KherveFitting Help Guide

Contents

Copyright

Authors

Dr. Gwilherm Kerherve, Elwen Kerherve (colors) & William Skinner, Department of Materials, Imperial College London, g.kerherve@imperial.ac.uk.
The software was tested by Mark A. Issacs (HarwellXPS), Arthur Graf (HarwellXPS), Benjamin Reed (NPL) and David J. Morgan (HarwellXPS)

Overview

KherveFitting, see Fig. 17, is an open-source software developed in Python, using wxPython for the graphical user interface, MatplotLib for data visualization, NumPy and lmfit for numerical computations and curve fitting algorithms, and Panda for manipulating Excel files.
It is aimed at users who want to analyse single or multiple samples with multiple core levels, perform automated batch fitting, depth profiling, and advanced statistical analysis including PCA. KherveFitting is designed to be elegant and simple to use.

Note

KherveFitting is currently under heavy improvements and so some of the Figures shown here does not correspond to the current version and are from a previous version. After version 2.0, the software should have found its permanent look and feel.
The name Kherve is short in Britanny language (Celtic part of France) for Kerherve.

Installation Instruction

Note: To keep the software free of charge, no signing certificate or security key was purchased. All executable files and scripts are delivered unsigned.

1. Windows (Installer)

- Start the KherveFitting launcher.
- Approve to execute the unsigned software
- Choose the File location. Do not choose the Program Files location as it would require to be administrator to run.
- Do not run under administrator as the drag and drop function would not work.

2. Windows (Binary file from the Beta folder)

- Make sure you had previously downloaded and installed KherveFitting from the installer mentioned in section above.
- Copy this new executable in the KherveFitting folder.

3. MacOS

- Drag the KherveFitting app to your Applications folder.
- Double-click the remove quarantine.command script.
- NOTE: When you try to open the script, macOS may show a security warning:

  If it says "cannot be opened because it is from an unidentified developer" Right-click (or Control-click) the script and select "Open".

  If a second warning appears, click "Open" to confirm - If completely blocked, go to System Preferences>Security & Privacy Look for a message about the blocked script and click "Open Anyway".

  The script will remove security restrictions from KherveFitting.

- Launch KherveFitting from your Applications folder (You may need to right-click and select "Open" the first time).

Why is this needed? - This application is free and so it does not have a security key. - macOS applies security restrictions to applications downloaded from the internet. The helper script safely removes these restrictions for K herveFitting only.
Note: A beta version is also available under the same Beta folder as Windows OS.

Getting Started

1. Instrument Settings

Before starting the analysis, ensure that you select the correct sensitivity factor for the instrument used to measure the data. This can be found in *Edit* → *Preferences* → *Instrument Settings*, highlighted in red in Fig. 1. The following configurations are required for some instruments:

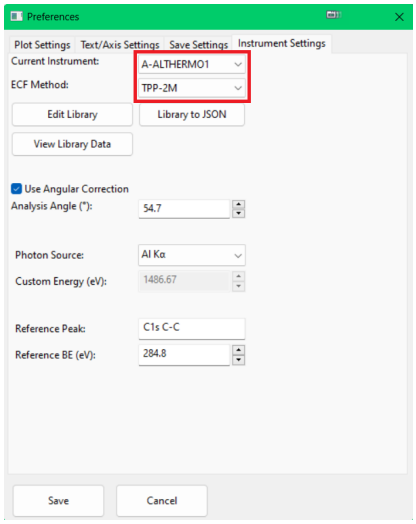


Figure 1: Instrument settings tab in the Preferences window.

- **General settings:** C-Al1486 and TPP-2M
- **Thermo Kalpha and Nexsa:** A-ALTHERMO1 and TPP-2M
- **Kratos (new instrument):** C-KRATOSF1S - Al1486 and TPP-2M
- **Kratos (older instrument):** C-KRATOSC1S - Al1486 and TPP-2M

Depending on your instrument, the angle from the X-ray source to the analyzer can also be adjusted, with the default value being the magic angle (54.7°). The Doublet Splitting (DS) values are stored in C-Al1486 and used for all instruments.

2. Open Files

Drag the XPS file (.xlsx, .vms, .kal, .spe) into the plot area. If the file is not in KherveFitting format, the program will create an Excel file in the correct format. Transmission data will also be exported, and raw data will be corrected, as shown in Fig. 2.
As an example, drag the file named "STO.xlsx" located in *KherveFitting* → *Data*. Using the middle mouse button, sroll to the Sr3d core level. This file shows XPS data obtained on a $SrTiO_3$ thin film on a XPS Thermo Kalpha. Make sure you have selected the RSF A-ALTERMO01 from the preference window.

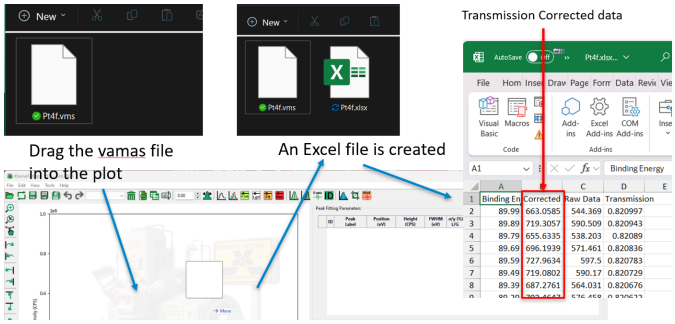


Figure 2: Opening a file: Example of a Vamas file.

Supported File Formats

KherveFitting supports importing data from a wide variety of instruments and file formats:

- **KherveFitting native:** Excel (.xlsx) with JSON metadata
- **Thermo Scientific:** Avantage Excel (.xlsx), AVG files (.avg)
- **Thermo Scientific VGD:** VGD files (.vgd)
- **VAMAS:** Standard format (.vms)
- **Kratos:** KAL files (.kal)
- **PHI/ULVAC-Phi:** SPE files (.spe)
- **Scienta:** Scienta files, Scienta Maps
- **Igor Pro:** .dat and .itx files
- **VG Microtech:** Multiple format support
- **Generic formats:** CSV, ASC (Surface Science Spectra)
- **Raman:** TXT files
- **XAS:** Diamond B07 beamline format

Multiple files can be imported simultaneously using the Import menu or by dragging and dropping multiple files onto the plot canvas.

3. Plot and Core Level Control

To familiarize yourself with KherveFitting, it is important to learn the different shortcuts. Scroll down the mouse button to switch between different core levels. Alternatively, use `Ctrl+[` or `Ctrl+]`. Pressing the `Ctrl` key allows you to change plot properties. Below is a list of the most useful shortcuts:

1. **`Ctrl+Left` or `Ctrl+Right`:** Move left or right along the X-axis.
2. **`Ctrl+Up` or `Ctrl+Down`:** Zoom in or out along the Y-axis.
3. **`Ctrl+"+"` or `Ctrl+"-"`:** Zoom in or out along the X-axis.
4. **`Ctrl+Shift+Left`:** Zoom in and out along the X-axis while keeping the Low BE minimum constant.

Alternatively, you can zoom in and out using the right-click menu or the zoom toolbar.

4. Prepare for Peak Fitting

Press the peak fit icon to open the peak fitting window. The fitting window (see Fig. 3) consists of two tabs: *Background* and *Peak Fitting*. Select the *Background* tab to create a background. The default method, *Multi-Regions Smart*, is suitable for most fitting applications.
To create peaks, select the *Fitting* tab. The default fitting method is *least squares*, which is appropriate for most models. The default fitting model is the product of Gaussian and Lorentzian GL(Area), a simple model useful for users new to XPS. However, the recommended fitting model is *Voigt (Area, L/G, σ)*, as it is the most physically meaningful. The *LA (Area, σ/γ, γ)* model lacks physical meaning but is familiar to users experienced with CasaXPS.

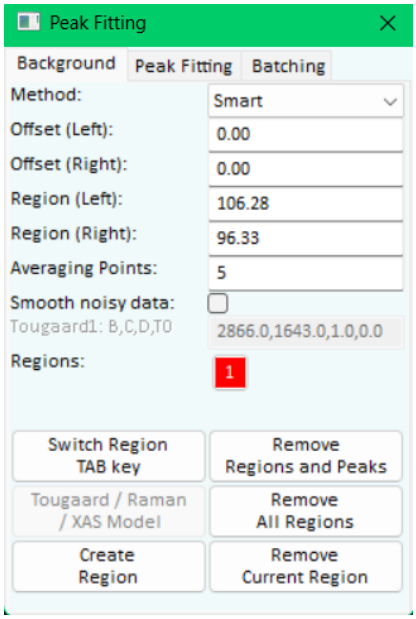


Figure 3: Peak fitting screen (KherveFitting v1.4).

5. Create a Background

To create a background, click on the left side (high BE) and right side (low BE) of the plot, ideally in a flat region about 1-2 eV away from the peaks. Press the *Create*

Region button. When using *Smart* or *Shirley*, it will generate a Shirley background between the two vertical lines and a region noted '1' will be created, see Fig. 4.

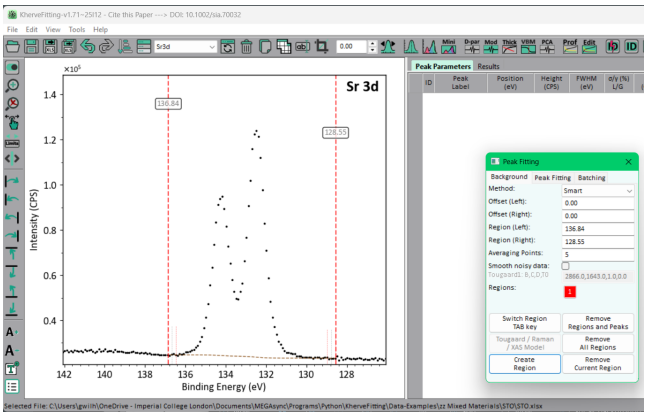


Figure 4: Create a Shirley background.

6. Create a Peak Model

Press the peak fitting tab of the peak fitting window. The fitting model is set by default to the SGL model. In this case, the Sr3d core level is composed of two peaks (doublet) of width (FWHM) around 1 eV split by about 1.7 eV. Press the `Add 2 Peaks` button 5. This will create 2 peaks namely A and B where peak B is linked to peak A with the following characteristics:

- `Position of` $A + 1.7\#0.2$`:` Peak B will be spaced 1.7 eV away from peak A with a possible variation of $\pm$ 0.2 eV.
- `FWHM of` $A \times 1$`:` The width or FWHM of peak B is fixed to the one of peak A. No variation is given here.
- `Area of` $A \times 0.667\#0.05$`:` The area of peak B is constrained to the one of peak $A \times 0.667$ or /1.5 with a possible variation of $\pm$ of 0.05. In a d shell, the number of electrons in the 5/2 shell is 6 and the number of electrons in the 3/2 shell is 4 so the ratio is therefore 0.667.

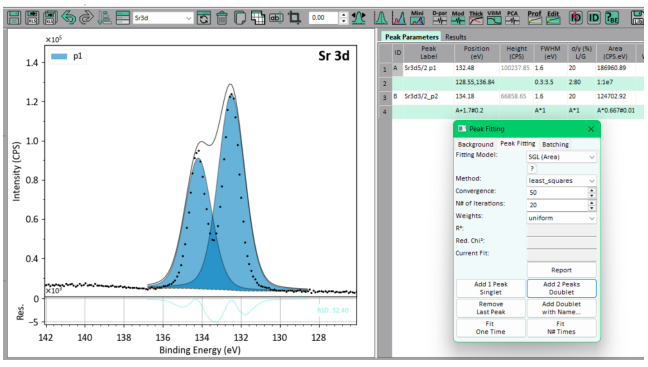


Figure 5: Add two SGL peaks.

7. Fit the Peak Model

Press the `Fit N# times` button and wait for the 20 iterations to complete, see Fig. 6. Once the fit complete, The Residual standard deviation (RSD) is around 2.0-3.4 which is acceptable for a SGL model. The results show that the peaks have a FWHM of around 1.0 eV and a L/G ratio of about 62%.

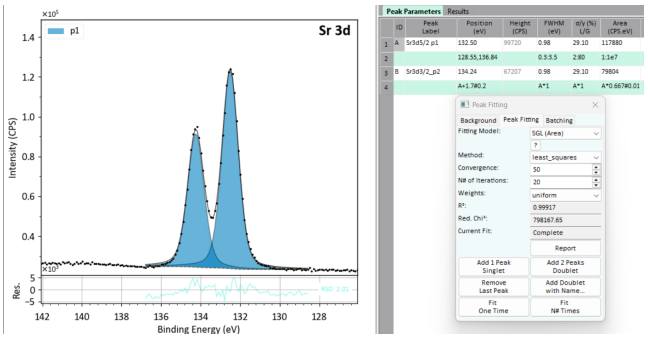


Figure 6: Fit two SGL peaks.

Please note that the L/G ratio changes with the width of the peak. A sharper peak will tend to be more Lorentzian while a wider peak would tend to be more Gaussian. It is not advisable to keep the peak shape to 30%

8. Move the Peak Model

Use `Tab` or `Q` to select the peak A. When a peak is selected, the label is on top of the peak. drag peak A by pressing the left mouse button and with the mouse on top of the cross, see Fig. 7. Note that the peak B moves with peak A as it is constrained to A with position and area. Dragging peak B moves only peak B. You can also drag the peaks by pressing the `Alt` key + `Left` or `Right` or `Down` or `Up`

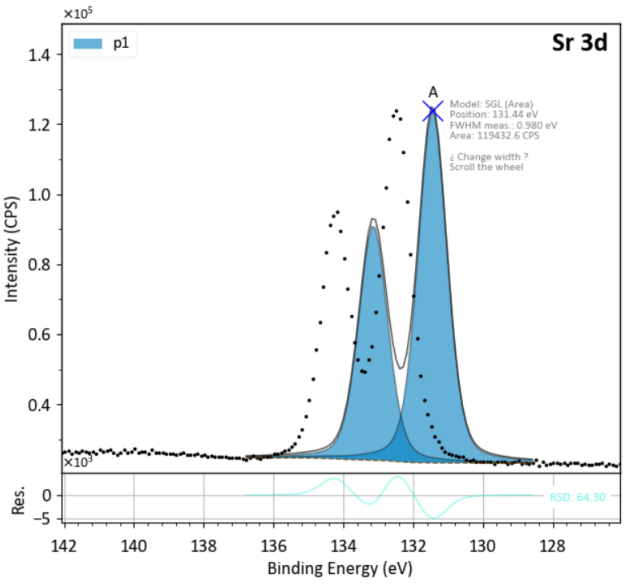


Figure 7: Drag the doublet.

