Single-Ion Deconvolution of Mass-Peak Overlaps for Atom Probe Microscopy

Andrew J. London*, Daniel Haley*, Michael P. Moody*

Corresponding author: andrew.london@materials.ox.ac.uk

*University of Oxford, Department of Materials Science,
16 Parks Rd, Oxford, UK and OX1 3PH

December 21, 2016

Abstract

Due to the intrinsic evaporation properties of the material studied, insufficient mass-resolving power and lack of knowledge of the kinetic energy of incident ions, peaks in the atom probe mass-to-charge spectrum can overlap and result in incorrect chemical measurements. Contributions to these peak overlaps can be deconvoluted globally, by simply examining adjacent peaks combined with knowledge of natural isotopic abundances. However, this strategy does not account for the fact that the relative contributions to this convoluted signal can often vary significantly in different regions of the analysis volume; e.g. across interfaces and within clusters. Some progress has been made with spatially localised deconvolution in cases where the discrete microstructural regions can be easily identified within the reconstruction, but this means no further point-cloud analyses are possible. Hence, we present an ion-by-ion methodology where the chemical identity of each ion, normally obscured by peak overlap, is resolved by examining the isotopic abundance of their immediate surroundings. The resulting peak-deconvoluted data is a point cloud and can be analysed with any existing tools. We will present the detailed case studies and discussion of the limitations of this new technique.

Keywords: atom probe tomography, mass spectrum analysis, peak overlaps, peak deconvolution, atomic-scale analysis.

1 Introduction

Atom probe tomography (APT) is a 3D atomistic characterisation technique which relies on time-of-flight mass spectrometry to infer elemental identities (Müller et al., 1968; Kelly and Larson, 2012). Therefore correct identification of the peaks in the mass-to-charge-state (m/z) spectrum is crucial in determining the correct measured composition (Haley et al., 2015). Due to the limited mass-resolving power of APT, there is a difficulty in distinguishing between certain ionic species. This is particularly challenging in organic (Narayan et al., 2012), oxide and ceramic materials (Kirchhofer et al., 2013; Mancini et al., 2014), which can produce complex mass spectra with molecular (Tsong, 1984) and multiply charged ions (Haydock and Kingham, 1980). However, peak overlaps can cause difficulties even with routine analysis of steels (Takahashi et al., 2011). With APT being applied to an increasing number of more complex materials (Valley et al., 2014; Seidman, 2007), there is a need to improve our analysis of the mass spectra.

One area for improvement is the deconvolution of peak overlaps. Peaks in the m/z spectrum may overlap directly (direct overlap) or a smaller peak may overlap the tail of a preceding peak (tail overlap). Tail overlap is often observed in laser pulsed mode due to the thermal transport from the tip (Vella et al., 2011) or in voltage mode due to an energy deficit (Müller and Krishnaswamy, 1974). In some cases an isobaric overlap occurs, such as $^{54}\text{Fe}/^{54}\text{Cr}$, where the atomic masses are very similar. Direct overlaps often occur when the separation of two peaks is smaller than a value which depends on the mass resolving power, but typically <0.1 Da. Direct overlaps can lead to incorrect measurements of the composition, and tail overlap reduces the signal-to-background ratio (contrast) of peaks. Therefore resolving any mass peak overlaps is critical to ensure an accurate compositional measurement.

In other spectral analyses, where the peak shape or position is known, peak fitting can be used to recover the total counts in each overlapped peak (Wojdyr, 2010). However, in APT, the peak shape is dependent on the ionic species and the position may be inexact due to inaccuracies during the calibration step. The peak shape can be estimated by machine learning to fit a peak shape to an experimental spectrum (Johnson et al., 2013), but this method requires a large quantity of data to produce a reliable fit. Peak overlaps may be resolved if they vary spatially and can be revealed by multivariate statistical analysis (Parish and Miller, 2010). However, in most cases the peak area may be estimated simply by integrating the counts from a specific m/z window or range (Miller, 2000). These ranged counts for each peak and knowledge of the natural isotopic abundances can be used to estimate the contribution of each ion to the overlapped peaks. These methods are well established for calculating the composition of

the whole data set, but this discards any spatial information entirely. Therefore we seek to improve the spatial resolution of this peak deconvolution method.

