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Adaptive Peak Fitting for Isotope Analysis via Atom Probe Mass Spectrometry

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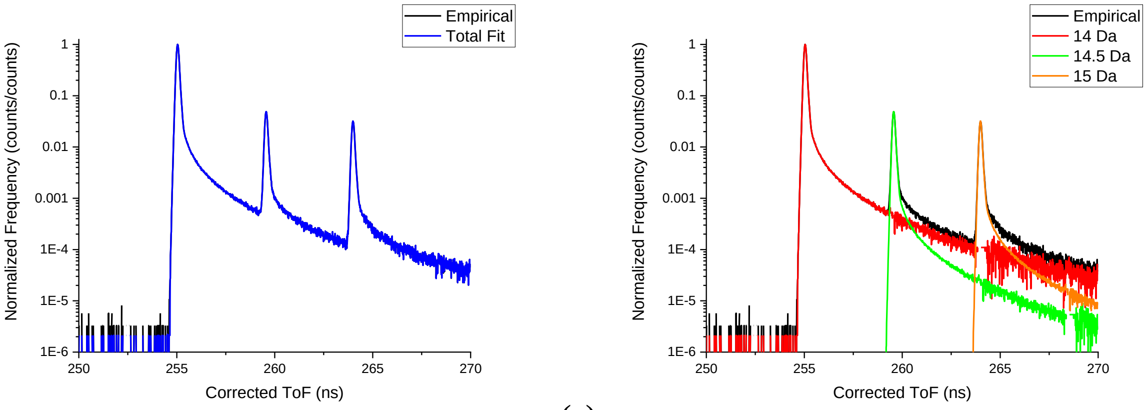
Atom probe tomography (APT) is an emergent characterization technique that has begun to see widespread use within the last 15 years. The technique offers the highest spatial resolution of any mass spectrometry technique for solid-state specimens, as well as a mix of advantages that set it apart from the other forms of mass spectrometry. Specimens are field evaporated, not dissolved in a liquid, ablated, or sputtered. Further, the combined ionization and detection efficiencies of APT can approach 80%, making it possible to achieve a level of accuracy and precision - without sensitivity factors or matrix correction factors - that would require an analysis volume roughly an order of magnitude larger with other techniques. However, the advancements in instrumentation and hardware have significantly outpaced the measurement science required for APT to realize its full potential. A significant challenge to performing accurate APT analyses lies with the peak forms encountered in the spectra. Since the peak forms can vary significantly between ion species and between data sets, no model peak form can be applied universally to every peak in the spectra [2]. Further, multi-hit detection events can be a cause for significant measurement bias in analyses [3].

We have been exploring a custom machine learning-based adaptive peak fitting method for assigning ions in the spectrum to specific ion species, as an alternative approach to the traditional ion ranging strategies. The goal is to produce an accurate, repeatable, and mathematically defensible method for determining peak shapes and peak intensities for the isotopic variants associated with each ion species in a spectrum. Rather than fit a continuous analytical form to each isotopic variant in a family of peaks, the optimization algorithm uses all of the information provided in a specified region of the spectrum, channel by channel, to determine the “best fit” peak form that is shared between the isotopic variants. The peak form is not assumed *a priori*, but rather is determined by the algorithm, subject to the constraint that all isotopic variants of a single ion species will have the same peak form. The sum of squared residuals is used as a cost function in an alternating least squares approach to capture peak fit and position.

A CAMECA local electrode atom probe (LEAP™ - 4000XSi) was used for all data acquisition. Subsequent data processing, prior to peak fitting and isotopic analysis, was done through IVAS v3.6.14, IVAS v3.8.2, and custom analysis scripts. The APT specimens were prepared in either a FEI Nova NanoLab™ 600 or a FEI Helios NanoLab™ 660 FIB-SEM. A number of natural materials (boron, tungsten, cubic boron) and isotopic abundance reference materials (common lead - SRM 981, triuranium octoxide – CRM129A, SRM U030, SRM U350, SRM U900) were used as “known” isotopic abundance values against which our analysis results could be compared to permit a quantitative statement of accuracy. The variety of different materials offered a wide range of analysis conditions under which to evaluate the performance of our methods. Analyses using timing-signal-only-based single-hit detection events were found to greatly improve accuracy on data sets containing a large fraction of multi-hit detection events [2]. Our methods have achieved accuracies limited predominantly by counting statistics, for these materials, even in the absence of any deadtime corrections and in the presence of high multi-hit fractions. The repeatability of the results obtained on the uranium reference materials permitted calibration to further ameliorate remaining measurement bias. While these initial results are encouraging (Figure 1), we will discuss some specific analysis situations in which our methods have had some difficulty. Our code continues to evolve as we seek to address these open issues.



(a) (b)

Figure 1. Figure 1: Adaptive peak fitting example. (a) Corrected time-of-flight spectrum for silicon in the region of the Si2+ ion species (black = empirical data, blue = total fit). (b) The three component peak fits associated with the isotopic variants of the Si2+ ion species (28Si2+, 29Si2+, 30Si2+).

References

[1] Disclaimer: Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

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