9. Other Models

Press the `Remove Last Peak` button twice to remove the two SGL peaks. Select The LA (Area, σ/γ, γ) model and press the `Add 2 Peaks` button where two LA peaks are created. Press the `Fit N# times` button. Note that the RSD is around 1.8-2.4 which is lower than for the GL model. In contrast to the GL model, the LA model is a full Lorentzian model that is powered on the right side by γ and on the left side by σ. The bigger the power, the more gaussian is the model. Fig. 8 shows the peak fitting grid obtained after fitting the Sr3d. The value for σ and γ gives the shape of the peak and are optimised during the fit. A value of σ/γ of 50% ($\sigma = \gamma$) represents a fully symmetric peak (default value). A value of σ/γ of less than 50% is an asymmetric peak. Fit the `Pt4f file` if you wish to fit assymetric LA.

	ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ W_g	γ W_l
1	A	Sr3d5/2 p1	132.49	100737	0.96	50.00	111374	3.13	3.13
2			126.08,142.08		0.3:3.5	Fixed	1:1e7		0.01:10
3	B	Sr3d3/2 p2	134.24	69317	0.96	50.00	76884	3.13	3.13
4			A+1.7#0.2		A*1	A*1	A*0.667#0.05		A*1

Figure 8: Peak fitting grig for the LA model.

Press the `Remove Last Peak` button twice to remove the two LA peaks. Select The Voigt (Area, L/G, σ) model and press the `Add 2 Peaks` button where two Voigt peaks are created. Press the `Fit N# times` button. Note that the RSD is around 2.9-3.1 which is lower than for the GL model. In contrast to other models, the FWHM of the model cannot be changed or constrained. Instead, the user can control and constrain the Gaussian width part of the peak as well as its L/G ratio. The Lorentzian width is then calculated from the L/G ratio. This allows the user to constraint the L/G ratio to other peak. It has to be noted that:

- A peak with a FWHM of 1.0 to 1.5 eV leads to a L/G ratio around 20%.
- A peak of width above 1.5 eV leads to a L/G ratio between 10-20%.
- A peak of width below 1.0 eV leads to a quick increase of the L/G ratio from 20% to 50-60%.

Fig. 9 shows the peak fitting grid obtained after fitting the Sr3d. The value for W_g and W_l are the width of the Gaussian and Lorentzian, respectively. The column with grey values are for indication only and cannot be changed while the one in black can be changed.

	ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ W_g	γ W_l
1	A	Sr3d5/2 p1	132.49	99246	0.98	25.28	116321	0.82	0.28
2			126.08,142.08			2:80	1:1e7	0.01:3	
3	B	Sr3d3/2 p2	134.24	67847	0.99	26.37	80466	0.82	0.29
4			A+1.7#0.2			A*1	A*0.667#0.05	A*1	

Figure 9: Peak fitting grig for the Voigt model.

Repeat the same fitting process using the Voigt model on Ti2p, see Fig. 11. Note that when adding a doublet for Ti2p or V2p, KherveFitting does not constrain the FWHM of peak B with peak A, as for an oxide the width of $Ti2p_{1/2}$ is wider than that of $Ti2p_{3/2}$ due to the kœster kronig effect.

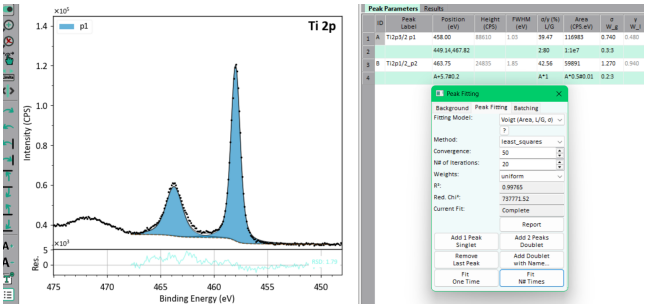


Figure 10: Fit of Ti2p using the Voigt model.

10. Export to Results Grid

The comparison between different core level in term of atomic concentration can be done in the Results grid. Note that the correct RSF library and method needs to be selected prior to this process. To export to the Results grid, Press the `Export` icon in the toolbar. Export Ti2p and Sr3d data into the Results grid. Tick the $Ti2p_{3/2}$ and the $Sr3d_{5/2}$ and see Fig. 11 for the example.

	Peak Label	Position (eV)	FWHM (eV)	Area (CPS.eV)	Atomic (%)		RSF	TXFN	ECF	Instr.	Norm. Area An (a.u.)
1	Ti2p3/2 p1	458.00	1.03	113274.80	53.84	☑	4.42	1.0	TPP-2M	A-ALTHERMO1	404.75
2	Ti2p1/2 p2	463.74	1.97	61769.81	0.00	☐	2.06	1.0	TPP-2M	A-ALTHERMO1	476.14
3	Sr3d5/2 p1	132.50	0.98	115384.40	46.16	☑	4.25	1.0	TPP-2M	A-ALTHERMO1	346.85
4	Sr3d3/2 p2	134.24	0.99	79363.51	0.00	☐	2.93	1.0	TPP-2M	A-ALTHERMO1	346.62

Figure 11: Results grid showing the atomic concentration of $Ti2p_{3/2}$ against $Sr3d_{5/2}$

Note that the results grid is still under development and sometimes the tick does not refresh. A simple solution is to click on the plot and the correct tick state is shown.

11. Load a Peak Table

Peaks table can be saved as a .json file to be re-used. Scroll down to C1s and press the `Load Peaks Parameter` icon on the right of the horizontal toolbar. Select the

`C1s_C-C_4peaks_Voigt_GK_xxxx.json` peak table, see Fig. 13. Note that 4 peaks have been created in the peak fitting grid.

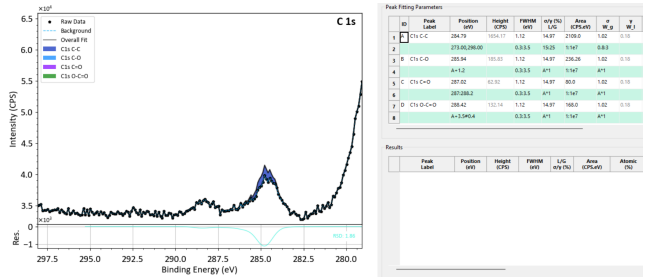


Figure 12: Loading of the C1s peak table using the Voigt model.

The background needs to be created next. Go onto the background Tab and place the vertical lines 1-2 eV away from the peaks. Press on `Create Region` and a Shirley background is created. Next go back to the Peak Fitting tab and press `Fit N# times`. C1s should be fitted with a RSD of about 1 eV.

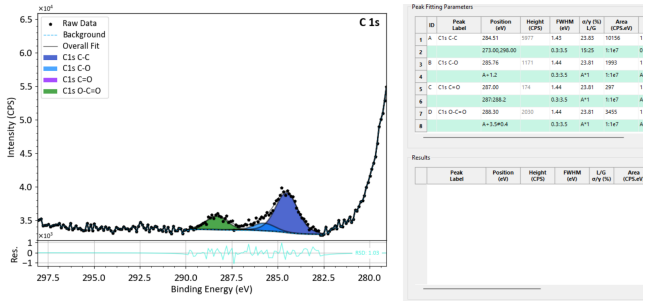
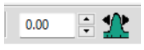


Figure 13: Final result of the fitted C1s core level.

Repeat the same process for the O1s core level but this time using the `O1s_O-Lat_3peaks_Voigt_GK_xxxx.json`. Set the background between 527.3 eV and 535 eV. Note that the O-surf peak is almost insignificant and can be removed from the peak table.

12. Binding Energy Correction



KherveFitting looks by default for a peak called `C1s C-C` and calculate the difference between the current peak position and 284.8 eV. Note that this can be changed in the Preferences window under Instrument Settings. Press the green peak as shown above and take note of the new corrected value of around 0.29 eV. Now all the peaks in the Peak Fitting grid and in the Results grid have shifted by +0.29 eV. The binding energy correction can be reversed by writting 0.00 in the Numeric control shown above and by clicking on the plot.

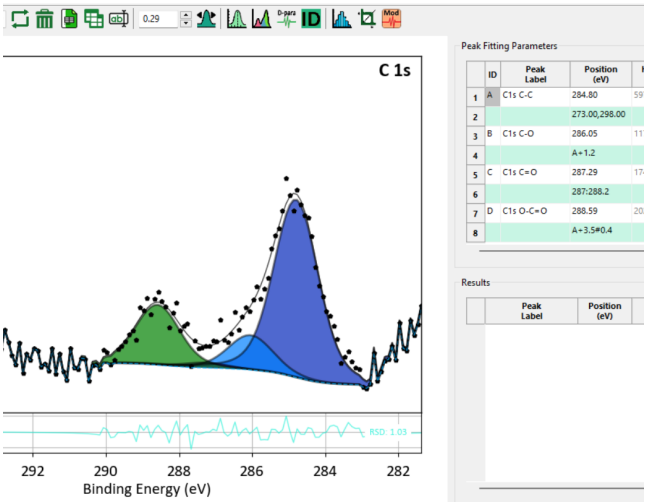


Figure 14: C1s core level corrected to C-C at 284.8 eV.

13. Background Offset

KherveFitting allows to offset the background by mouse control. Scroll down to O1s core level. Zoom down (`Ctrl+Down`) to the background level. You should get to a plot similar to Fig. 15

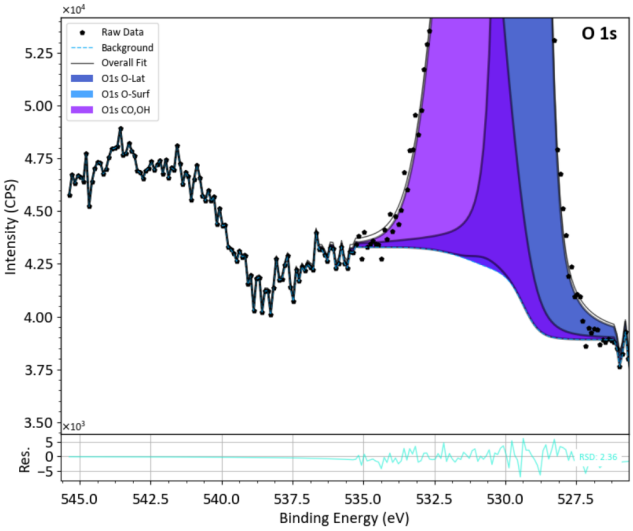


Figure 15: O1s core level zoomed down to background level.

Go on the Background tab and make sure the Vertical Lines are reset by pressing on `Reset Vertical Lines` button. Select a range between 527.3 and 537.5 eV, then press `Shift` and hold the background at high binding energy and shift it down as per Fig. 16

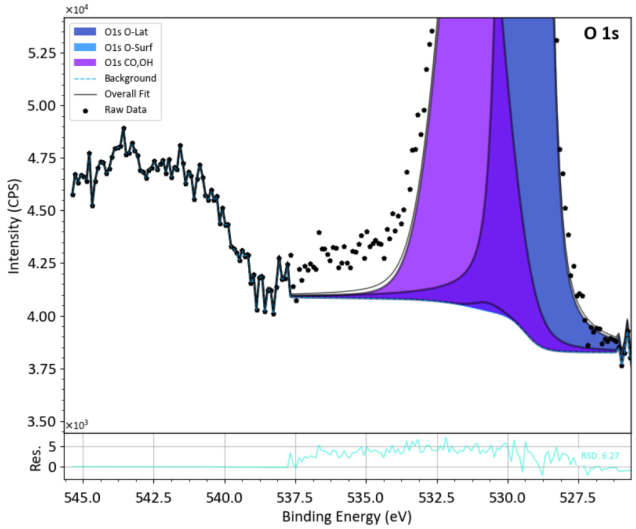


Figure 16: O1s core level zoomed down to background level.

In more details

The software interface (Fig. 17) features three main sections: a plot area on the left showing spectral data, a peak parameter grid on the upper right for adjusting fitting parameters, and a results grid on the lower right displaying calculated values. Two toolbars provide quick access to essential functions. The horizontal toolbar includes tools for opening files, selecting spectra, adjusting plot components, fitting peaks, calculating noise, identifying elements, and exporting results. The vertical toolbar allows easy adjustment of the plot's x- and y-axis limits.

Process Worklow

The software workflow follows a structured process for XPS data analysis (Fig. 18). Users start by importing data through either drag-and-drop functionality or the open button, with automatic conversion of various file formats to the KherveFitting Excel format.

After loading the data, users select specific spectra using the mouse wheel or dropdown menu. The software offers two main analysis paths: element identification for survey spectra through a periodic table interface accessed via the "ID" button, or peak fitting for narrow scans to identify chemical states and determine sample composition.

For survey spectra, the periodic table displays binding energies and intensity ratios for each element. A practical example is shown in Figure 19, featuring a hard carbon survey scan with identified elements and their characteristic peaks.

When creating a peak model, the peak fitting window first prompts the fitting of a background over a selected range, with models that currently include linear, Shirley , Smart and Tougaard. Further details of each of these methods are included in the Background Models section.

After establishing the background, users can create peaks of varying shapes and configurations. The software offers multiple peak models based on Gaussian-Lorentzian combinations, optimized for XPS data analysis. Common models include GL, SGL, Voigt, LA, and DS functions, with detailed descriptions provided in the Peak Models section of the manual.

The peak parameter grid (Fig. 23) enables interactive adjustment of peak properties and constraint settings. Parameters like position, area, LG ratio and FWHM can be modified either through grid inputs or by direct peak manipulation using click-and-drag operations.

Fitting is performed using the variety of fitting algorithm via the LMFIT Python library [1]. Fit quality indicators (R^2, reduced Chi^2) appear in the parameter grid, while RSD values are shown in the residual plot. Users can refine fits through manual adjustments or by adding/removing peaks, with undo/redo functionality supporting experimental flexibility.

The process can be repeated across multiple core levels within a file. Binding energy correction is available through either manual adjustment or automatic detection of reference peaks (default: C1s C-C at 284.8 eV), with customisable reference values in the preferences screen.

Final analysis includes atomic concentration calculations using Scofield sensitivity factors with additional correction factors as detailed in the Theoretical background section.

