Development of Python-based Toolkit to Improve Analysis of Atom Probe Tomography Data

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Toolkit Capabilities

- Generate initial CSV files from proxigram XLSX.
- Take user-input for manual peak decomposition in proxigrams.
- Convert proxigram atom counts to at% values.
- Generate profiles of proxigram data after discarding irrelevant isotopes.
- Create core statistics file from user identification of matrix and precipitate of profile.
- Turn large POS files into workable CSVs.
- Calculate and display spatial error statistics for proxigram and CSV.
- Take inputs for calculating average radius, vol fraction, and number density, do the calculation, and report the uncertainty.
- Generate a mass spectrum graph and analysis from POS CSV.
- Consolidate programs into GUI using Py2App and *tkinter* for better user experience.
- Calculate statistics such as Gibbsian interfacial excess of solute and distributions of atoms within matrix, precipitate, and core

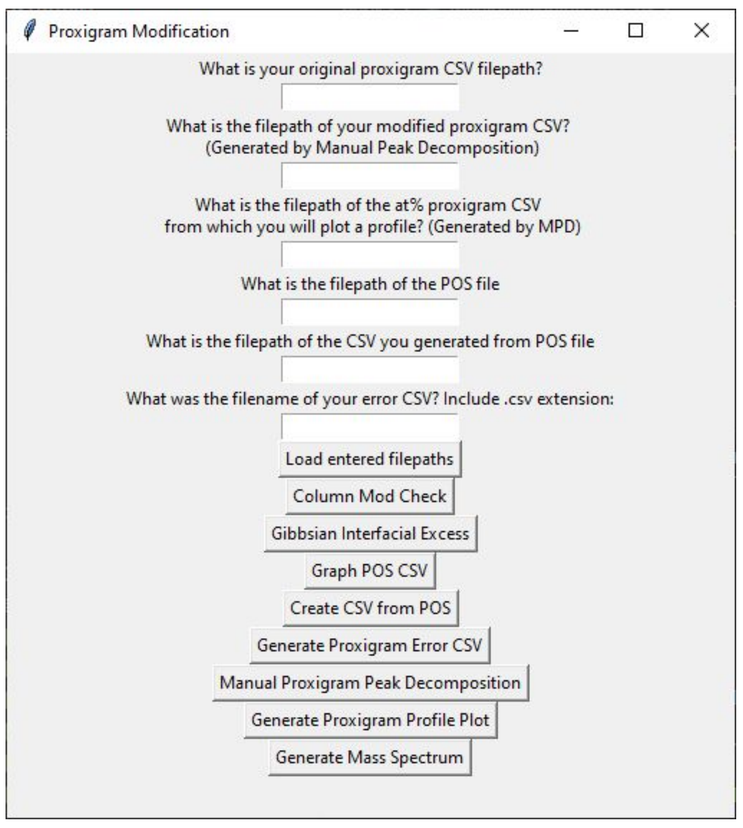
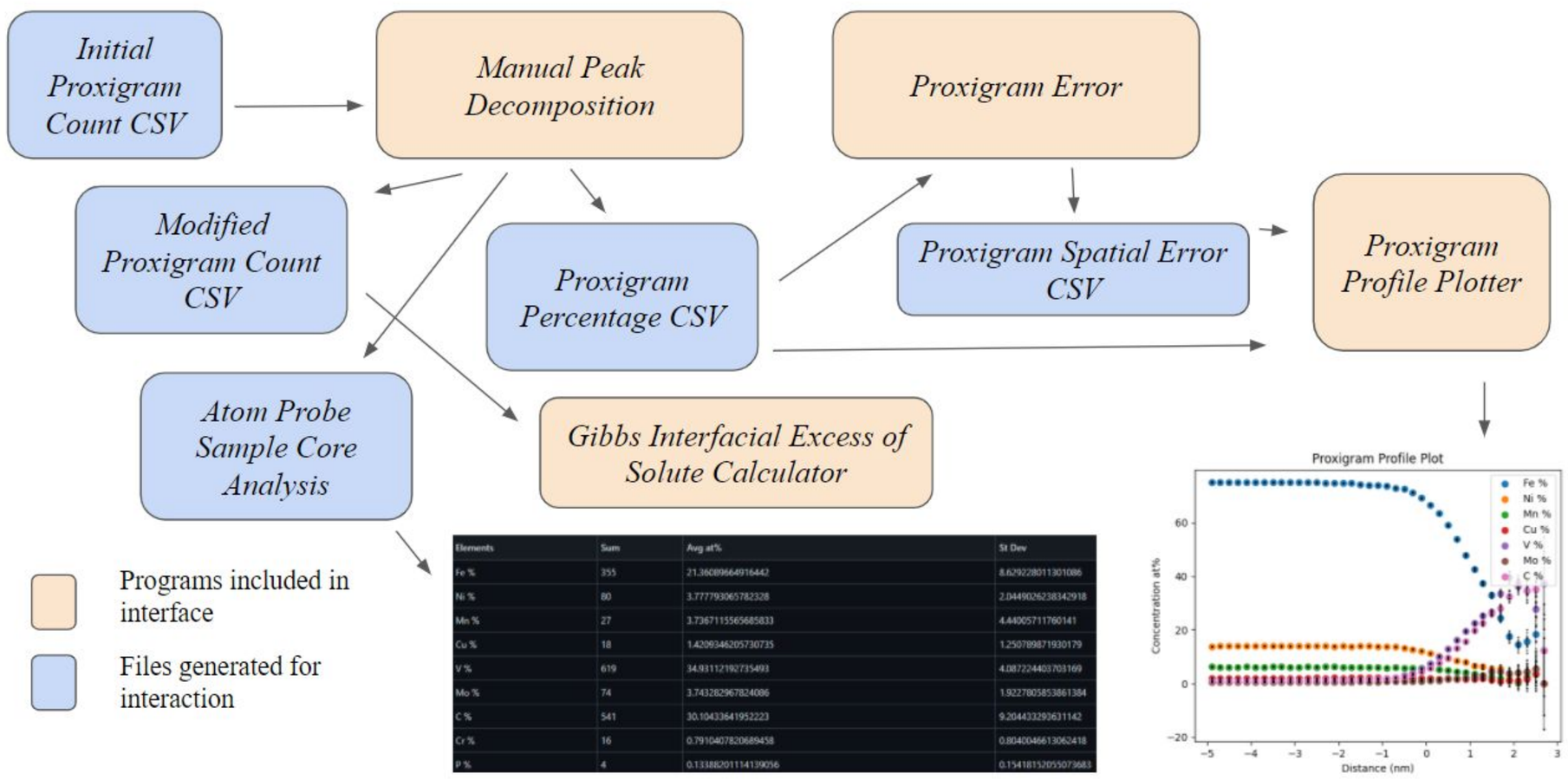