Kuduz et al. showed that corrections to the m/z spectrum applied to a specific volume can yield improved composition measurements (Kuduz et al., 2004), and similarly London et al. implemented a method for deconvoluting peak overlaps of individual clusters (London et al., 2015a). Therefore it is possible to use the additional spatial information available in the data to improve the reliability of the mass spectrum analysis. This is especially important when the extent of peak overlaps varies spatially across an analysed volume.

Recently, algorithmic development has allowed measurements of local concentration (Chen et al., 2014), solute distribution (Stephenson et al., 2014) and spectral analysis (Cairney et al., 2015), made at the *atomic-scale*. These analyses use the ions themselves as the spatial basis of the calculations. This transfers the selection of the scale of the digitization of the data from a voxel size (Miller, 1992) to an environment around every ion, such as by a sphere size or number of nearest neighbours.

Therefore we aim to couple this local, atomic-scale, spatial basis with mass spectrum analysis to resolve peak overlaps with the maximum possible spatial resolution. As such, we detail an implementation of a new ion-by-ion methodology where the chemical identity of each ion, obscured by peak overlap, is resolved by examining the isotopic abundance of their immediate surroundings. By confining the deconvolution to the smallest volume possible we retain the best possible spatial resolution. Equipped with this new tool, we demonstrate how existing compositional and spatial analysis can be improved. The new method is explained and applied to real data, and discussions of the limits are given.

2 Materials and Methods

We present two case studies from two different materials. One material is an oxide dispersion strengthened (ODS) steel (Fe-0.3Ti-0.3Y₂O₃wt%, (London et al., 2015b)), which contains Y-Ti-oxide clusters, and the other is a maraging steel (Fe-7Ni-10Cr-8Co-3Mo-1.80Al wt%, (Martin et al., 2016)), which contains Mo and NiAl particles. Both datasets were acquired on a LEAP 3000X HR in laser pulsing mode with a 0.4 nJ pulse energy and 532 nm laser. In the ODS steel, the principal overlaps occur between the oxide-containing species of the oxide clusters (e.g. TiO²⁺ and O₂⁺). In the maraging steel, an overlap exists between the Al⁺ and Fe²⁺ ions.

Now we turn to the per-ion deconvolution method, which has four main steps, detailed below, which include: (1) defining the ions whose chemical identities are obscured by peak overlap in the mass spec-

trum, (2) characterising the local environment around each of these ions in the reconstruction, (3) deconvoluting the overlap and (4) assigning the new ionic identity. The required inputs are the 3D positions and m/z values, a definition of what constitutes a peak overlap, and a definition of the ions present in the data.

2.1 Defining overlaps

The initial step of the per-ion deconvolution is the same as any other method that deconvolutes peak overlaps: all possible “direct” overlaps must be defined from: (1) a list of potential ion species likely to be observed in the analysis of the specific specimen, and (2) a given minimum peak spacing. It is very difficult to derive, from the data alone, what ions are present; therefore a list of ion species should be specified by the user. The criteria for two peaks to be considered overlapped is based on a minimum spacing of the peaks in the m/z spectrum, below which two or more peaks cannot be resolved as separate peaks. Practically this value depends on many individual variable including the specimen, experimental parameters (e.g. flight length and evaporation voltage) and the measured m/z for the peak position. The peaks have approximately constant width in the time-of-flight spectrum and therefore peaks in the m/z spectrum get wider as the measured m/z increases, $\delta m \propto \sqrt{m}$ (Larson et al., 2013). Therefore, we define the width of a specific peak by two upper and lower bounds which confine a particular peak window:

$$-P_1 \times \sqrt{\left(\frac{m}{z}\right)_i} < \text{peak window} < P_2 \times \sqrt{\left(\frac{m}{z}\right)_i}$$

where P_1 and P_2 are the lower and upper bound parameters and $\left(\frac{m}{z}\right)_i$ is the m/z value of the i th peak. If the resulting peak windows of two or more peaks overlap, those ions are considered directly overlapped. The positions and identities of overlapped ions can be visualised as per figure 1. This example illustrates Fe_2O^{2+} and TiO^+ overlap at four m/z positions, TiO^+ and CrO^+ overlap at 65.9 Da, and CrO^+ and Ga^+ overlap at 68.9 Da. Although Fe_2O^{2+} and CrO do not overlap, because TiO^+ overlaps with both Fe_2O^{2+} and CrO^+ , the solutions of these overlaps are interdependent and form an overlap group. However, the solution to each overlap group is independent of other groups of ions. Thus, the groups may be considered separately, which simplifies the peak deconvolution.