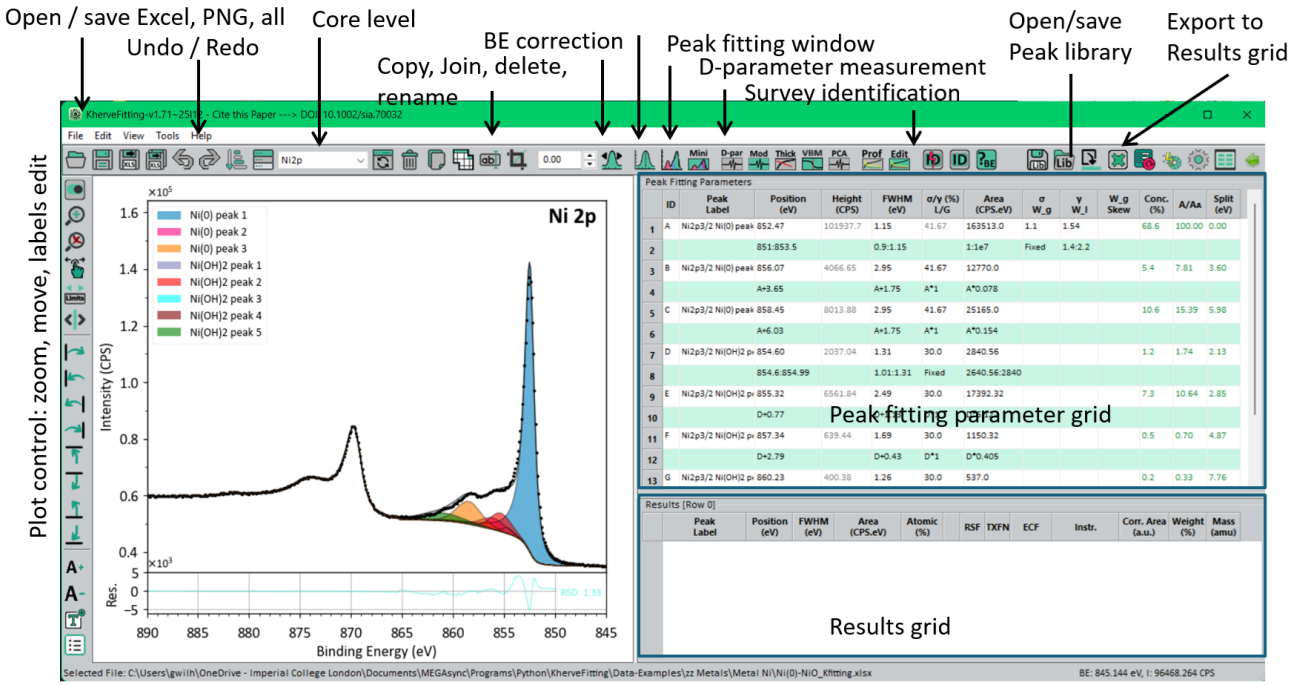


Figure 17: KherveFitting interface showing peak fitting parameters, constraints, quantitative results, and plot controls.

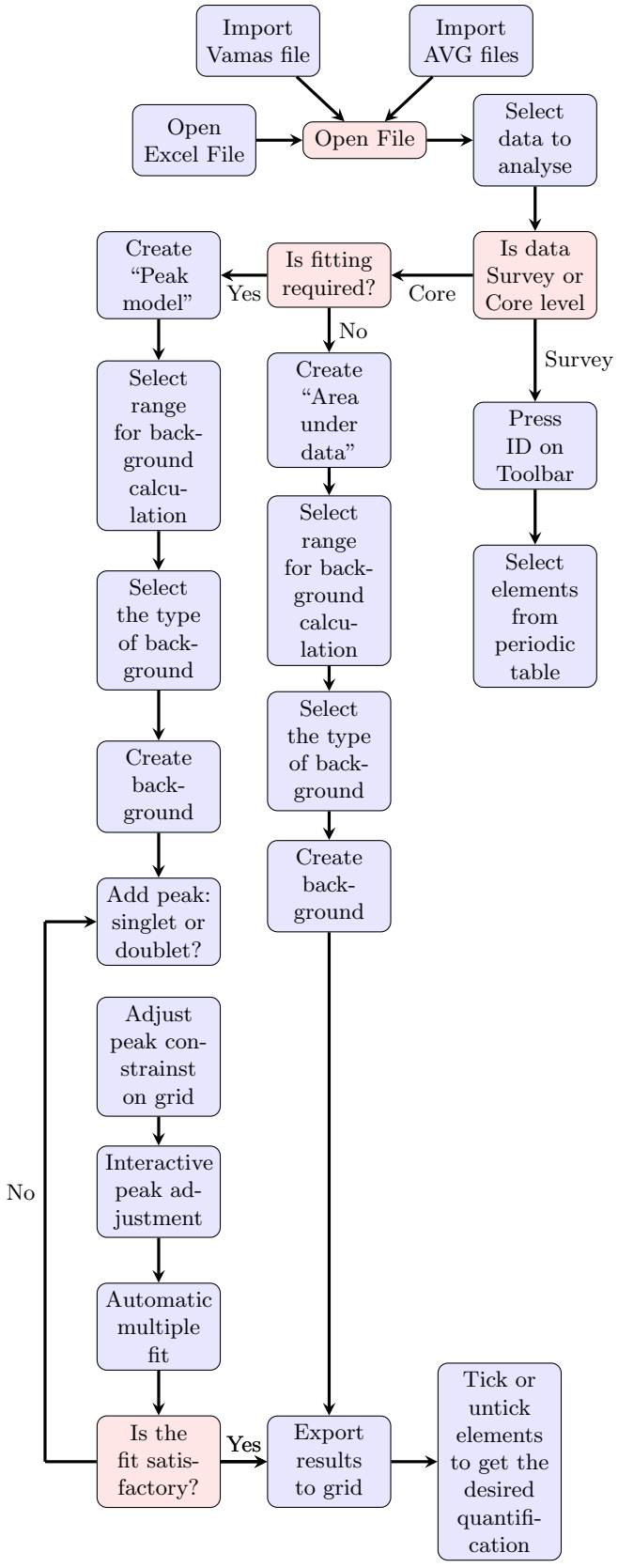


Figure 18: Workflow to analyse XPS data using KherveFitting

Results are exported to the grid (Fig. 24) and saved in Excel format for compatibility with other software platforms.

Opening Files

KherveFitting can open Excel files (.xlsx) and import/convert Avantage Excel (.xlsx), VAMAS (.vms), Kratos (.kal), Thermo (.avg) and Phi (.spe) files and Avantage files into Excel format. For best results:

- Place raw data (X,Y) in Columns A and B, starting at row 0
- Use the row offset control in the horizontal toolbar if needed
- Save each core level in a separate sheet named after the core level. Do not use white spaces, e.g. Si2p, Al2p, C1s, O1s.

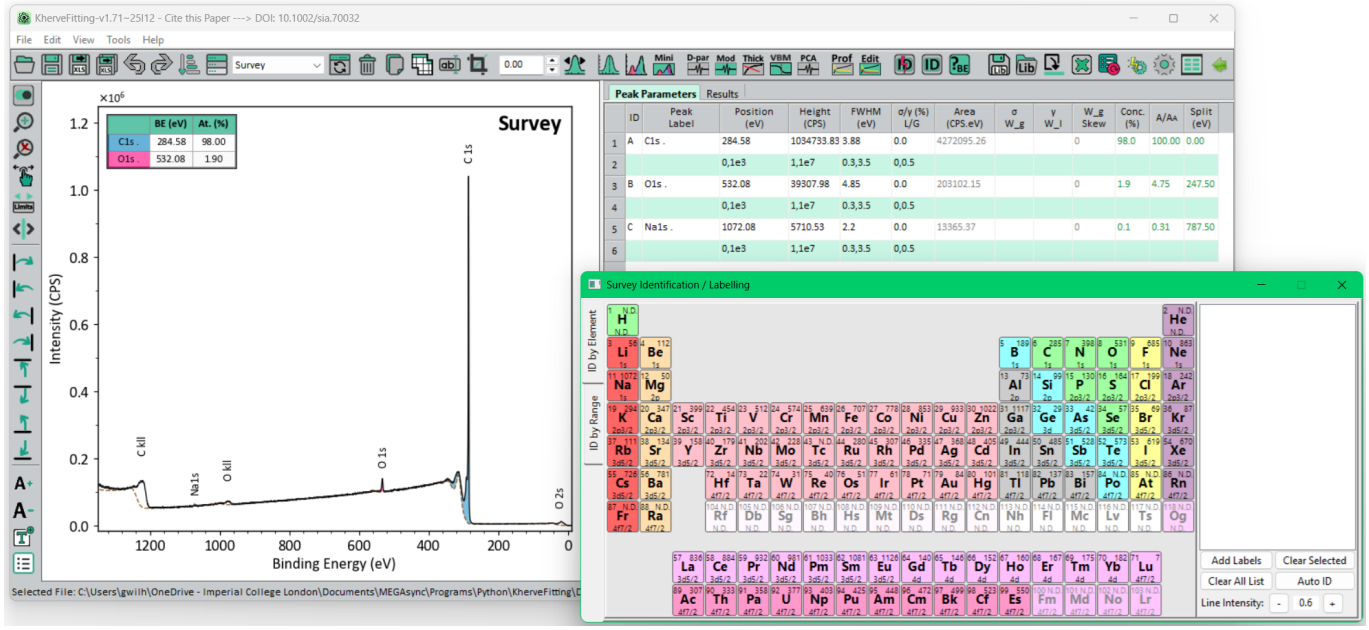


Figure 19: Survey spectrum of a hard carbon sample showing the presence of O, C and Na. KherveFitting allows the labeling and the measurement of each species.

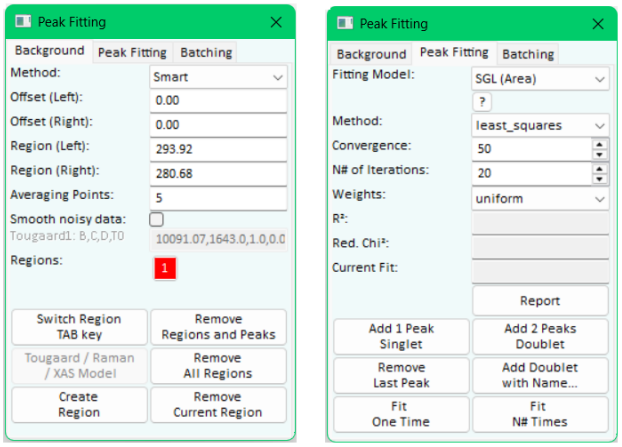


Figure 20: Representation of the Fitting screen window consisting of the background tab (left) and the fitting tab (right).

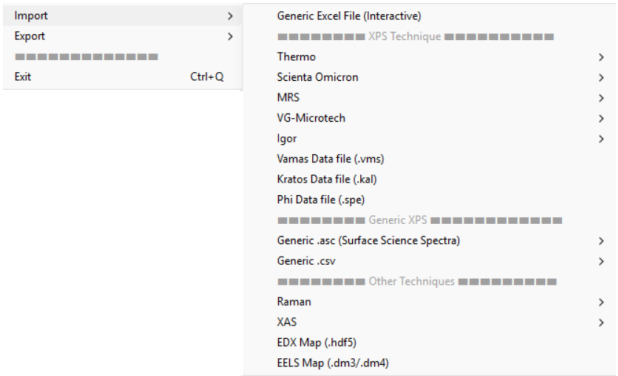


Figure 21: Import File Menu.

When reopening a saved fitting, KherveFitting also looks for a JSON file of the same name containing all the required properties.

KherveFitting also supports drag and drop functionality for opening files. Users can simply drag and drop KherveFitting or Avantage Excel (.xlsx), VAMAS (.vms), Kratos (.kal), Thermo (.avg or .vgd) and Phi (.spe) files directly onto the plot canvas, and the software will automatically open and process the files. This convenient feature allows users to quickly import data without having to navigate through file menus or dialogs. KherveFitting will detect the file type and handle the appropriate opening and conversion process, making the data immediately available for analysis. The drag and drop functionality applies to both single files and multiple files. Users can select one or more Excel or VAMAS files and drop them onto the canvas to have them all loaded and processed by KherveFitting.

Saving Files

KherveFitting offers three saving options:

1. Save corrected binding energy, background, envelope, residuals, and fitted peak data of the active core level to columns Donwards in the corresponding json file. No Excel sheet is saved at this point.

2. Save the Excel sheet and the figure of the active core level to the corresponding Excel sheet and as a PNG file.

3. Save all fitted core level data, including figures, to the Excel file. Peak fitting properties for all core levels are saved in a JSON file.