Figure 3. Image of user interface application with integrated programs. Packages used in this project and thus system requirements are *struct*, *pandas*, *tkinter*, *numpy*, and *matplotlib*.



Elements	Sum	Avg at%	St Dev
Fe %	355	21.36089664916442	8.629228011301086
Ni %	80	3.777793065782328	2.0449026238342918
Mn %	27	3.7367115565685833	4.440057117601 41
Cu %	18	1.4209346205730735	1.250789871930179
V %	619	34.93112192735493	4.087224403703169
Mo %	74	3.743282967824086	1.9227805853861384
C %	541	30.10433641952223	9.204433293631142
Cr %	16	0.7910407820689458	0.8040046613062418
P %	4	0.13388201114139056	0.15418152055073683

Figure 4. Programs written to interact with proxigram data.

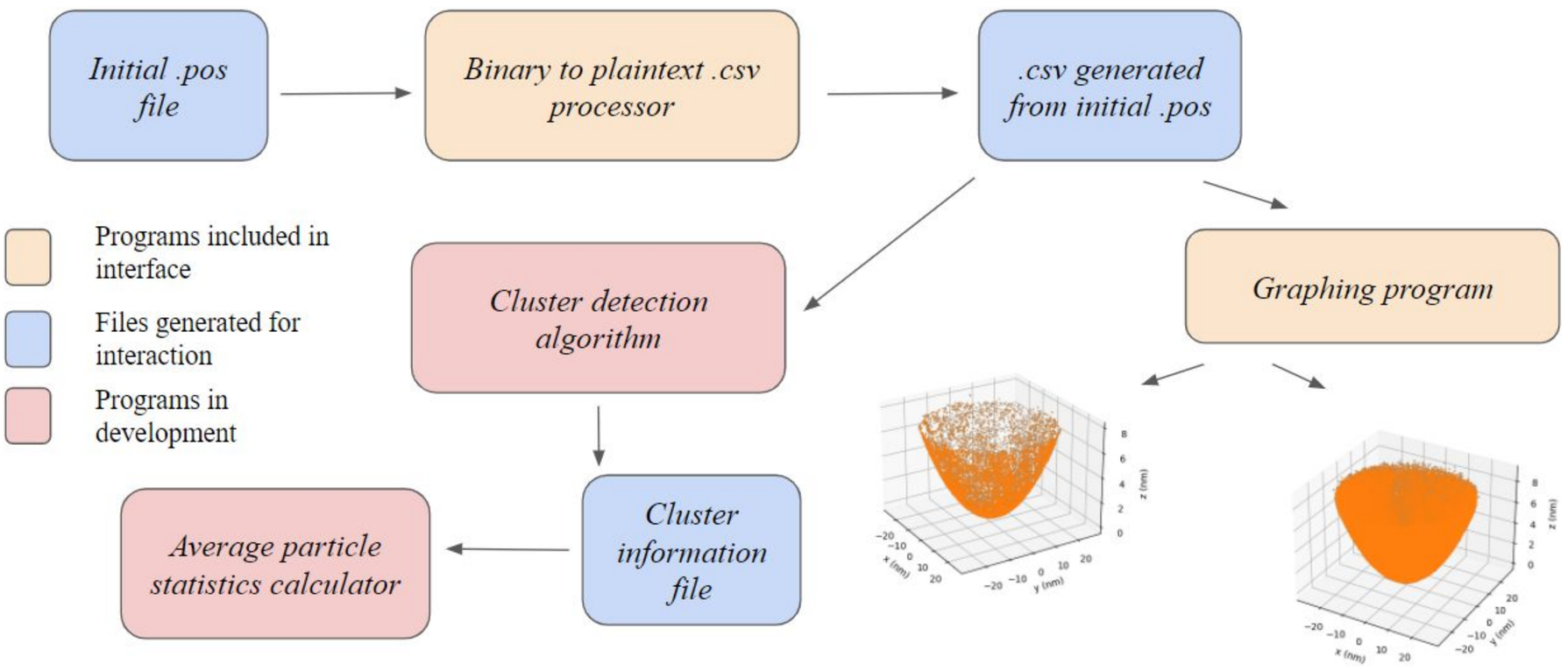


Figure 5. Programs written to interact with initial raw .pos and .epos data. A major bottleneck with interaction with .pos files is the large amounts of data, often totaling hundreds of millions of atoms to parse. Therefore, optimization and implementation of SQL along with more algorithms are a high priority to moving forward in work on .pos files. The graph is a sample of 10,000 and 100,000 atoms in a sample APT run.

Project Overview

The purpose of the project was to develop a Python-based toolkit to automate, optimize, and streamline analysis of data produced by Atom Probe Tomography (APT). This project addresses many issues with the raw data and proximity histogram analysis processes conducted after APT, such as the difficulties of mass spectrum peak decomposition, mass spectrum ranging, determining statistics such as Gibbs interfacial excess of solute, and error calculation in reported values.

This was achieved by using established Python libraries such as *Pandas* to process large amounts of binary data generated by APT into workable CSV files and addressing each issue in APT analysis with discrete scripts, finally compiling them into a toolkit available on Github. In addition to this project holistically addressing APT data analysis using Python and moving APT data analysis away from proprietary software, future goals include improving existing data analysis techniques by implementing various algorithms employing optimization and machine learning.

