

Background Recovery through the Quantification of Delayed Evaporation Multi-Ion Events in Atom-Probe Data

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The reliable quantitative analysis of oxides by atom probe tomography (APT) is an on-going issue. Analysis conditions have been shown to dramatically affect the measured composition, while rarely achieving a completely satisfactory measurement. In most cases, the optimal analysis conditions have been identified as a combination of low laser energy and high electric field. However, these analysis conditions also result in a relatively high probability for multi-ion evaporation within a single pulse, which can degrade the overall analysis and possibly introduce an unintentional compositional bias.

Saxey proposed graphical methods for interpreting multi-ion evaporation events (multihits) through correlation histograms [1,2]. An example of these so-called “Saxey plots” is shown in Figure 1 for NiO (LEAP 4000XHR, $\lambda=355$ nm, T=40K, 2-50 pJ/pulse laser energy range) in addition to conventional mass spectra for these same data. Color coding identifies ordinarily ranged (red) and unranged (green) portions of the data. Note that the data have been filtered to events with exactly two detected ions/pulse to maximize the S/N ratio in this representation. When the mass spectra is filtered to only unranged ions in Figure 1c, what remains is unidentifiable background that is typically discarded. However, when plotted on the correlation histogram these same data are readily identifiable as correlated, delayed evaporation events by the diagonal green lines extending from the lower-left to upper right of Figure 1a.

Identification of these background ions is enabled by leveraging the shared delay in evaporation (Δt) of the correlated ion pair, as described by Saxey[1]. This is accomplished by plotting the mass-to-charge state ratio (m/n) of one ion versus the difference in the square roots of the two m/n ratios and creating a histogram, as shown in Figure 2a for the same NiO data. Identification and quantification of the various peaks follows, enabling reliable recovery of >80 % of the “background” present in the original unranged portion of the multihit mass spectrum. Similar data are also displayed for Fe₃O₄ in Figure 2b.

The results of these quantifications are summarized in Table 1. Given the small percentage of unranged ions that are part of an event consisting of exactly two detected ions, it is unsurprising that the overall impact on the measured composition is minimal. However, careful implementation of these new analysis methods could provide novel insights into the origins of non-stoichiometric oxide measurements by APT and more broadly explore the role of background and multihit events in systematic composition errors for other materials that exhibit a propensity for correlated evaporation.

References:

- [1] Saxey, D W, Ultramicroscopy **111**, (2011) p. 473-479
- [2] Santhanagopalan, D et al., Ultramicroscopy **148**, (2015) p. 57-66.