Plot Window

Vertical Toolbar:

The vertical toolbar located on the left side of the plot window provides essential plot manipulation tools:

Zoom Tools

-  Zoom In: Click to enable zoom mode, then drag to select area
-  Zoom Out: Returns to full view
-  Drag: Enables plot panning

Binding Energy Controls

-  High BE adjustment
-  Low BE adjustment

Intensity Controls

-  High intensity adjustment
-  Low intensity adjustment

Text Controls

-  Increase font sizes
-  Decrease font sizes

Toggling Display Elements

Use toggle buttons to show or hide various plot elements:

- Raw data points
- Background line
- Individual fitted peaks
- Overall envelope
- Residuals
- Legend

Keyboard Controls for Plot Manipulation

XPS spectra manipulation and peak fitting can be efficiently controlled through keyboard shortcuts:

Peak Navigation and Selection

- Tab/Q: Navigate through peaks (next/previous)
- Alt+Arrow keys: Adjust selected peak
- Alt+Up/Down: Increase/decrease Peak intensity
- Alt+Left/Right: Move peak position to higher/lower BE
- Alt+Shift+Left/Right: Increase/decrease peak FWHM
- Shift+scroll wheel: Drag to adjust FWHM

Plot Navigation

- Ctrl+[or]: Switch between core levels (previous/next)
- Ctrl+Up/Down: Adjust plot intensity scale
- Ctrl+Left/Right: Shift plot to higher/lower BE
- Ctrl+Plus/Minus: Zoom in/out
- Shift+Left/Right: Adjust high BE range

General Controls

- Ctrl+Z/Y: Undo/Redo (up to 30 events)
- Ctrl+S: Save (grid data only)
- Ctrl+P: Open peak fitting window
- Ctrl+A: Open area calculation window
- Ctrl+K: Display keyboard shortcuts

Plot Preferences

The plot preferences window, see Fig. 22 provides comprehensive control over the visual appearance of XPS spectra through three main tabs. The Plot Settings tab is the primary interface for customizing data visualization. Use the Preferences window to customize the plot appearance, including:

- Colors for raw data, background, fitted peaks, and residuals
- Line styles (solid, dashed, dotted)
- Marker types for data points
- Font sizes and styles
- Axis labels and titles

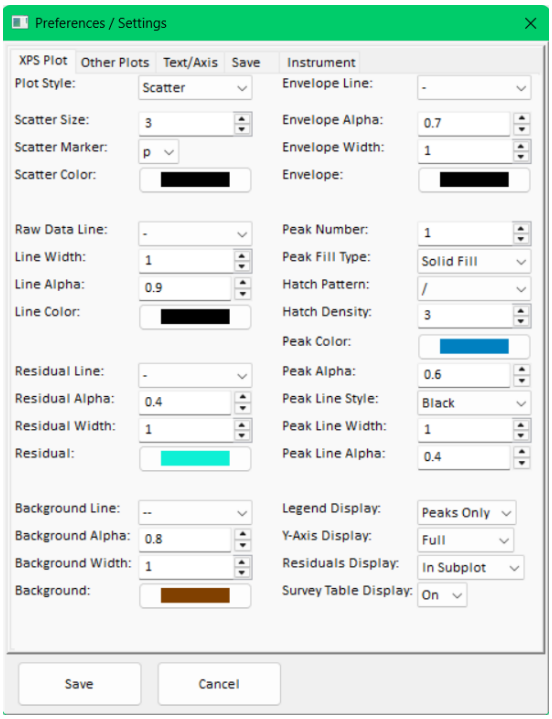


Figure 22: The preference window under the plot settings tab

- Instrument settings with various RSFs and ECF methodologies

Plot Settings Tab

`Raw Data Display:` Raw XPS data can be displayed either as scattered points or continuous lines. In scatter mode, customize point size (1-50), marker style (circle, square, triangle, diamond, or star), and color. Line mode offers width control (1-10 pixels) and transparency adjustment through the alpha parameter (0-1). These options allow clear visualization of experimental data points while maintaining a clean presentation.

`Peak Display:` Fitted peaks can be represented with either solid fills or customizable hatch patterns. The hatch density (1-10) controls pattern spacing, while peak transparency is adjusted via the alpha parameter (0-1). Peak outlines can be hidden, colored (black, same as fill, grey, or yellow), with adjustable thickness (1-5 pixels) and transparency. These options enable clear differentiation between multiple peaks while maintaining visual clarity.

`Component Display:` Additional spectral components - background, envelope, and residuals - each have customizable line styles and colors. The background can be shown as solid, dashed, or dotted lines with adjustable color and opacity. The envelope (overall fit) and residuals follow similar customization options, allowing for clear visualization of fit quality and individual spectral components.

Text/Axis Settings Tab: This is the Settings for fonts, axis labels, and tick marks

Instrument Settings Tab: These are the XPS instrument-specific parameters.

Peak Fitting Grid

The peak fitting grid displays parameters for each fitted peak across two rows - one for values and one for constraints. The primary visible columns include: Peak ID (A, B, C...), Peak Label, Position (eV), Height (CPS), FWHM (eV), σ/γ ratio or L/G ratio (%), Area (CPS.eV), σ, γ, Skew. Additional columns, including the fitting model, background parameters, and offset values, are hidden by default but can be displayed using the Toggle Column button in the toolbar. Cell colors indicate editable parameters (white) versus derived values (gray) for different fitting models. The grid automatically updates when peaks are modified through direct plotting manipulation.

`Constraints:` Constraints can be specified numerically (e.g. "0.3:3.5" or "0.3,3.5") or relative to other peaks from the same peak fitting grid (e.g. "A*0.667" or "A/1.5"). Variance can be inserted to allow the linked peak to move around the set value (e.g. "A*0.667#0.01"). To fix a peak to a known value "fi" or "Fixed" can be inserted. A list of known nomenclature is shown below:

- 'a', 'b', 'c' → 'A*1', 'B*1', 'C*1' (follow peak A, B, or C)
- 'fi' or 'fix' or 'fixe'→ 'Fixed'
- '#0.5' → Variance to ±0.5 eV
- Allowed nomenclature: A*1.5, A/1.5, A+1.5, A-1.5, A*1.5#0.01, #0.1, 'fi'

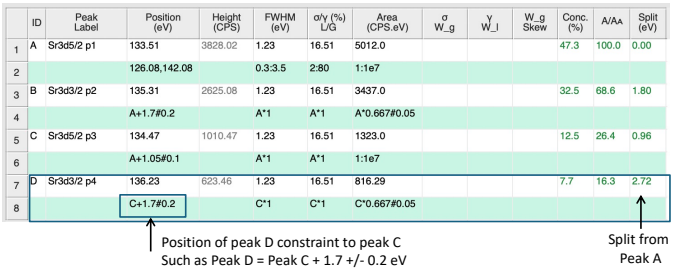


Figure 23: Peak Fitting grid. The atomic concentration shows almost a 1 to 1 to 3 ratio between Sr, Ti and O.

Results Grid

The results grid provides a summary of all fitted peaks across all core level spectra. Each row represents one peak with columns for: Peak Label, Position (eV), Height (CPS), FWHM (eV), L/G ratio (%), Area (CPS.eV),

Atomic (%), selection checkbox, RSF value, fitting model, relative area, model-specific parameters (σ, γ), background type and range, sheetname, and peak constraints. Peak selection via checkboxes enables atomic percentage calculations based on peak areas normalized by RSF values.

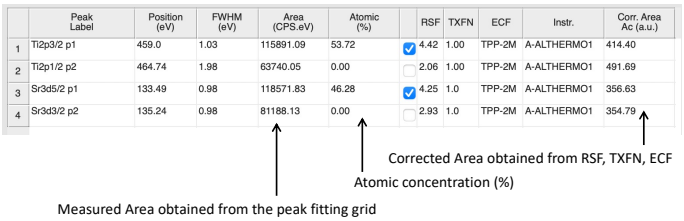


Figure 24: Results grid after the fitting of the Sr3d and Ti2p of $SrTiO_3$ crystal. The atomic concentration shows almost a 1 to 1 ratio between Sr and Ti.

New peaks can be added into the Results Grid by pressing the "Export to Results Grid" Icon.

Sample Manager

The Sample Manager in KherveFitting provides an intuitive interface for organizing, visualizing, and manipulating multiple core level spectra across different samples. This tool simplifies data management for complex datasets and enables efficient comparative analysis of XPS data, see Fig 25.

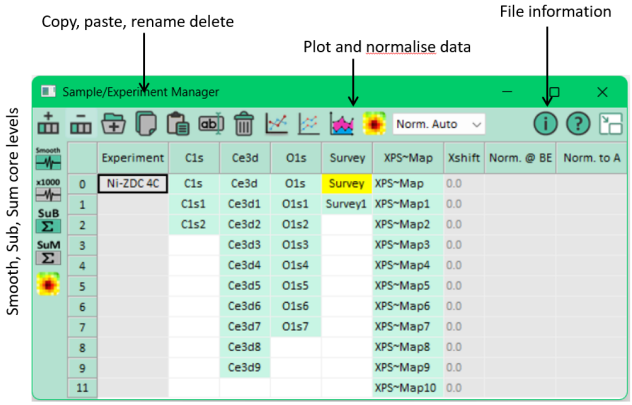


Figure 25: Representation of the Sample manager window. The samples loaded in the manager are CeO2 with narrow scans C1s, O1s, Ce3d and wide scans.

Accessing the Sample Manager: The Sample Manager can be accessed through the main toolbar or via the menu system:

- Click the Sample Manager icon in the toolbar
- Alternatively, select "Tools → Sample Manager" from the menu

Interface Overview: The Sample Manager presents spectra in a grid format where:

- Rows represent samples or experiments (numbered 0, 1, 2, etc.)
- Columns represent different core levels (C1s, O1s, etc.)
- Cells contain the sheet names for individual spectra

Additional columns provide critical functionality:

- Experiment: Labels for sample groups or experimental conditions
- Xshift: Binding energy correction values for each sample row
- Norm. @ BE: Binding energy value for intensity normalization
- Norm. to A: Area normalization factor

Basic Functionality: The Sample Manager supports the following operations:

`Sample Organization`

- Add rows: Add 10 additional rows to accommodate more samples
- Delete rows: Remove the last two rows when needed
- Sort sheets: Reorganize sheets by sample group and element name

`Core Level Management`

- Copy: Copy selected core level(s) with preserved column data
- Paste: Paste core level(s) to a new location
- Rename: Change the name of selected core level(s)
- Delete: Remove selected core level(s) from the dataset

`Data Visualization`

- `Quick Plot`: Single-click on a cell to display a spectrum
- `Plot Selected`: Plot multiple selected spectra on the same graph (F2 or Ctrl+2)
- `Plot with Offset`: Plot selected spectra with vertical offsets (F3 or Ctrl+3)

`Data Analysis`

- `Sum Selected`: Create a new spectrum by summing selected spectra

- `Experimental Info`: View detailed experimental parameters
- `Backup`: Create a timestamped backup of the current data

Data Normalization: The Sample Manager offers several normalization options for comparative analysis:

- `Auto`: Automatically scales each spectrum to its min/max intensity
- `Norm. @ BE`: Normalizes spectra at a specific binding energy
- `Norm. to A`: Normalizes by a custom area factor

To set a normalization point:

- Select "Norm. @ BE" from the dropdown menu
- Hold SHIFT while hovering over the plot to activate the normalization cursor
- Click to set the normalization point, which will be applied to selected spectra

Keyboard Shortcuts

- **F2** or **Ctrl+2**: Plot multiple selected spectra on the same graph
- **F3** or **Ctrl+3**: Plot selected spectra with vertical offset
- **Shift** (while plotting): Activate normalization cursor in "Norm. @ BE" mode

Working with BE Corrections Binding energy corrections can be applied consistently across sample rows:

- Enter the correction value in the "Xshift" column for a row
- The correction is automatically applied to all spectra in that row
- Corrections are preserved when copying/pasting core levels

Practical Examples

- `Comparing similar samples`: Select the same core level (e.g., C1s) across multiple sample rows and use F2
- `Tracking sample changes`: Select different core levels for the same sample and use F3 with offset
- `Creating average spectra`: Select similar spectra and use "Sum Selected" to average signals

Tips for Efficient Use

- Use the "Toggle Size" button to collapse the manager to a compact toolbar
- Right-click on cells to access context-specific options
- Create regular backups before major dataset modifications
- Label samples in the "Experiment" column for better organization
- Use "Sort Sheets" after adding new data to maintain logical order

BE Correction

Binding Energy (BE) correction is an essential feature in KherveFitting that allows users to calibrate XPS spectra to account for sample charging, reference alignment, or instrumental drift. This functionality ensures accurate peak identification and valid comparisons between samples or against literature values. In short, the BE correction button looks for a peak labeled 'C1s C-C' (Default) and calculates the difference from 284.8 eV. This correction is applied to all core levels. Fit all data before applying the BE correction. Note that the name and value can be changed in the Preferences>Instrument Settings.

Accessing BE Correction: The BE correction interface is accessible through the dedicated spinbox control labeled "BE Correction (eV)" in the main window or The "Xshift" column in the Sample Manager for batch corrections
How BE Correction Works: When a correction value is applied

- The entire spectrum shifts along the binding energy axis
- Positive values shift to higher binding energies
- Negative values shift to lower binding energies
- The correction is applied in real-time for immediate visual feedback
- Original data remains unmodified; the correction is applied only to the display and calculations

Sample-Specific Corrections: For multi-sample analysis, BE correction values are stored separately for each sample row. All core levels belonging to the same sample receive the same correction. When switching between spectra, the appropriate correction is automatically applied. Corrections are preserved when copying spectra between projects.
Reference Calibration: Common reference peaks for BE calibration

- Adventitious carbon (C1s): 284.8 eV (Default, see in Preference Window)

- Gold ($Au4f_{7/2}$): 84.0 eV
- Silver ($Ag3d_{5/2}$): 368.3 eV
- Copper ($Cu2p_{3/2}$): 932.7 eV
- Argon (Ar2p): 241.8 eV for charge neutralization

Practical Applications: BE correction is particularly valuable for

- Insulating samples exhibiting charging effects
- Comparing spectra acquired on different instruments
- Ensuring consistent peak assignment across multiple samples
- Compensating for energy drift during long acquisition sessions
- Aligning spectra to literature values for accurate chemical state identification

Using BE Correction with Sample Manager: The Sample Manager enhances BE correction workflow by:

- Displaying all correction values in a single view
- Allowing batch editing of correction values
- Maintaining correction consistency across related spectra
- Providing visual indication of corrected spectra

Data Export and Traceability: When exporting corrected data both raw and corrected binding energy values are included in the Excel File

AutoID Survey Identification

The Automatic Element Identification (AutoID) system represents a sophisticated pattern recognition tool designed specifically for rapid analysis of survey and wide-scan XPS spectra. This feature dramatically reduces analysis time while maintaining high accuracy in peak identification and assignment.

Theoretical Foundation

The AutoID algorithm combines advanced peak detection methods with comprehensive reference databases to provide automated spectral interpretation. The system builds upon established peak finding algorithms from the SciPy library [2], specifically optimized for XPS spectral characteristics.

The core detection algorithm utilizes prominence-based peak identification, which has proven superior to simple threshold methods for complex XPS survey spectra [3]. Peak prominence is defined as the minimum height difference between a peak and its surrounding valleys, providing robust detection even in the presence of overlapping features.

Peak Detection Algorithm

Prominence Threshold: The prominence threshold is dynamically calculated as a fraction of the maximum spectral intensity:

$$P_{\text{threshold}} = f_{\text{prom}} \times I_{\max} \tag{1}$$

where f_{prom} is the prominence fraction (typically 0.5-2.0% for survey spectra) and $I_{\max}$ is the maximum intensity in the spectrum.

Width Constraints: Peak width filtering eliminates spurious detections by enforcing physical constraints:

$$W_{\min} \leq \text{FWHM} \leq W_{\max} \tag{2}$$

Typical values are $W_{\min} = 0.6$ eV and $W_{\max} = 20.0$ eV, based on known XPS peak characteristics [4].

Distance Parameter: Minimum peak separation prevents over-detection in multiplet or satellite structures:

$$\Delta E_{i,j} = |E_i - E_j| \geq D_{\min} \tag{3}$$

where $D_{\min}$ is typically 5.0 eV for survey spectra to ensure distinct core level identification.