During this step, a check for rank deficiency is made as there needs to be at least as many m/z ranges as ions in each overlap group. For example, if the mono-isotopic P^+ and P_2^{++} ions overlap, there are two ions and only one peak; therefore this overlap group is rank deficient and cannot be resolved. Some isotopes have a very low isotopic abundance (below the quantification limit of the atom probe) and may

reduce the reliability of the overlap separation. Thus a minimum isotopic abundance is required for the isotope to be considered present, e.g. a value of approximately 0.2 % to exclude the ^{18}O isotope.

2.2 Local environment

To define the local environment around each overlapped ion, either a sphere centred around the ion or a number of that ion's nearest neighbours is used. Ions from this local neighbourhood are used to create a mass spectrum and the counts of the ions from this spectrum are used to deconvolute the peak overlaps. A sphere of fixed radius gives a fixed spatial resolution around each ion, however this sphere will contain a variable number of ions and hence have a varying degree of compositional uncertainty. Alternatively, specifying a number of nearest neighbours gives a fixed number of ions (fixed compositional certainty) but a variable spatial resolution.

2.3 Separating overlaps

The counts for each mass peak are given by specific ranges of m/z values (section 2.1). This has the advantage over spectral fitting methods used by Cairney and co-workers (Cairney et al., 2015), which require a pure reference spectrum to perform the fitting. The approach used here assumes a linear combination of ion counts $\{\mathbf{n}\}$ divided into separate peaks as described by their isotopic abundance $[\mathbf{A}]$. The counts $\{\mathbf{r}\}$ from each peak are contained within the specified range windows. For example, for two ions producing three mass peaks, this can be expressed in matrix algebra as:

$$\begin{bmatrix} A_{i,1} & A_{j,1} \\ A_{i,2} & A_{j,2} \\ A_{i,3} & A_{j,3} \end{bmatrix} \begin{Bmatrix} n_i \\ n_j \end{Bmatrix} = \begin{Bmatrix} r_1 \\ r_2 \\ r_3 \end{Bmatrix} \quad (1)$$

If the ions have a natural isotopic abundance, then $[\mathbf{A}]$ is known. $[\mathbf{A}]$ contains one column for each ion and each row contains the contribution of that ion to one specific m/z position. $\{\mathbf{r}\}$ contains the counts for each peak observed from the atom probe data. This leaves the ion counts $\{\mathbf{n}\}$, which is unknown. Unless equation (1) is rank deficient (section 2.1), then there are at least as many ranges as unknown ions, meaning this is an over-constrained mathematical problem. The simplest method to solve for $\{\mathbf{n}\}$ is to minimise the squared residual; this is called least squares (LS) (Lawson and Hanson, 1995). The application of LS to solve peak overlaps is described elsewhere (Gault et al., 2012; Larson et al., 2013). However, (Miller et al., 1996) describe solving the same mathematical problem using maximum likelihood estimation (MLE). MLE is superior to LS when treating discrete data with limited counts

(Maus et al., 2001), but is less numerically stable and somewhat more computationally intensive than LS. In our implementation, MLE was roughly ten times slower than LS, but was considered an acceptable trade-off for the improved result. The formalism given by (Miller et al., 1996) was an analytical solution for a specific species overlap and therefore of limited applicability. However, we have devised a method to solve any arbitrary set of overlapping peaks using the following likelihood function:

$$L(\mathbf{r}, \mathbf{n}) = -\log(\{\mathbf{r}\} \times [\mathbf{A}]') \cdot \{\mathbf{n}\}$$

For any particular set of overlapping peaks (any $[\mathbf{A}]$) and an initial guess of $\{\mathbf{n}\}$, this function can be maximised by a numerical method to return the most likely $\{\mathbf{n}\}$, for a given $\{\mathbf{r}\}$. From $\{\mathbf{n}\}$, the most likely ionic composition of the overlapped mass peak is calculated.

