantification of Delayed Evaporation Multi-Ion Events in Atom-Probe Data. *Microscopy and Microanalysis*, 21(S3), 857-858. doi:10.1017/S1431927615005085

[3] Meisenkothen, F., & Steel, E. (2017). Exploring Artifact Signals in Atom Probe Mass Spectra. *Microscopy and Microanalysis*, 23(S1), 634-635. doi:10.1017/S143192761700383X

[4] Fathidoost, M., Stephenson, L., Raabe, D., Gault, B., & Katnagallu, S. (2019). Hough Transform Based Accurate Composition Extractions From Correlation Histograms in Atom Probe Tomography. *Microscopy and Microanalysis*, 25(S2), 324-325. doi:10.1017/S1431927619002356

[5] Chen, Y., Geiser, B., Oltman, E., Rice, K., Ulfig, R., & Prosa, T. (2020). Study of Correlative Evaporation and Ion Dissociation in Atom Probe Data. *Microscopy and Microanalysis*, 26(S2), 2882-2882. doi:10.1017/S1431927620023090