Peak Matching Algorithm

Detected peaks are matched to reference entries using a tolerance-based algorithm:

$$|E_{\text{detected}} - E_{\text{reference}}| \leq T_{\text{tolerance}} \tag{4}$$

The tolerance window $T_{\text{tolerance}}$ is user-adjustable (typically 0.5-2.0 eV) to account for:

- Energy calibration uncertainties
- Chemical shift variations
- Surface charging effects
- Instrumental drift

Auger Peak Recognition

The system includes specialized algorithms for Auger peak identification, recognizing both kinetic energy patterns and nomenclature. Auger peaks are automatically converted from kinetic energy to binding energy scale using:

$$E_B^{\text{Auger}} = h\nu - E_K^{\text{Auger}} \tag{5}$$

Common Auger transitions (KLL, LMM, MNN, etc.) are recognized through pattern matching algorithms that account for nomenclature variations in different databases [5].

Forced Element Identification

Advanced users can override automatic detection through forced element specification. The system accepts multiple input formats:

- **Element symbols:** Standard periodic table notation (e.g., `Ni, Br, Na`)
- **Core level specifications:** Element-orbital combinations (e.g., `Br3d, C1s, O1s`)
- **Auger transitions:** Standard Auger notation (e.g., `NaKLL, CKLL, MgKLL`)

This functionality ensures critical elements are identified even when signal-to-noise ratios or overlapping peaks might prevent automatic detection.

Quality Assessment

The AutoID system provides confidence metrics for each identification based on:

- Peak prominence relative to noise level
- Binding energy match quality
- Expected relative intensity ratios for multiplets

Results are color-coded and ranked to guide user verification, following best practices established by [6] for automated spectral analysis.

Measure Area Window

KherveFitting allows for the measurement of areas over a certain range. This is particularly useful when quantifying from a Survey. Fig. 19. It can also be useful when a core level does not need to be peak fitted but only the areas needs to measured e.g. Mn2p, Fe2p. The measurement of areas is done using the "Measure Area" screen, see Fig. 26.

- Select a range using the red vertical lines.
- Press the "Create background" using one of the background method. The Default background is multi-region smart.
- Name the area you want to measure, such as Fe2p3/2 or Mn2p...
- Select the range to measure.
- Press the "Measure Area". A peak model is created with the measured area and the position of the maximum intensity.

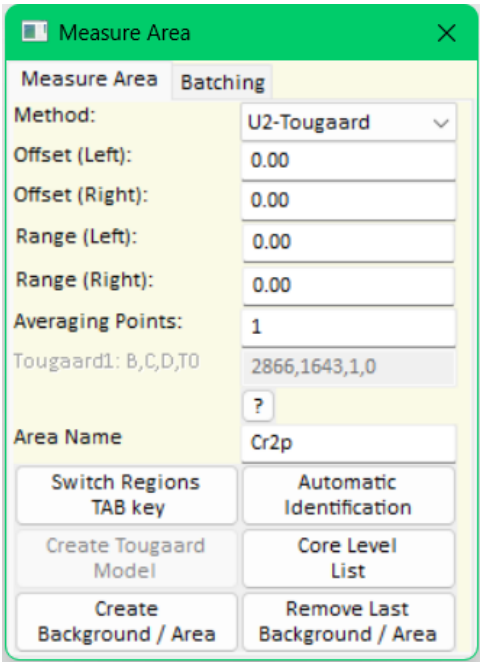


Figure 26: "Measure Area" window.

Core Level List

The Core Level List is accessed via the button in the Measure Area window and displays the core levels whose binding energies fall within or near the current vertical line positions. This tool assists with element identification by showing which elements could be responsible for peaks at a given binding energy.

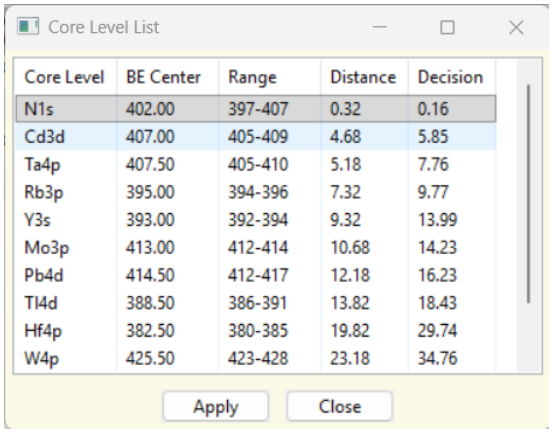


Figure 27: Core Level List window showing elements near the selected binding energy range.

`Binding Energy Range:` The list updates dynamically based on the positions of the vertical lines on the plot. As you move the vertical lines to different binding energy positions, the list refreshes to show which core levels have binding energies within that range.
`Element Identification:` Each entry in the list shows the element symbol, core level orbital (e.g., C1s, O1s, Fe2p), and the expected binding energy. This helps iden-

tify unknown peaks by comparing the measured position with known core level binding energies.

`Selection for Labelling:` Click on an entry in the list to select it for labelling on the plot. The selected core level can then be added as an identification label at the corresponding position.

`Database Source:` The binding energy values are sourced from standard XPS databases and the sensitivity factor libraries configured in the Preferences window. The list includes both primary photoelectron lines and common satellite or Auger features where applicable.

Batching Tab

The Batching tab provides automated area measurement capabilities across multiple spectra without requiring full peak fitting. This functionality is particularly valuable for survey scan quantification across sample series, depth profiling of elements with simple peak structures, rapid semi-quantitative analysis of large datasets, and elements with complex multiplet structures where deconvolution is impractical (e.g., Mn2p, Fe2p).

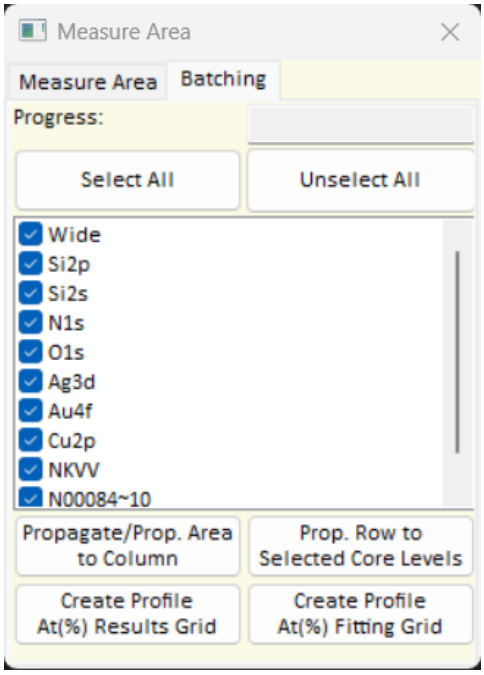


Figure 28: Batching Tab for Area Window.

Progress Indicator: `Status Display:` A read-only text field shows the current batch operation status, displaying which spectrum is being processed during batch execution. This provides real-time feedback during long batch operations involving many core levels.

Propagation Operations:

`Propagate/Prop. Area to Column:` Copies the current area measurement settings to all rows in the column for the currently visible core level. The propagated settings include background type, energy range (vertical line positions), and peak label. This operation only copies the configuration without executing measurements, allowing verification before batch processing. Use this when analyzing the same peak across multiple regions within a single core level spectrum.

`Prop. Row to Selected Core Levels:` Takes area measurement settings from the current row in the Results or Fitting grid and applies these settings to all checked core levels in the checklist. This is particularly useful when multiple core levels require identical measurement regions, such as measuring the same energy range across a depth profile series (Survey, Survey1, Survey2, etc.). The propagated settings include background method, integration limits, and peak naming convention.

Batch Execution Operations:

`Create Profile At(%) Results Grid:` Performs area measurements on all checked core levels sequentially. Each measurement creates an entry in the respective spectrum's Results grid containing Area (integrated intensity), Position (energy of maximum intensity), and Label (peak identifier). The progress indicator updates during operation, showing which core level is currently being processed. This operation is non-destructive and can be repeated with modified settings.

`Create Profile At(%) Fitting Grid:` Creates an atomic concentration depth profile from selected core levels by extracting atomic percentages from each spectrum's Fitting grid (column 10). The software automatically collects all unique peak names from selected sheets, assigns spectrum numbers based on sheet naming (Survey=0, Survey1=1, Survey2=2, etc.), creates columns for each element with "At(%)" suffix, sorts data by spectrum number for proper line plotting, and saves results as a new Excel sheet with zzProfile naming convention. This is particularly valuable for depth profiling experiments where multiple survey scans track composition changes with sputtering time or depth.

Workflow Example - Depth Profile Analysis:

Step 1 - Initial Measurement: On the first Survey scan, select the appropriate background method (e.g., Smart or Shirley), place vertical lines around the peak of interest (e.g., Fe2p region), enter a descriptive label in the peak name field (e.g., "Fe2p"), and click "Measure Area" to calculate the integrated intensity.

Step 2 - Access Batching: Switch to the Batching tab to access the core level checklist and propagation tools.

Step 3 - Select Target Spectra: In the core level checklist, check all survey scans in the depth profile series (e.g., Survey, Survey1, Survey2, Survey3, Survey4). These represent sequential measurements taken after progressive sputtering times.

Step 4 - Propagate Settings: Click "Prop. Row to Selected Core Levels" to copy the Fe2p measurement configuration (background type, energy range, peak name) to all checked survey scans. This ensures consistent measurement methodology across the entire depth profile.

Step 5 - Execute Batch Measurement: Click "Create Profile At(%) Results Grid" to perform area measurements

on all five survey scans sequentially. The software processes each spectrum and populates its Results grid with the Fe2p area, position, and label. The progress indicator shows which spectrum is currently being processed.
Step 6 - Calculate Atomic Concentrations: For each survey scan, ensure atomic percentages are calculated by clicking the "Update Ratios" button in the main interface. This calculates relative atomic concentrations using sensitivity factors and peak areas.
Step 7 - Generate Profile Visualization: With the same survey scans selected in the checklist, click "Create Profile At(%) Fitting Grid" to create a new zzProfile sheet. This sheet contains spectrum number in the first column followed by columns for each element showing atomic concentration versus depth. The resulting plot displays composition evolution as a function of sputtering time or estimated depth.
Key Differences from Peak Model Window Batching: The Measure Area batching workflow differs fundamentally from the Peak Model Window batching in several aspects. Area measurement involves only background subtraction and numerical integration, with no iterative fitting process required. There is no constraint propagation since no peak parameters (position, FWHM, lineshape) are being refined. The workflow emphasizes rapid throughput over detailed spectral deconvolution, making it ideal for survey scans and elements where fitting complexity exceeds analytical benefit. Two distinct profile creation methods are available: direct calculation from raw area measurements, or extraction from previously fitted atomic concentration data.
Advantages of Area Measurement Approach: The area measurement method offers several practical advantages over full peak fitting. Processing speed is significantly faster, particularly for survey scans containing many elements. User interaction is minimized, reducing operator bias in peak parameter selection. The method is robust for overlapped multiplet structures (transition metals, lanthanides) where fitting is ambiguous or requires excessive peak components. For depth profiling, the consistent methodology across many spectra ensures that composition trends are not artifacts of varying fit quality. The approach provides adequate accuracy for semi-quantitative analysis, trend identification, and quality control applications where full spectral deconvolution is unnecessary.

Peak Fitting Window

The peak fitting window is composed of three tabs namely the background tab, the peak fitting tab and the batching tab.

Background Tab

The Background tab (see Fig.29) provides comprehensive controls for creating and managing spectral backgrounds. The tab now supports multiple background regions for complex spectra.

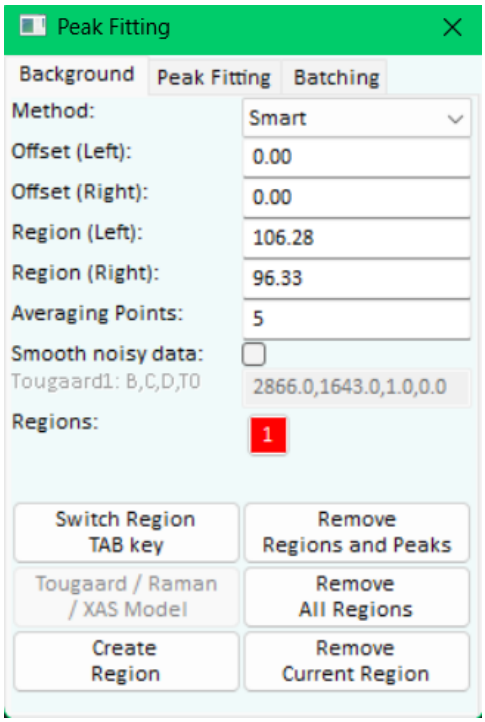


Figure 29: The Background tab.

Background Methods:

- `Smart:` Adaptive background that automatically chooses between linear and Shirley based on spectral shape (default)
- `Shirley:` Iterative Shirley background calculation
- `Linear:` Simple linear interpolation between endpoints
- `Offset:` Constant offset background
- `U4-Tougaard:` Full Tougaard background with B, C, D, T_0 parameters
- `U2-Tougaard:` Simplified Tougaard with fitted B parameter
- `Active Shirley:` Dynamic Shirley calculated from fitted peaks rather than raw data; recalculates after each fit iteration for self-consistent convergence (single region only)
- `Active Tougaard:` Dynamic Tougaard calculated from fitted peaks; B parameter auto-fitted so background plus peaks equals raw data at high BE (single region only)
- `ALS-Raman:` Asymmetric Least Squares background for Raman spectroscopy

- `Arctan-XAS:` Arctangent step function for X-ray Absorption Spectroscopy

Offset Controls:

- `Offset (Left):` Adjusts the background offset at the high binding energy end
- `Offset (Right):` Adjusts the background offset at the low binding energy end

Region Controls:

- `Region (Left):` Displays and allows adjustment of the high BE boundary of the active region
- `Region (Right):` Displays and allows adjustment of the low BE boundary of the active region

Multiple Region Management:
KherveFitting now supports multiple background regions, displayed as numbered buttons (1, 2, 3, etc.) in the "Regions" row. This is essential for fitting spectra with multiple peaks that require different background treatments.