2.4 Identity Assignment

Using the local ionic composition, computed by the method above, the identity of an overlapped ion can be reassigned. This reassignment is made probabilistically and weighted by the deconvoluted ionic composition. If an ion has a composition of 10% X and 90% Y, then ionic identity is assigned as X or Y at random but with a 10/90 weighted probability. Relabeling probabilistically gives the advantage that the resulting data can be used with conventional workflows such as composition line profiles and proximity histograms as demonstrated in the following section.

3 Results

3.1 Case Study 1

ODS steels contain complex oxide phases which produce molecular oxygen-containing species during the atom probe experiment. Due to the differing chemistry of the oxide clusters, different ionic species can evaporate from different clusters. Figure 3a shows the mass spectrum from the 31–33 Da range of two different clusters. These two clusters have very different ionic compositions, with one containing predominantly TiO^{++} ions and the other containing only O_2^+ ions in the 32 Da peak. The ions from the 32 Da peak of an ODS steel are shown in figure 3b. Inspection of the global mass spectrum experiment shows small peaks from TiO^{2+} ions as well as a significant additional contribution to the 32 Da peak from O_2^+ ions overall. Figure 3c shows the per-ion deconvoluted data using a 1 nm spherical local environment. The deconvoluted data shows that most of the oxide clusters contain TiO^{2+} ions, however

a O₂-rich cluster is shown at the top of figure 3c. This apparently O₂-rich region is a Y₂O₃ oxide, unlike the surrounding clusters which are mixed Y-Ti-O oxides.

3.2 Case Study 2

Figure 4a shows ions from the 27 Da peak from a maraging steel. The steel contains Cr, Al and Fe, and the globally deconvoluted m/z histogram is shown in figure 4b. This global peak deconvolution shows that the 27 Da peak contains a 50/50 mixture of Fe²⁺ and Al⁺ ions. The Fe and Al elements are partitioned between the Fe-rich matrix and the NiAl particles, however this is not clear from figure 4a due to the peak overlap. After the per-ion deconvolution, the Al-rich particles are much more clear, as seen in the atom-map in figure 4c. As well as improving the visualisation of the atom map, the proximity histogram analysis is also corrected.

Prior to the deconvolution, the 27 Da could be assigned to either Al⁺ or Fe²⁺, and the results of this assignment are shown in figure 4d. Al-assignment is correct for the Al-rich particle centre but this overestimates the Al-content of the surroundings. Fe-assignment gives the correct Al-content of the predominantly Fe-rich matrix, however, this results in very little Al detected in the particles. The black line shows the proximity histogram measured from the per-ion deconvoluted data and this has the expected Al-concentration for the Al-rich centre of the particles and a much lower Al-content in the surrounding matrix.

4 Discussion

In both the examples above, the per-ion deconvolution method works to resolve the overlaps while maintaining a spatial resolution in the range of a few nanometers. For the oxide clusters in an ODS steel (figure 3) it is possible to separate out the clusters before performing the deconvolution (c.f. (London et al., 2015a)), but the per-ion method described here allows differences between the clusters to be clearly visualised, as well as the opportunity to refine the cluster selection. In the maraging steel, the simplest method of quantification of the interface between the particles and the matrix is a proximity histogram (Hellman et al., 2003) which provides spatially averaged information from many particles. Without modification of the proximity histogram method, it is not possible to extract accurate compositional information about the interface region because of the dramatic differences in the ionic composition of the 27 Da peak. Using the per-ion deconvolution method, we have obtained a more accurate measurement of the composition of the particle in the core, interface and matrix region without modification of the

proximity histogram method. This has been achieved without the need for a “pure spectral reference” as required previously to perform this analysis (Cairney et al., 2015). The per-ion deconvolution method is best applied when there is a spatial variation of the peak overlaps of the m/z spectrum.