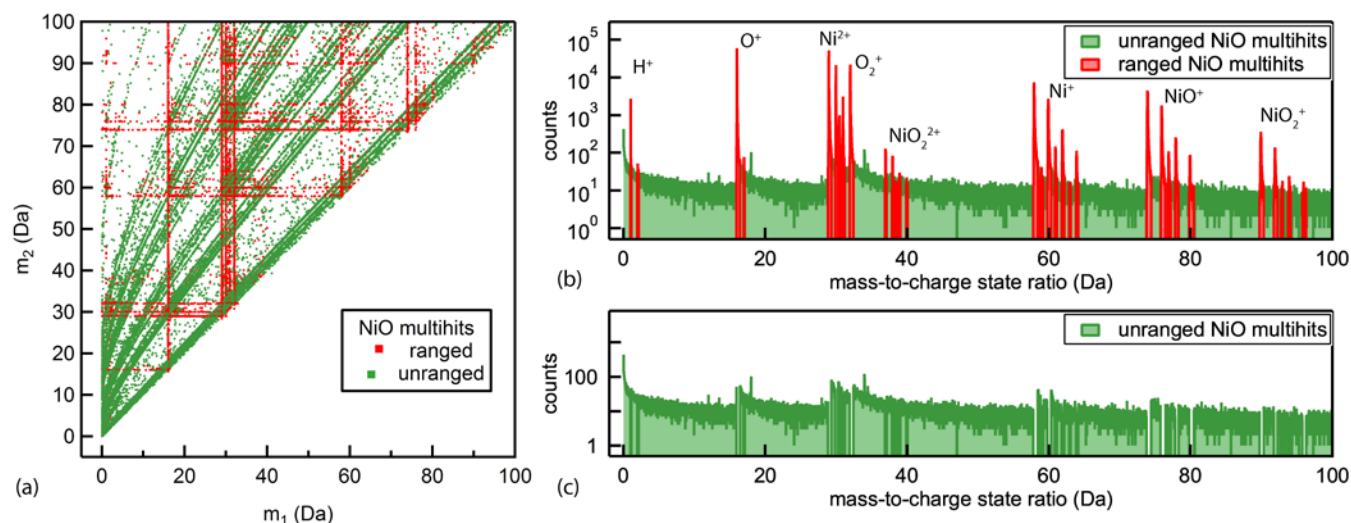


Figure 1. (a) Correlation histogram and (b)-(c) corresponding mass spectra for NiO wherein the data is filtered to only display data from exactly 2 detected ions in a given pulse. Color coding indicates ions that were identified by conventional ranging (red) and ion pairs that were not identifiable (green).

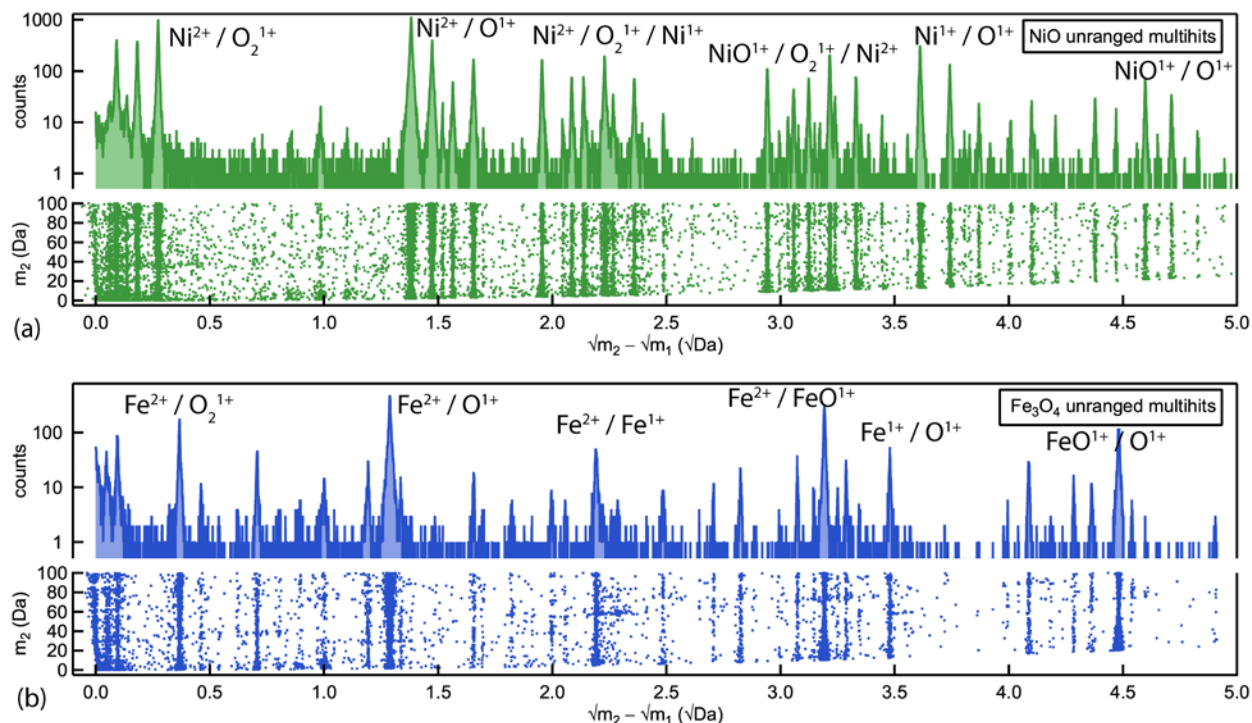


Figure 2. Recovered mass spectra from the unranged portions of NiO and Fe₃O₄ multihit data.

	O Concentration As-Ranged	O Concentration Unranged Multihits	Corrected O Concentration	Recovered Background
NiO	47.5 ± 0.1 at. %	57.4 ± 0.1 at. %	47.8 ± 0.1 at. %	82%
Fe ₃ O ₄	51.7 ± 0.1 at. %	49.6 ± 0.1 at. %	51.7 ± 0.1 at. %	67%

Table 1. O concentration using standard ranging and by adding unranged, identifiable multihit ions.