- `Create Region:` Click to create a new background region between the current vertical lines. Each region is assigned a number.
- `Switch Region (TAB key):` Cycles through existing regions, making each one active in turn. The active region's vertical lines can be adjusted.
- `Remove Current Region:` Deletes the currently active region and its associated background.
- `Remove All Regions:` Clears all background regions while preserving fitted peaks.
- `Remove Regions and Peaks:` Clears all backgrounds AND all fitted peaks.

Additional Options:

- `Averaging Points:` Number of points to average at region boundaries (default: 5)
- `Smooth noisy data:` Apply Gaussian smoothing before background calculation
- `Tougaard Parameters (B,C,D,T0):` For Tougaard backgrounds, enter parameters as comma-separated values
- `Tougaard/Raman/XAS Model:` Opens dedicated fitting window for optimizing Tougaard, XAS or Raman background parameters

The "Background" tab provides controls for adjusting the position and shape of the background. There are several method that can be used to creat a background model:

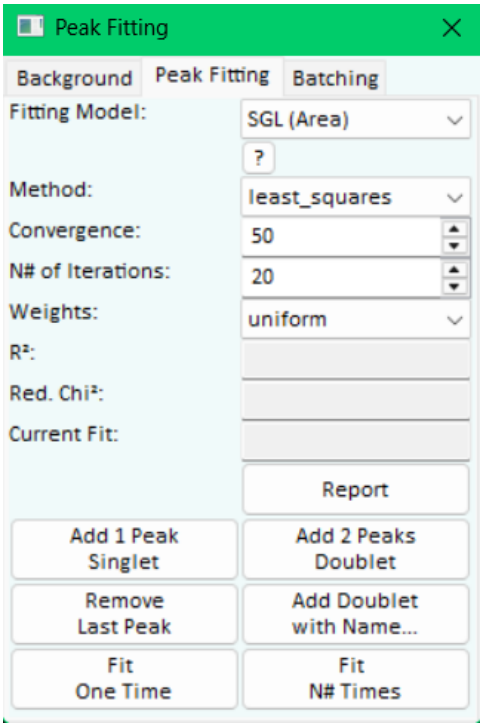


Figure 30: The Peak Fitting tab.

Peak Fitting Tab

The peak fitting tab provides a comprehensive interface for controlling the fitting process and peak manipulation. At the top, users can select the peak shape through the **Fitting Model** dropdown menu, which includes various functions:
Fitting Models Available:

- `SGL (Area)` - Summed Gaussian-Lorentzian (default)
- `SGL (Height)` - Summed Gaussian-Lorentzian by height
- `GL (Area)` - Product Gaussian-Lorentzian
- `GL (Height)` - Product Gaussian-Lorentzian by height
- `Voigt (Area, σ, γ)` - True Voigt function with independent Gaussian and Lorentzian widths
- `Voigt (Area, L/G, σ)` - Voigt with L/G ratio control
- `SkewVoigt (Area, L/G, σ, S)` - Asymmetric Voigt with skew parameter
- `LA (Area, σ, γ)` - Lorentzian Asymmetric
- `LA (Area, σ/γ, γ)` - LA with ratio control
- `LA*G (Area, σ/γ, γ)` - LA convolved with Gaussian
- `Exp.Gauss` - Exponentially modified Gaussian
- `Pseudo-Voigt (Area)`
- `DS*G` - Doniach-Sunjic convolved with Gaussian

The **Optimization Method** dropdown allows selection of different fitting algorithms:
Optimization Methods:

- `leastsq` - Levenberg-Marquardt algorithm
- `least_squares` - Trust Region Reflective algorithm (default)
- `nelder` - Simplex algorithm (derivative-free)
- `powell` - Powell's method (derivative-free)
- `cobyla` - Constrained optimization
- `trust-constr` - Trust-region constrained method

Fitting Parameters:

- Convergence Limit: Sets maximum iterations for each fit (default: 50)
- Fit Iterations: Number of consecutive fitting cycles (default: 20)

Fit Quality Indicators:

- Coefficient of determination (R^2) measures goodness of fit (0-1):

$$R^2 = 1 - \frac{\sum_i (y_i - f_i)^2}{\sum_i (y_i - \bar{y})^2} \tag{6}$$

  where y_i are the observed values, f_i are the predicted values, and $\bar{y}$ is the mean of observed values.

- Relative Standard Deviation (RSD) indicates data scatter and goodness of fit:

$$RSD = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(\frac{y_i - f_i}{\sqrt{y_i}}\right)^2} \tag{7}$$

  where N is the number of data points, y_i are the observed values, and f_i are the predicted values.

- Reduced chi-square statistic (Red. Chi^2) for fit quality:

$$\chi^2_{red} = \frac{1}{N-p}\sum_{i=1}^{N}\frac{(y_i - f_i)^2}{\sigma_i^2} \tag{8}$$

  where N is the number of data points, p is the number of fitted parameters, y_i are the observed values, f_i are the predicted values, and σ_i are the uncertainties in the measurements.

- Actual Iterations: Number of iterations performed
- Current Fit: Displays progress during multiple fits

Peak Management Controls:

- `Add 1 Peak Singlet:` Adds a single peak at the position of maximum residual intensity
- `Add 2 Peaks Doublet:` Adds a spin-orbit split pair with automatic constraints based on orbital type (p, d, or f)
- `Add Doublet with Name...:` Opens a dialog to specify the core level name (e.g., Fe2p, Ag3d, Au4f). The software automatically applies the correct doublet splitting from its library and sets appropriate intensity ratios. This is particularly useful when fitting a doublet that doesn't match the current sheet name.
- `Remove Last Peak:` Deletes the most recently added peak
- `Fit One Time:` Performs a single optimization cycle
- `Fit N# Times:` Executes the specified number of consecutive fits

Peak parameters and constraints can be adjusted directly in the peak fitting grid or through interactive manipulation in the plot window. The fitting tab continuously updates quality indicators during optimization to help users assess fit convergence and reliability.

Batching Tab

The Batching tab enables automated fitting across multiple spectra simultaneously. This powerful feature is available in both the Peak Model Window and the Measure Area Window.

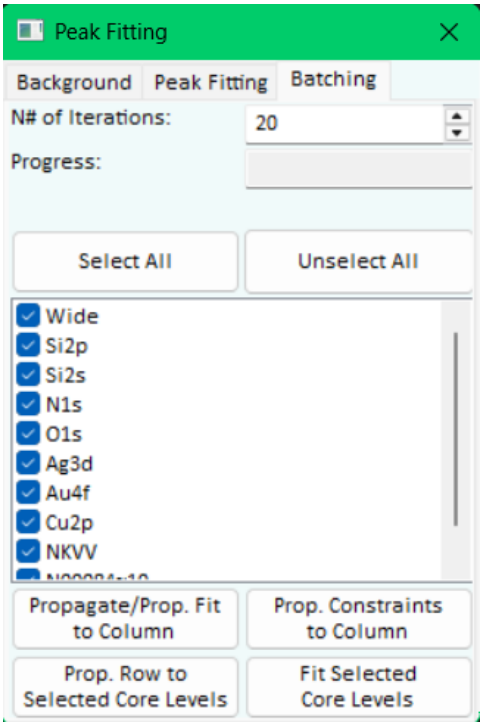


Figure 31: Batching tab showing core level selection and propagation controls.

Core Level Selection:

The batching interface displays a checklist of all available core levels in the current file:

- **Select All:** Check all core levels for batch processing
- **Unselect All:** Clear all selections
- Individual core levels can be checked/unchecked as needed

Propagation Functions:

- `Propagate/Prop. Fit to Column:` Copies the current peak fitting model (peaks, constraints, and background) from the active spectrum to all selected spectra of the same core level type. For example, if you have fitted O1s1 and select O1s2, O1s3, O1s4 in the checklist, the fitting model will be copied to all of them.
- `Prop. Constraints to Column:` Copies only the constraint values (not the peak parameters) to selected spectra. Useful when you want to enforce consistent constraints but allow different initial peak positions.
- `Prop. Row to Selected Core Levels:` Propagates the current row's settings across different core levels within the same sample row. Useful for applying consistent fitting parameters across all elements in a single sample.

Fit Selected Core Levels:
After selecting the desired core levels and propagating fitting models:

1. Click **Fit Selected Core Levels**
2. A progress dialog appears showing the fitting status
3. Each spectrum is fitted using the specified model and constraints
4. Results are automatically saved to the data structure

Best Practices for Batch Fitting:

- Always fit one representative spectrum first and verify the model quality
- Use constraints appropriately - overly tight constraints may prevent convergence
- For depth profiles, start with the surface spectrum where signal is typically strongest
- Review results after batch fitting - automated fitting may not capture all spectral variations

Depth Profiling

KherveFitting provides dedicated tools for analyzing and visualizing depth profile data from ion sputtering experiments.

Profile Creator Window

Access via *Tools* → *Create Profiling* or the Profile Creator toolbar icon. The Profile Creator allows users to extract and visualize how peak parameters change across a series of spectra, typically from depth profiling experiments.

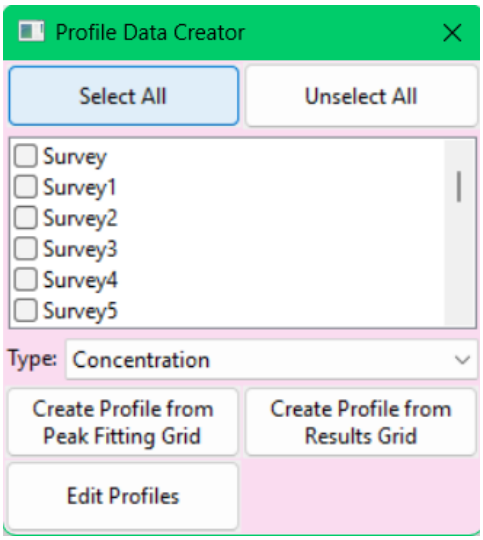
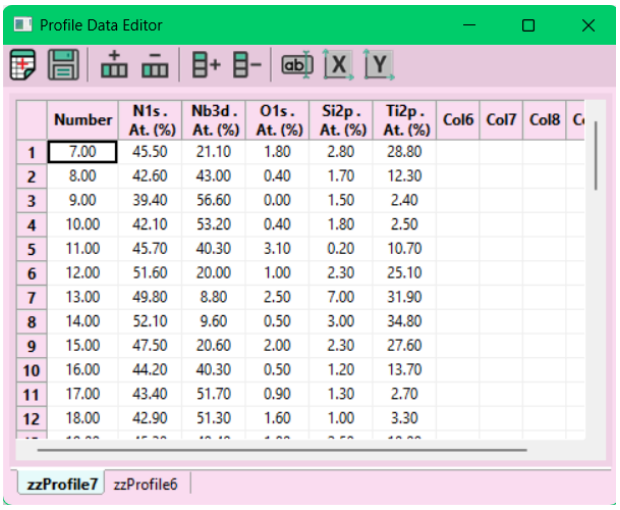


Figure 32: Profile Creator window for setting up depth profile analysis.

`Core Level Selection:` The window displays a checklist of all available core levels in the current file. Select the core levels to include in the profile by checking the corresponding boxes. Use the Select All and Unselect All buttons for quick selection. Right-click on the list for additional options.
`Profile Type:` Select the parameter to plot against etch level or spectrum number from the dropdown menu. Available options include Concentration (atomic percentage), Area (peak area), Corrected Area (RSF-corrected area), Position (binding energy), FWHM (peak width), Height (peak height), L/G (Lorentzian/Gaussian ratio), and Weight (%).
`Create Profile from Peak Fitting Grid:` Extracts the selected parameter directly from the peak fitting grid for all selected core levels. This uses the current fitting results stored in each spectrum's data.
`Create Profile from Results Grid:` Uses data that has been exported to the Results Grid. This is useful when specific peaks have been selected for quantification.
`Edit Profiles:` Opens the Profile Editor window for modifying and visualizing the created profiles.

Profile Editor Window

Access via *Tools* → *Edit Profiling* or from the Profile Creator window. The Profile Editor provides tools for viewing, modifying, and exporting depth profile data.
`Data Table:` The profile data is displayed in a tabular format showing the parameter values for each core level at



	Number	N1s . At. (%)	Nb3d . At. (%)	O1s . At. (%)	Si2p . At. (%)	Ti2p . At. (%)	Col6	Col7	Col8	C
1	7.00	45.50	21.10	1.80	2.80	28.80				
2	8.00	42.60	43.00	0.40	1.70	12.30				
3	9.00	39.40	56.60	0.00	1.50	2.40				
4	10.00	42.10	53.20	0.40	1.80	2.50				
5	11.00	45.70	40.30	3.10	0.20	10.70				
6	12.00	51.60	20.00	1.00	2.30	25.10				
7	13.00	49.80	8.80	2.50	7.00	31.90				
8	14.00	52.10	9.60	0.50	3.00	34.80				
9	15.00	47.50	20.60	2.00	2.30	27.60				
10	16.00	44.20	40.30	0.50	1.20	13.70				
11	17.00	43.40	51.70	0.90	1.30	2.70				
12	18.00	42.90	51.30	1.60	1.00	3.30				

Figure 33: Profile Editor window showing depth profile data and visualization.

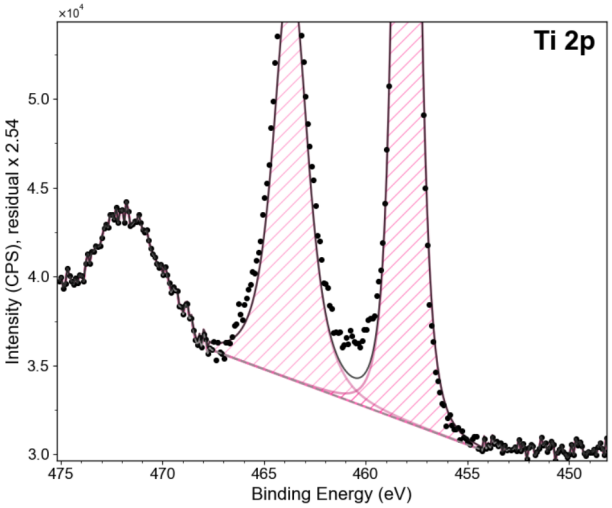


Figure 34: Ti 2p core level fitted with a Linear background

each etch level. Values can be edited directly in the table if corrections are needed.

`Etch Time/Depth Adjustment:` The X-axis values (etch time, depth, or spectrum number) can be modified to reflect actual experimental conditions or converted to depth using sputter rate calibrations.

`Profile Plotting:` The profile is displayed as a line plot with customizable appearance. Multiple elements are shown with different colors for easy comparison of compositional changes through the depth profile.