Having discussed the utility of this method, we now consider the limitations. Fundamentally, any atomistic method will be limited by counting error, the variation which comes from having a limited amount of data. Figure 5 illustrates the measured compositional variance as a function of the local environment sampling size for a typical atom probe data set (density of 30 overlapped ions/nm³). Therefore a specific sampling volume can be selected to provide a specified minimum level of compositional certainty. Figure 5 also compares the compositional error from using MLE and LS. The MLE method consistently outperforms LS and gives a smaller error but at the cost of an increased computation time.

The new method also introduces some spatial uncertainty because each overlapped ion is now delocalised over the volume of the local environment selected. In every atom probe experiment there is some small amount of spatial uncertainty (Vurpillot et al., 2000), which is quantifiably compounded with this error by using the per-ion deconvolution method. We set out a demonstration of the effective spatial uncertainty below.

Two hypothetical ions, A and B, both have equal isotopic abundances. A has peaks at 1 and 2, and B has peaks 2 and 3, as shown in figure 6a. Equal amounts of A and B were used to form a sharp interface shown in figure 6b. The per-ion deconvolution method (1 nm radius sphere sampling volume) was applied to resolve the overlap in the 2nd peak, and a composition profile across the interface is shown in figure 6c. Both the LS and MLE methods were applied for comparison.

The deconvoluted line profile has been blurred from the original step function in both the LS and the MLE results (figure 6c), with the spatial uncertainty being equal to twice the radius of the sampling volume. This spatial uncertainty is comparable to that introduced by voxelisation and delocalisation when calculating isoconcentration surfaces (Hellman et al., 2003). The deconvolution using LS shows some additional composition variations in the pure A and pure B regions. This shows the limitation of least squares when working with limited discrete data; in the pure A region, statistical fluctuations can cause the 2 peak to contain more counts than the 1 peak. LS estimates that some B must be present, even if there are no counts in the 3 peak. MLE however, is not subject to these errors, and correctly predicts the most likely composition in the pure regions and across the interface.

A further limitation of atomic-based analysis is the inability to readily capture the background signal present in the data. Atom probe data is always subject to some background signal, which represents a relatively small fraction of the total data, and appears as spurious points in 3D with arbitrary m/z values

(Gault et al., 2012). In the global spectrum this background is routinely subtracted from the total signal (Larson et al., 2013), however there are insufficient counts in each local environment to reliably correct for the background in the per-ion deconvolution method. While it is possible to estimate the background or noise contribution globally it is not reliable to assume the noise level will be constant throughout the 3D data, this is specially true of peak-tail overlaps. The result of not applying any form of background correction can be seen in the Al concentration of the matrix in figure 4d, which is higher than expected, 1.0 at% in the per-ion deconvolution but 0.6 at% from the global deconvolution. The over-estimated counts of Al result from tail overlaps of the Fe and Cr peaks near the 27 Da peak. To overcome this problem we suggest that the background level could be estimated using a similar local environment approach, but with a larger scale, to that detailed in figure 2, and a probabilistic assignment made to either a signal ion or background ion in the same way that ion identity was stochastically assigned.

5 Summary

We have developed a new method for solving peak overlaps at the atomic-scale which uses the surrounding ions to determine the ionic identity using known isotopic abundances. The use of a flexible local environment and deconvolution by maximum likelihood estimation mitigate some of the existing challenges of working limited discrete data. We demonstrated the utility of the technique for studying clusters and interfaces where the extent of the overlapping ions varied spatially. This per-ion deconvolution technique is particularly useful when the geometry of the feature of interest is not easily isolated for “bulk” analysis or when analysis of an interface between features containing different overlaps is required. This new technique produces standard point-cloud data, meaning it can be exploited further using existing techniques such as proximity histograms, composition line profiles, isosurfaces or cluster identification without further modification. Implementations of the programs described, written in MATLAB, are available at <http://AtomProbeLab.sourceforge.net>.

Acknowledgments

Many thanks to T. Martin of the University of Oxford for the use of the maraging steel alloy data. AJL is funded by EPSRC project EP/I012400/1 and EP/I003274/1. D. Haley acknowledges EPSRC funding from EP/L014742/1.