Atom Probe Tomography

- Atom-by-atom dissection of a material volume
- Sub-nanometer resolution, and chemical sensitivities approaching 10 atomic ppm
- Breakdown by field evaporation
- Time-of-flight mass spectrometry and impact recordings create reconstruction
- Mass-to-charge ratio and (x, y, z) recorded in large binary .pos files
- Proximity histogram (proxigram) details at% composition of thin ~.1 nm shells of sample about predetermined surface

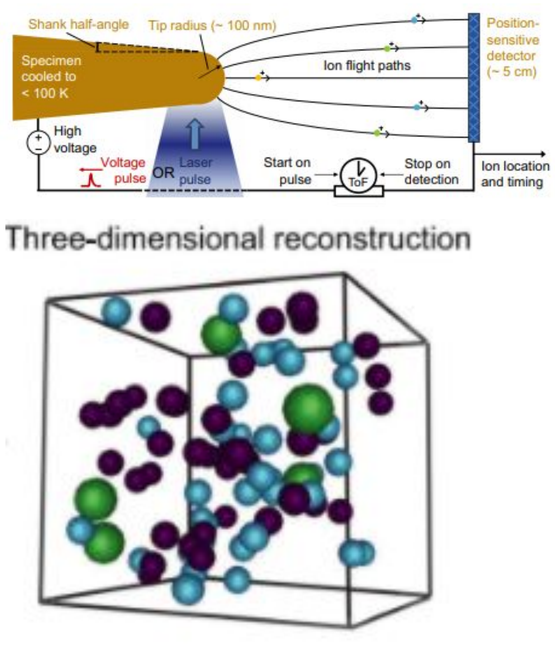


Figure 1. The schematics above represent the process of atom probe tomography, and demonstrate how reconstructions can be developed from a position-sensitive detector. Image sourced from Reddy, S. M., Saxey, D. W., Rickard, W. D. A., Fougerouse, D., Montalvo, S. D., Verberne, R., & van Riessen, A. (2020).

The Challenges of Atom Probe Tomography

- Leaves molecular artifacts in sample through FIB milling and other processing (Tamura, M., Shukuri, S., Moniwa, M., & Default, M. (1986))
- Isotopic overlaps left inherent to time-of-flight mass spectrometry
- Mass spectrum ranging and peak identification is difficult
- Maximum separation algorithm heavily dependent on user-input parameters, could use optimization (Vincent, G. B., Proudian, A. P., & Zimmerman, J. D. (2020))
- Lack of algorithms to calculate error statistics and relevant thermodynamic quantities such as Gibbs interfacial excess of solute for which APT is easily applicable (Hellman, O. C., & Seidman, D. N. (2002), Krakauer, B. W., & Seidman, D. N. (1993))
- Large amounts of data make processing generally tedious - optimization and automation of the process is a viable direction for development

Distance (nm)	Rn % (27Da)	Fe %	Mn %	Cr %	C %	Ni %	Al %	Cu %	NiH %	C2 %	C3 %	C4 %	Ca %	Ga %	H %	Sample Count
-4.949999809	120248	865188	270480	85353	32141	91196	61543	28948	0	0	0	0	242	211	141	1555691
-4.849999905	124861	897409	281636	88476	33029	94206	63305	29901	0	0	0	0	253	215	157	1613448
-4.75	129342	929743	290383	91072	33607	97102	65665	30660	0	0	0	0	243	238	160	1668215
-4.650000095	133474	961079	300279	94948	34926	100530	68102	31499	0	0	0	0	241	218	153	1725449

Figure 2. Unmodified proxigram of atom counts. Note Rn % (27Da), raw data for the 27 Dalton which could be $27Al^{1+}$, $54Fe^{2+}$, or $54Cr^{2+}$. This ambiguity of isotopic overlap requires further resolution, one of the tasks executed by the toolkit. The gallium implanted by FIB milling will also requires resolution by the toolkit

Gibbsian Interfacial Excess of Solute

- Γs, concentration of solute within an infinitesimally small interface, a "Gibbs dividing surface," between two bulk phases of a material
- Atom probe proxigram data is very well suited for this calculation, already binned shells
- Prior formulations require knowledge of area of shell thickness, possible to bypass
- Circumvented *a priori* requisites for ρ using lattice parameter of molecular species and assumption of Bravais crystal lattice structure

$$\Gamma_s = \left(\sum_{n=1}^{N} \frac{(C_n - C_0)}{A_n} \right) / (1 - C_0)$$

$$A_i = \frac{N_i}{\rho \Delta l}$$

Figure 6 . Hellman & Seidman (2002) determined the above formulations that eliminated the need for *a priori* knowledge of slice area, and through dimensional analysis substituted a formula