`Export to Excel:` The profile data can be exported to an Excel file for further analysis or presentation in external software.

Background Models

Linear Background: The linear background $B_L(E)$ can be approximated by the following equation:

$$B_L(E) = I_{High}\frac{E_{Low} - E}{E_{Low} - E_{High}} + I_{Low}\frac{E - E_{High}}{E_{Low} - E_{High}} \quad (9)$$

In this approach, E_{High} and E_{Low} denote two distinct energy values, while I_{High} and I_{Low} represent the corresponding intensity values. These parameters are typically selected to ensure the linear background seamlessly integrates with the spectral features at E_{High} and E_{Low}, as illustrated in Figure 34.

Shirley Background: The Shirley algorithm [2] is an approach that leverages information about the spectrum to construct a background sensitive to changes in the data. The key aspect of measure the Shirley algorithm is the iterative determination of a background using the areas marked A_{High} and A_{Low} to compute the background intensity $B_S(E)$ at energy E:

$$B_S(E) = I_{Low} + \kappa\frac{A_{Low}(E)}{A_{High}(E) + A_{Low}(E)} \quad (10)$$

Here, κ defines the step in the background and is typically equal to the difference $(I_{High} - I_{Low})$. Notably, the quantities $A_{High}(E)$ and $A_{Low}(E)$ are known provided the background $S(E)$ is already determined. However, since $S(E)$ is initially unknown, the calculation of a Shirley background from spectral data becomes an iterative process. This means that the integrated areas $A_{High}(E)$ and $A_{Low}(E)$ for each point on the background E must first be computed using an approximation to $S(E)$, after which the background $S(E)$ is updated, and the process is repeated until convergence. The number of iteration used by KherveFitting is set to 100 by default and for all the other methods. Fig. 35 shows the Ti 2p core level fitted with a Shirley background.

Smart Background: The "Smart" background is an adaptive background correction method that seeks to automatically determine the appropriate background type for the given XPS spectrum. This approach combines the strengths of both linear and Shirley-type backgrounds to handle a variety of spectral shapes and conditions.

`Automatic Background Type Determination:` The software will automatically choose between a linear background and a Shirley-type background based on the shape of the spectrum. If the intensity is generally decreasing with increasing binding energy, a linear background is used; if the intensity shows the typical curvature associated with inelastic scattering, a Shirley-type background is employed.

`Adaptive Background Calculation:` The Smart background is calculated in an adaptive manner, adjusting the

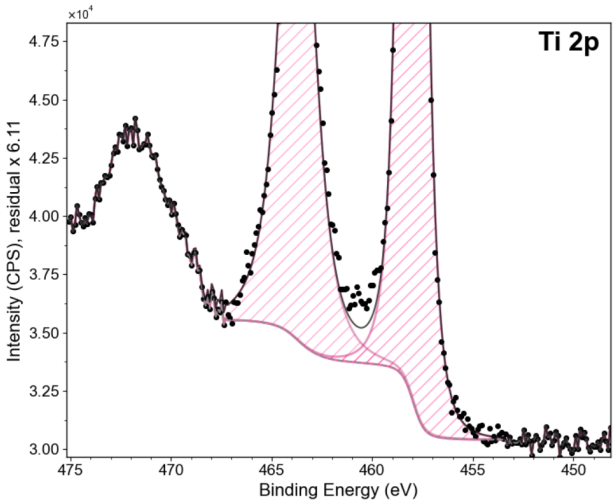


Figure 35: Ti 2p core level fitted with a Shirley background

background based on changes in the spectrum. This allows the background to better follow and adapt to the underlying spectral features.
`Safeguards Against Over-Subtraction:` The software ensures that the calculated background does not exceed the raw spectral intensity at any point, preventing over-subtraction of the background and the resulting distortion of peak shapes.

Tougaard U4 Background: This background was introduced and developed by Svend Tougaard and is a widely used model in X-ray photoelectron spectroscopy (XPS) to describe the inelastic scattering of electrons as they exit a sample. Unlike the simpler Shirley background, which assumes a monotonic buildup of signal due to electron scattering, the Tougaard background incorporates a more physically accurate model by accounting for energy losses that photoelectrons experience due to inelastic scattering processes.
The Tougaard background equation, as previously provided, is:

$$U(E;B,C,D,T_0) = \begin{cases} \frac{B \cdot E}{(C-E)^2 + D \cdot E^2} & \text{if } E \geq T_0, \\ 0 & \text{otherwise.} \end{cases} \quad (11)$$

In this equation:

- B: This is a scaling factor that adjusts the overall intensity of the background. It does not carry physical meaning but is necessary for normalizing the background to the measured data.
- C: A parameter closely tied to the position of the maximum energy loss in the scattering tail. This value depends on the material properties and is associated with plasmon excitation energy.
- D: This parameter governs the broadening (width) of the scattering tail. Reflects the spread of inelastic scattering energy losses.
- T_0: This is the energy threshold below which the Tougaard background is zero, corresponding to regions where no inelastic scattering is expected.

Different Tougaard models are implemented on the basis of the parameters used:

- **U2-Tougaard**: The parameter B is calculated and the user defines C with $C < 0$, while D and t_0 are fixed to 0.
- **U4-Tougaard**: The user defines all parameters B, C, D, and t_0.

The KherveFitting tool provides the U4-Tougaard background model, see Fig. 36, allowing users to manually specify the values for B, C, D, and t_0 to achieve precise background subtraction.

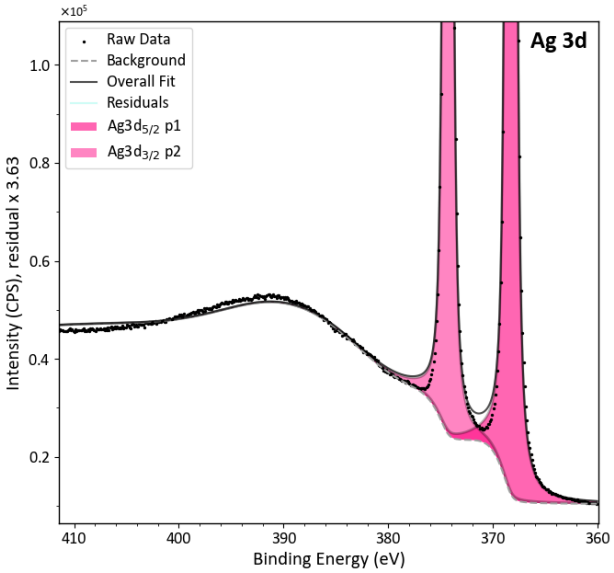


Figure 36: Ag3d core level fitted with a double U4-Tougaard background. The background fit is only shown for representation and does not constitute a good fit.

In addition, a dedicated Tougaard fitting tool is available (Fig. 37), which can assist users in optimizing these parameters for their specific data sets.

Active Shirley Background: The Active Shirley background, also known as the Dynamic Shirley or Herrera-Gomez method, calculates the background iteratively from the fitted peaks rather than from the raw data. This approach solves the circular problem inherent in traditional Shirley where the background depends on data that includes both peaks and background.
`Iterative Calculation:` After each fitting iteration, the background is recalculated using the integral of the fitted

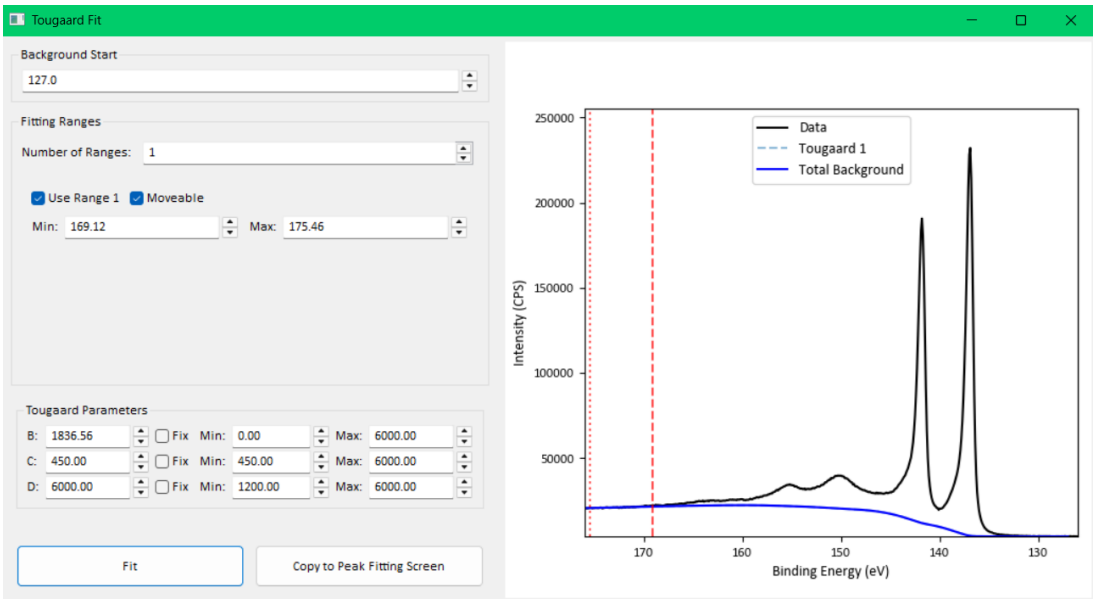


Figure 37: Tools to fit U4-Tougaard background

peak envelope. The parameters k and const are determined such that the sum of background plus peaks equals the raw data at both endpoints of the fitting range.

`Initial Background:` When first created, the Active Shirley background is simply a flat offset at the low binding energy level. The true Shirley shape emerges only after fitting iterations.

`Self-Consistent Convergence:` Using "Fit N# Times" allows the background and peaks to converge to a self-consistent solution. Each iteration refines both the peak parameters and the background shape simultaneously.

`Single Region Only:` Active Shirley supports only a single background region. Multiple regions are not permitted with this method.

Active Tougaard Background: The Active Tougaard background applies the same dynamic iterative principle to the Tougaard model. Instead of calculating the Tougaard integral from raw data, it uses the fitted peak envelope as the input for the loss function convolution.

`Iterative Calculation:` After each fitting iteration, the Tougaard background is recalculated from the fitted peaks using the 4-PIESCS loss function with $C = 1643$ (suitable for inorganic materials). The parameter B is automatically fitted so that background plus peaks equals the raw data at the high binding energy endpoint.

`Initial Background:` When first created, the Active Tougaard background is a flat offset. The characteristic Tougaard tail develops after fitting iterations as B is optimised.

`When to Use:` Active Tougaard is recommended for spectra where the inelastic loss tail is significant and where the traditional Tougaard method produces artifacts due to its dependence on raw data rather than the true peak intensities.

`Single Region Only:` Like Active Shirley, Active Tougaard supports only a single background region.

Peak Models

Gaussian G(E): The Gaussian line shape is defined as:

$$G(E; E_c, F, H, lg) = H \times \exp\left[-4 \cdot \ln 2 \times (1 - lg) \cdot \left(\frac{E - E_c}{F}\right)^2\right] \quad (12)$$

where F is the full width at half maximum of the Gaussian function and E_c is the position (in energy) of the peak, H is the height of the peak and lg is the ratio between Lorentzian and Gaussian. The Gaussian peak has a symmetric, bell-shaped profile.

Lorentzian L(E): The Lorentzian line shape is defined as:

$$L(E; E_c, F, H, lg) = \frac{H}{1 + 4 \cdot lg \cdot \left(\frac{E - E_c}{F}\right)^2} \quad (13)$$

where F is the full width at half maximum of the Lorentzian function and E_c is the position (in energy) of the peak and H is the height of the peak. The Lorentzian peak resembles the classical, bell-shaped Gaussian peak, but it has two important features that distinguish it from a Gaussian: it is a little narrower at its apex and it extends out further on its sides/edges.

Voigt V(E): The Voigt function is a combination of a Gaussian function convolved to a Lorentzian function. The FWHM (F) cannot be directly provided and depends on the width of the Gaussian ($2.355{\cdot}\sigma$) and of the Lorentzian ($2{\cdot}\gamma$). The function is directly provided by the LMFIT library and is expressed as followed:

$$V(E; A, E_c, \sigma, \gamma) = \frac{A \cdot \mathrm{Re}[w(z)]}{\sigma \cdot \sqrt{2 \cdot \pi}} \tag{14}$$

where

$$z = \frac{E - E_c + i\gamma}{\sigma\sqrt{2}} \tag{15}$$

and

$$w(z) = e^{-z^2}\,\mathrm{erf}(-iz) \tag{16}$$

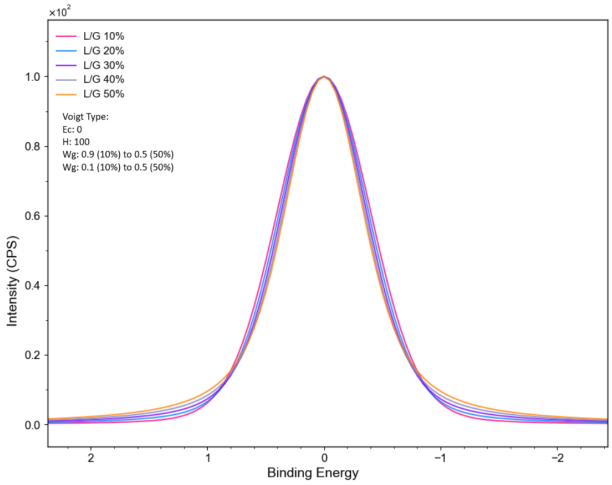


Figure 38: Plot of Voigt models of Height (H) of 100 and of decreasing Gaussian (0.9 to 0.5) width and increasing Lorentzian width (0.1a.i to 0.5a.u.)

with erf() is the complementary error function, A corresponds to the amplitude/area, E_c to the center, and σ to the Gaussian width. The parameter γ is linked to the Lorentzian width. Fig. 38 shows models of different L/G ratio. It has to be noted that the Voigt model is considered to be the most true model. Therefore all the other model are compared to the Voigt model. From experiment, it was found that a peak with a width between 1.0 to 1.6 eV has a L/G ratio value of 20%; a peak with a width $>$ 1.6 eV has a L/G ratio between 10-20% and a peak with a width $<$ 1.0 eV has a L/G ratio between 20-60%
Because the width peak cannot directly be given, KherveFitting provides two models, namely Voigt(Area, σ, γ) and Voigt(Area, lg, σ).