Figure 1: A schematic showing which ion species overlap and at which m/z positions. Ions are named in ovals, the overlapping positions are shown by labelled lines and connected ions form an “overlap group”. The line thickness indicates the product of the isotopic abundances of the overlapped peaks, and therefore “overlap intensity” if the ionic quantities were equal. All values in Da.

Figure 2: The local environment may be defined by (a), a sphere around the target ion, or (b) a number of nearest neighbours.

Figure 3: Ions from the 32 Da peak in a Y-Ti-O containing ODS steel. Approximately 30% of all ions from the oxide clusters have a m/z of 32 Da. (a) selected m/z spectra from two different oxide clusters, one TiO^{2+} -rich and the other O_2^+ -rich. Atom maps: (b) all ions from the 32 Da peak, (c) ions from the 32 Da peak after per-ion deconvolution and identity reassignment using a local environment sphere of radius 1 nm: TiO^{2+} ions (lighter) and O_2^+ ions (darker). Scale bar 20 nm.

Figure 4: Atom maps from a FeCrAl steel which contains Al-rich precipitates (a) showing all ions from the 27 Da peak (b) showing only Al ions in the 27 Da peak after per-ion deconvolution (c) proximity histogram from the per-ion deconvoluted data (local environment = 100 nearest neighbours) using an Al iso-concentration surface of 10 at%. Scale bar 20 nm.

Figure 5: Variation of error with local environment size, comparing the least squares method (LS) and the maximum likelihood estimation (MLE) method.

Figure 6: Simulated point cloud of two ions (A, B) each with isotopes of equal abundance (total composition shown in (a)). (b) the sharp interface between two regions of pure A and pure B. (c) the measured composition after per-ion peak deconvolution (1 nm local environment radius) using either least squares (LS) or maximum likelihood estimation (MLE).

References

- Cairney, J. M., Rajan, K., Haley, D., Gault, B., Bagot, P. A., Choi, P.-P., Felfer, P. J., Ringer, S. P., Marceau, R. K., and Moody, M. P. (2015). Mining information from atom probe data. *Ultramicroscopy*, 159, Part 2:324 – 337, DOI: [10.1016/j.ultramic.2015.05.006](https://doi.org/10.1016/j.ultramic.2015.05.006). 1st International Conference on Atom Probe Tomography & Microscopy. 3, 5, 8
- Chen, Y., Chou, P. H., and Marquis, E. A. (2014). Quantitative atom probe tomography characterization of microstructures in a proton irradiated 304 stainless steel. *Journal of Nuclear Materials*, 451(1-3):130–136, DOI: [10.1016/j.jnucmat.2014.03.034](https://doi.org/10.1016/j.jnucmat.2014.03.034). 3
- Gault, B., Moody, M. P., Cairney, J., and Ringer, S. (2012). *Atom Probe Microscopy*, volume 160. Springer-Verlag, New York, ISBN: 978-1-4614-3435-1, DOI: [10.1007/978-1-4614-3436-8](https://doi.org/10.1007/978-1-4614-3436-8). 5, 9
- Haley, D., Choi, P., and Raabe, D. (2015). Guided mass spectrum labelling in atom probe tomography. *Ultramicroscopy*, 159, Part 2(""):338–345, DOI: [10.1016/j.ultramic.2015.03.005](https://doi.org/10.1016/j.ultramic.2015.03.005). 2
- Haydock, R. and Kingham, D. R. (1980). Post-Ionization of Field-Evaporated Ions. *Phys. Rev. Lett.*, 44(23):1520–1523, DOI: [10.1103/PhysRevLett.44.1520](https://doi.org/10.1103/PhysRevLett.44.1520). 2
- Hellman, O. C., du Rivage, J. B., and Seidman, D. N. (2003). Efficient sampling for three-dimensional atom probe microscopy data. *Ultramicroscopy*, 95(0):199–205, DOI: [10.1016/S0304-3991\(02\)00317-0](https://doi.org/10.1016/S0304-3991(02)00317-0). 7, 8
- Johnson, L., Thuvander, M., Stiller, K., Odén, M., and Hultman, L. (2013). Blind deconvolution of time-of-flight mass spectra from atom probe tomography. *Ultramicroscopy*, 132:60–64, DOI: [10.1016/j.ultramic.2013.03.015](https://doi.org/10.1016/j.ultramic.2013.03.015). 2
- Kelly, T. F. and Larson, D. J. (2012). The second revolution in atom probe tomography. 37:150–158, ISBN: 0883-7694, DOI: [10.1557/mrs.2012.3](https://doi.org/10.1557/mrs.2012.3). 2
- Kirchhofer, R., Teague, M. C., and Gorman, B. P. (2013). Thermal effects on mass and spatial resolution during laser pulse atom probe tomography of cerium oxide. *Journal of Nuclear Materials*, 436(1–3):23 – 28, DOI: [10.1016/j.jnucmat.2012.12.052](https://doi.org/10.1016/j.jnucmat.2012.12.052). 2
- Kuduz, M., Schmitz, G., and Kirchheim, R. (2004). Investigation of oxide tunnel barriers by atom probe tomography (tap). *Ultramicroscopy*, 101(2–4):197 – 205, DOI: [10.1016/j.ultramic.2004.06.003](https://doi.org/10.1016/j.ultramic.2004.06.003). 3