Conclusions

Confirmation of the ability of toolkit to automate analysis of data in APT

Implementation of calculators for specific thermodynamic quantities

Identifiable room for development in areas dealing with large amounts of data through implementation of optimization algorithms and different data structures

Results and Discussion

- The main application interface and related programs can be found at https://github.com/sakanak/apt-csv-work
- Current algorithms in the application are those written expressly for the sake of automation of manual tasks, with the exception of the calculation software for the Gibbs interfacial excess of solute
- All programs were checked to have complete accuracy through comparison with past files available at the Naval Research Laboratory
- The formulation used for Gibbs interfacial excess relies on estimations made for number density using an assumed lattice parameter and structure - further development could reduce such error as proposed in Krakauer & Seidman et al. (1993) for an APFIM TEM calculation of Gibbsian excess

Further Perspectives

A few tasks for the toolkit currently in development include:

- Optimizing cluster detection
- Generating volume and radii calculations with particle info
- Executing peak detection and automatic ranging and isotope assignment using available isotope abundances table
- Modelling matrix composition to track precipitation as a function of time
- Additional tasks are to be determined

Further implementation of different techniques; one example includes utilizing Ripley's K-function and machine learning to optimize the maximum separation algorithm for cluster detection, while another involves optimizing existing simulations for field evaporation such as TAPSim

Citations

Reddy, S. M., Saxey, D. W., Rickard, W. D. A., Fougerouse, D., Montalvo, S. D., Verberne, R., & van Riessen, A. (2020). *GGR Cutting‐Edge Review Atom Probe Tomography: Development and Application to the Geosciences. Geostandards and Geoanalytical Research.* doi:10.1111/ggr.12313

Lefebvre-Ulrikson, W., Vurpillot, F. & Sauvage, X. (2016). *Atom Probe Tomography*. London: Academic Press.

Kelly, T. F., & Miller, M. K. (2007). *Atom probe tomography. Review of Scientific Instruments, 78(3), 031101*. doi:10.1063/1.2709758

Tamura, M., Shukuri, S., Moniwa, M., & Default, M. (1986). *Focused ion beam gallium implantation into silicon. Applied Physics A Solids and Surfaces, 39(3), 183–190*. doi:10.1007/bf00620733

Dhara, S., Marceau, R. K. W., Wood, K., Dorin, T., Timokhina, I. B., & Hodgson, P. D. (2018). *Atom probe tomography data analysis procedure for precipitate and cluster identification in a Ti-Mo steel. Data in Brief, 18, 968–982*. doi:10.1016/j.dib.2018.03.094

Vincent, G. B., Proudian, A. P., & Zimmerman, J. D. (2020). *Three dimensional cluster analysis for atom probe tomography using Ripley's K-function and machine learning. Ultramicroscopy, 113151*. doi:10.1016/j.ultramic.2020.113151.

Kühbach, M., Breen, A., Herbig, M., & Gault, B. (2019). *Building a Library of Simulated Atom Probe Data for Different Crystal Structures and Tip Orientations Using TAPSim. Microscopy and Microanalysis, 1–11*. doi:10.1017/s1431927618016252

Knipling, K. E., Narayana, P. U., & Nguyen, L. T. (2017). *Microstructures and Properties of As-Cast AlCrFeMnV, AlCrFeTiV, and AlCrMnTiV High Entropy Alloys. Microscopy and Microanalysis, 23(S1), 702–703*. doi:10.1017/s1431927617004172

Perea, D. E., Liu, J., Bartrand, J., Dicken, Q., Thevuthasan, S. T., Browning, N. D., & Evans, J. E. (2016). *Atom Probe Tomographic Mapping Directly Reveals the Atomic Distribution of Phosphorus in Resin Embedded Ferritin. Scientific Reports, 6(1)*. doi:10.1038/srep22321

Hellman, O. C., & Seidman, D. N. (2002). *Measurement of the Gibbsian interfacial excess of solute at an interface of arbitrary geometry using three-dimensional atom probe microscopy. Materials Science and Engineering: A,* 327(1), 24–28. doi:10.1016/s0921-5093(01)01885-8

Krakauer, B. W., & Seidman, D. N. (1993). *Absolute atomic-scale measurements of the Gibbsian interfacial excess of solute at internal interfaces. Physical Review B,* 48(9), 6724–6727. doi:10.1103/physrevb.48.6724

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