- Larson, D. J., Prosa, T. J., Ulfig, R. M., Geiser, B. P., and Kelly, T. F. (2013). *Local Electrode Atom Probe Tomography: A User's Guide*. Springer-Verlag New York, ISBN: 978-1-4614-8720-3, DOI: [10.1007/978-1-4614-8721-0](https://doi.org/10.1007/978-1-4614-8721-0). 4, 5, 9
- Lawson, C. and Hanson, R. (1995). *Solving Least Squares Problems*. Society for Industrial and Applied Mathematics, Philadelphia, DOI: [10.1137/1.9781611971217](https://doi.org/10.1137/1.9781611971217). 5
- London, A. J., Lozano-Perez, S., Moody, M. P., Amirthapandian, S., Panigrahi, B. K., Sundar, C. S., and Grovenor, C. R. M. (2015a). Quantification of oxide particle composition in model oxide dispersion strengthened steel alloys. *Ultramicroscopy*, DOI: [10.1016/j.ultramicroscopy.2015.02.013](https://doi.org/10.1016/j.ultramicroscopy.2015.02.013). 3, 7
- London, A. J., Santra, S., Amirthapandian, S., Panigrahi, B. K., Sarguna, R. M., Balaji, S., Vijay, R., Sundar, C. S., Lozano-Perez, S., and Grovenor, C. R. M. (2015b). Effect of Ti and Cr on dispersion, structure and composition of oxide nano-particles in model ODS alloys. *Acta Mater.*, 97:223–233, DOI: [10.1016/j.actamat.2015.06.032](https://doi.org/10.1016/j.actamat.2015.06.032). 3
- Mancini, L., Amirifar, N., Shinde, D., Blum, I., Gilbert, M., Vella, A., Vurpillot, F., Lefebvre, W., Lardé, R., Talbot, E., Pareige, P., Portier, X., Ziani, A., Davesne, C., Durand, C., Eymery, J., Butté, R., Carlin, J.-F., Grandjean, N., and Rigutti, L. (2014). Composition of wide bandgap semiconductor materials and nanostructures measured by atom probe tomography and its dependence on the surface electric field. *The Journal of Physical Chemistry C*, 118(41):24136–24151, DOI: [10.1021/jp5071264](https://doi.org/10.1021/jp5071264). 2
- Martin, T., Radecka, A., Sun, L., Simm, T., Dye, D., Perkins, K., Gault, B., Moody, M., and Bagot, P. (2016). Insights into microstructural interfaces in aerospace alloys characterised by atom probe tomography. *Materials Science and Technology*, 32(3):232–241, DOI: [10.1179/1743284715Y.0000000132](https://doi.org/10.1179/1743284715Y.0000000132). 3
- Maus, M., Cotlet, M., Hofkens, J., Gensch, T., De Schryver, F. C., Schaffer, J., and Seidel, C. (2001). An experimental comparison of the maximum likelihood estimation and nonlinear least-squares fluorescence lifetime analysis of single molecules. *Analytical chemistry*, 73(9):2078–2086, DOI: [10.1021/ac000877g](https://doi.org/10.1021/ac000877g). 6
- Miller, M. (1992). Implementation of the optical atom probe. *Surface science*, 266(1):494–500. 3
- Miller, M. K. (2000). *Atom probe tomography*. Plenum Pub Corp, New York, ISBN: 978-0-306-46415-7, DOI: [10.1007/978-1-4615-4281-0](https://doi.org/10.1007/978-1-4615-4281-0). 2

- Miller, M. K., Cerezo, A., Hetherington, M. G., and Smith, G. D. W. (1996). *Atom probe field ion microscopy*. Oxford Science Publications, Oxford, ISBN: 978-0-19-851387-2. 5, 6
- Müller, E. W. and Krishnaswamy, S. (1974). Energy deficits in pulsed field evaporation and deficit compensated atom-probe designs. *Review of Scientific Instruments*, 45(9):1053–1059. 2
- Müller, E. W., Panitz, J. A., and McLane, S. B. (1968). The Atom-Probe Field Ion Microscope. *Rev. Sci. Instrum.*, 39(1):83–86, DOI: 10.1063/1.1683116. 2
- Narayan, K., Prosa, T. J., Fu, J., Kelly, T. F., and Subramaniam, S. (2012). Chemical mapping of mammalian cells by atom probe tomography. *Journal of structural biology*, 178(2):98–107, DOI: 10.1016/j.jsb.2011.12.016. 2
- Parish, C. M. and Miller, M. K. (2010). Multivariate statistical analysis of atom probe tomography data. *Ultramicroscopy*, 110(11):1362–1373, DOI: 10.1016/j.ultramic.2010.07.006. 2
- Seidman, D. N. (2007). Three-Dimensional Atom-Probe Tomography: Advances and Applications. *Annu. Rev. Mater. Res.*, 37(1):127–158, DOI: 10.1146/annurev.matsci.37.052506.084200. 2
- Stephenson, L. T., Ceguerra, A. V., Li, T., Rojhirunsakool, T., Nag, S., Banerjee, R., Cairney, J. M., and Ringer, S. P. (2014). Point-by-point compositional analysis for atom probe tomography. *MethodsX*, 1:12–18, DOI: 10.1016/j.mex.2014.02.001. 3
- Takahashi, J., Kawakami, K., and Kobayashi, Y. (2011). Quantitative analysis of carbon content in cementite in steel by atom probe tomography. *Ultramicroscopy*, 111(8):1233–1238, DOI: 10.1016/j.ultramic.2011.03.024. 2
- Tsong, T. T. (1984). Pulsed-laser-stimulated field ion emission from metal and semiconductor surfaces: A time-of-flight study of the formation of atomic, molecular, and cluster ions. *Phys. Rev. B*, 30(9):4946–4961, DOI: 10.1103/PhysRevB.30.4946. 2
- Valley, J. W., Cavosie, A. J., Ushikubo, T., Reinhard, D. A., Lawrence, D. F., Larson, D. J., Clifton, P. H., Kelly, T. F., Wilde, S. A., Moser, D. E., and Spicuzza, M. J. (2014). Hadean age for a post-magma-ocean zircon confirmed by atom-probe tomography. *Nature Geoscience*, 7(3):219–223, DOI: 10.1038/ngeo2075. 2
- Vella, A., Mazumder, B., Costa, G. D., and Deconihout, B. (2011). Field evaporation mechanism of bulk oxides under ultra fast laser illumination. *Journal of Applied Physics*, 110(4):044321, DOI: 10.1063/1.3610523. 2

- Vurpillot, F., Bostel, A., Cadel, E., and Blavette, D. (2000). The spatial resolution of 3d atom probe in the investigation of single-phase materials. *Ultramicroscopy*, 84(3):213–224, DOI: [10.1016/S0304-3991\(00\)00035-8](https://doi.org/10.1016/S0304-3991(00)00035-8). 8
- Wojdyr, M. (2010). Fityk: a general-purpose peak fitting program. *Journal of Applied Crystallography*, 43(5):1126–1128, DOI: [10.1107/S0021889810030499](https://doi.org/10.1107/S0021889810030499). 2