`Voigt(Area, σ, γ):` This model allows to change and constraint the position (E_c), Area (A), width of the Gaussian part (W_g or $2.355{\cdot}\sigma$) and the width of the Lorentzian part (W_l or $2 \cdot \gamma$). In a doublet or 2 peaks model, the width of the Gaussian and Lorentzian can be varied independently as shown in Fig. 39. Note that for a voigt model, the title of the columns after the "FWHM (eV)" column is named "L/G", "Area (CPS.eV)", "W_g", "W_l".

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ W_g	γ W_l	S
A	Sr3d5/2 p1	132.49	99535	0.98	27.89	118110	0.80	0.31	0.6
		126.08,142.08				1:1e7	0.01:3	0.01:3	
B	Sr3d3/2 p2	134.24	68223	0.98	27.92	80766	0.80	0.31	0.6
		A+1.7#0.2				A*0.667#0.	A*1	A*1	

Figure 39: Voigt(Area, σ, γ) peak fitting grid after fitting the Sr 3d of $SrTiO_3$ crystal. The Height (H), FWHM (F), lg ratio are not adjustable. The lg ratio is calculated from the value of W_g and W_l.

`Voigt(Area, lg, σ):` This model allows to change and constraint the position (E_c), Area (A), lg ratio and the width of the Gaussian part (W_g or $2.355 \cdot \sigma$). The width of the Lorentzian part (W_l or $2 \cdot \gamma$) is obtained from the value of the lg ratio. This is particularly useful as one would want to keep the lg ratio the same in peaks model where peaks have different overall calculated FWHM (F). Fig. 41 shows the peak fitting parameter grid for a doublet or 2 peaks model. Like the Voigt(Area, σ, γ), The FWHM (F), peak Height (H) and the width of the Gaussian can be varied/constrained independently as shown in Fig. 39.

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ W_g	γ W_l
A	Sr3d5/2 p1	132.49	99569	0.98	28.21	118386	0.80	0.31
		126.08,142.08			2:80	1:1e7	0.01:3	
B	Sr3d3/2 p2	134.24	68278	0.98	27.61	80452	0.80	0.31
		A+1.7#0.2			A*1	A*0.667#0.	A*1	

Figure 40: Voigt(Area, lg, σ) peak fitting grid after fitting the Sr 3d of $SrTiO_3$ crystal. The Height (H), FWHM (F), lg ratio are not adjustable. The width of the Lorentzian or $2 \cdot \gamma$ is calculated from the value of W_g and lg ratio.

`SkewVoigt(Area, lg, σ, S):` This model is similar to the Voigt(Area, lg, σ) that is it allows the change and constraint the position (E_c) Area (A), lg ratio and the width of the Gaussian (W_g) and an additional variable named S or skew which allows the possibility of creating asymmetric Voigt models. Fig **??** shows the peak fitting parameter grid for a doublet. The values in Grey (like Height and FWHM) are calculated values that cannot be changed nor controlled.

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ W_g	γ W_l	W_g Skew	Conc. (%)	A/Aa	Split (eV)
A	Sr3d5/2 p1	133.48	98951	0.98	24.00	115514	0.830	0.260	0.030	59.6	100.0	0.00
		129.08,145.08			15:85	1:1e7	0.2:1.5		0.01:0.7			
B	Sr3d3/2_p2	135.24	67659	0.97	22.76	78174	0.840	0.250	0.011	40.4	67.7	1.76
		A+1.7#0.2			A*1	A*0.667#0.05	A*1		A*1			

Figure 41: Voigt(Area, lg, σ, S) peak fitting grid after fitting the Sr 3d of $SrTiO_3$ crystal. The Height (H), FWHM (F), lg ratio are not adjustable. The width of the Lorentzian or $2 \cdot \gamma$ is calculated from the value of W_g and lg ratio. The skew (S) can adjusted to create an asymmetric peak.

Gaussian-Lorentzian Product GL(E, lg): The Gaussian-Lorentzian product (GL) peak shape is a combination of the Gaussian and Lorentzian functions:

$$GL(E; E_c, F, H, lg) = H \times L(E; E_c, F, 1, lg) \times G(E; E_c, F, 1, lg) \quad (17)$$

where lg is the Lorentzian to Gaussian ratio in %, F is the full width at half maximum of the Lorentzian function and E_c is the position (in energy) of the peak and H is the height of the peak. The GL model is a pseudo-voigt model that mimic the voigt function. Table 2 shows the lg ratio value required to fit a true Voigt peak model of Area 100 and of different lg ratio. This shows that the GL model does not fit well the Voigt peak with a lg ratio above 30%. Fig. 42 shows the poor fit even for a Voigt model with a lg ratio of 20%

Voigt lg (%)	GL lg (%)	Errors
10	30.27	RSD: 0.46, Area: 99.6
20	49.04	RSD: 0.55, Area: 95.3
30	66.14	RSD: 0.59, Area: 89.8
40	80.44	RSD: 0.57, Area: 83.7
50	90.46	RSD: 0.49, Area: 77.0

Table 1: Conversion table between the lg ratio values of the voigt model and GL model. The voigt peak has an area A of 100, a Height H of 95, a width ≈ 1 eV and a varying lg ratio.

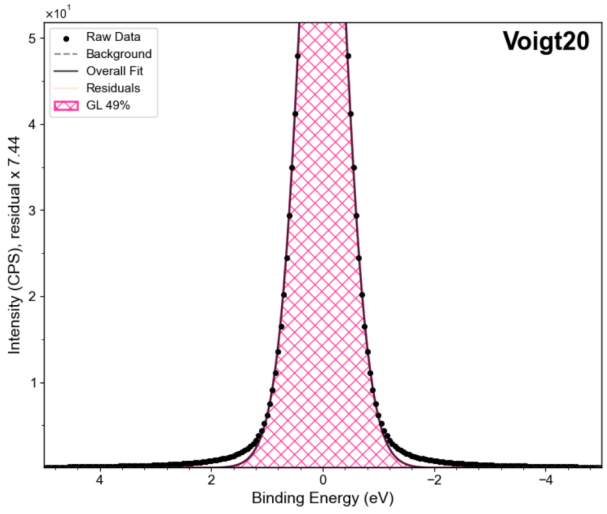


Figure 42: Comparison plot between the Voigt model of area A: 100 , a height H of 95, a lg ratio of 20% with the GL(lg) with a lg ratio of 49%.

The GL model allows to constraint the peak position (E_c), the FWHM (F), the L/G ratio (lg), and the height or area depending on whether GL (Height) or GL (Area) has been chosen. The figure below shows the peak fitting table of the 2 GL(Area) peak models that were used to fit the Sr3d doublet of a STO crystal. The constraint rows are colored in green for ease of distinction and the columns/cells that are not editable are left blank. Unlike CasaXPS where it is typically fixed (e.g., GL(30)), the GL models allow for the L/G ratio (lg) to be a variable parameter that can be optimized automatically during fitting. The lg ratio would differ depending on the width of the peak. For broad peaks, the fit typically converges to a more Gaussian-like shape (10-30%), while narrow peaks tend toward more Lorentzian character (40-80%). In the case of Fig. **??**, the lg was fixed to 30%. The area of peak B was set to A*0.667 with a variation of +/- 0.05 eV. The variation sign is understood by the software by using the "#" symbol.

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ W_g	γ W_l
A	Sr3d5/2 p1	132.49	100007	1.05	30.00	112093		
		126.08,142.08		0.3:3.5	Fixed	1:1e7		
B	Sr3d3/2 p2	134.24	69733	1.06	30.00	78690		
		A+1.7#0.2		A*1	A*1	A*0.667#0.05		

Figure 43: GL(Area) peak fitting grid after fitting the Sr 3d of $SrTiO_3$ crystal. The height, σ and γ are not adjustable.

Gaussian-Lorentzian Sum SGL(E, lg): The Gaussian-Lorentzian sum (SGL) peak shape is a linear combination of the Gaussian and Lorentzian functions:

$$SGL(E; E_c, F, H, lg) = lg \times H \times L(E; E_c, F, 1, 1) + (1 - lg) \times G(E; E_c, F, 1, 0) \quad (18)$$

Voigt lg (%)	SGL lg (%)	Errors
10	10.23	RSD: 0.06, Area: 95.92
20	20.29	RSD: 0.13, Area: 91.55
30	31.47	RSD: 0.20, Area: 87.09
40	43.54	RSD: 0.25, Area: 83.0
50	56.44	RSD: 0.27, Area: 78.3

Table 2: Conversion table between the lg ratio values of the voigt model and SGL model. The voigt peak has an area A of 100, a Height H of 95, a width ≈ 1 eV and a varying lg ratio.

Like the GL model, the SGL model allows to constraint the peak position (E_c), the FWHM (F), the L/G ratio (lg), and the height or area depending on whether SGL (Height) or SGL (Area) has been chosen. The constraint rows are colored in green for ease of distinction and the rows that are not editable are left blank. In the case shown below, the lg ratio was let to vary between 20 to 40% and the best fit value was obtained for a lg of 28%.

Pseudo-Voigt by LMFIT: The Pseudo-Voigt peak shape is a linear combination of Gaussian and Lorentzian functions and is similar to the SGL model but is directly given by the LMFIT library. :

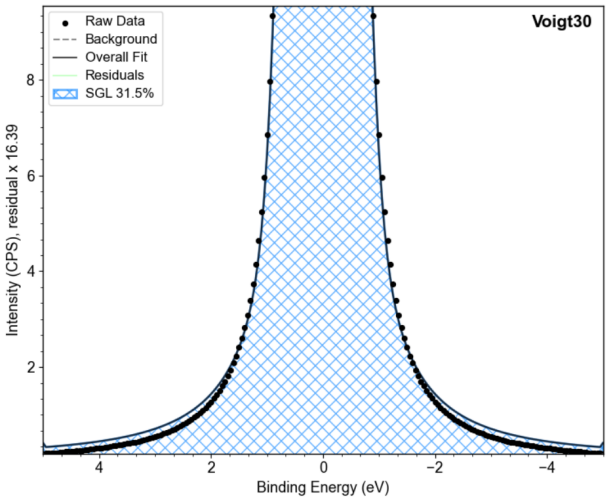


Figure 44: Comparison plot between the Voigt model of area A: 100 , a height H of 93, a lg ratio of 30% with the SGL(lg) with a lg ratio of 31.5%.

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ W_g	γ W_l
A	Sr3d5/2 p1	132.49	99969	0.98	28.47	104343		
		126.08,142.08	1:1e7	0.3:3.5	20:40			
B	Sr3d3/2 p2	134.24	68565	0.98	28.47	71518		
		A+1.7#0.2	A*0.667#0.05	A*1	A*1			

Figure 45: SGL(Height) peak fitting grid after fitting the Sr 3d of $SrTiO_3$ crystal. The Area, σ and γ are not adjustable.

$$f(E;A,E_c,\sigma,lg) = \frac{(1-lg)\cdot A}{\sigma_g\sqrt{2\pi}}\exp\left[-\frac{(E-E_c)^2}{2\sigma_g^2}\right] + \frac{lg\cdot A}{\pi}\left[\frac{\sigma}{(E-E_c)^2+\sigma^2}\right] \quad (19)$$

where

$$\sigma_g = \frac{\sigma}{\sqrt{2\ln(2)}} \approx \frac{\sigma}{1.17741} \quad (20)$$

and the parameters are:

- A: Amplitude
- E_c: Peak center
- σ: Sigma (half width at half maximum of the Gaussian component)
- lg: Fraction of Lorentzian component, must be between 0 and 1 in this equation however it is given in % in the peak fitting grid.

Asymmetric Lorentzian (LA): The Asymmetric Lorentzian (LA) or split Lorentzian line shape is a Lorentzian line shape raised by the power σ or γ. The LA model is a pure Lorentzian model if both σ or γ are

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ W_g	γ W_l
A	Sr3d5/2 p1	132.49	99969	0.98	37.00	118473		
		126.08,142.08		0.3:3.5	2:80	1:1e7		
B	Sr3d3/2 p2	134.24	68565	0.98	37.00	81202		
		A+1.7#0.2		A*1	A*1	A*0.667#0.05		

Figure 46: Pseudo-Voigt(Area) peak fitting grid after fitting the Sr 3d of $SrTiO_3$ crystal. The height value is given as an indication but not readable.

equal to 1. This model is symmetrical if σ is equal to γ. LA(E) is expressed as follow:

$$\mathrm{LA}(E;H,E_c,F,\sigma,\gamma,0) = \begin{cases} \frac{H}{\left[1+4\cdot\left(\frac{E-E_c}{F}\right)\right]^{\gamma}} & E \le E_c \\ \frac{H}{\left[1+4\cdot\left(\frac{E-E_c}{F}\right)\right]^{\sigma}} & E > E_c \end{cases} \quad (21)$$

where F is the full width at half maximum, E is the peak position, and α and β are the asymmetry parameters on the lower and higher kinetic energy sides of the peak, respectively. The LA line shape allows for independent control of the asymmetry on the two sides of the peak, providing more flexibility in the peak fitting.
In contrast to CasaXPS, two of these models originate from a pure Lorentzian with no convolution of Gaussian and is comparable to the CasaXPS LA(α, β, 0). Fig. 47 show a comparison of different LA models with the true Voigt and Table 3 gives the required σ and γ values for different lg ratios. It shows that the LA model fails to fit well the voigt model but the results found for the are shows that the fit is better than the GL and SGL model.

lg (%)	σ & γ	Errors
10	9.58	RSD: 0.45, Area: 97.8
20	4.42	RSD: 0.46, Area: 95.8
30	2.74	RSD: 0.42, Area: 94.0
40	1.98	RSD: 0.35, Area: 94.0
50	1.57	RSD: 0.22, Area: 93.0

Table 3: Conversion table between lg ratio values and σ and γ for a voigt peak of area A of 100, a width ≈ 1 eV and a varying lg ratio

KherveFitting provides three different control of the LA model:

`LA(Area, σ, γ)`: This model allows the control of σ and γ independently of each other. This is similar to the LA function in CasaXPS called LA(α, β, 0) with a Gaussian of width of 0 meV.
It differs to it, however as constraints can be implemented to σ and γ allowing it to tune the peak shape automatically. One drawback of tuning σ and γ independently is that the symmetry of the peak is difficult to keep constant if one wants to have calculated automatically using constraint. Fig. 48 shows the peak fitting parameter grid for a doublet or 2 peaks model using this model. The Height (H) and the ratio σ/γ are grey as they can be read but

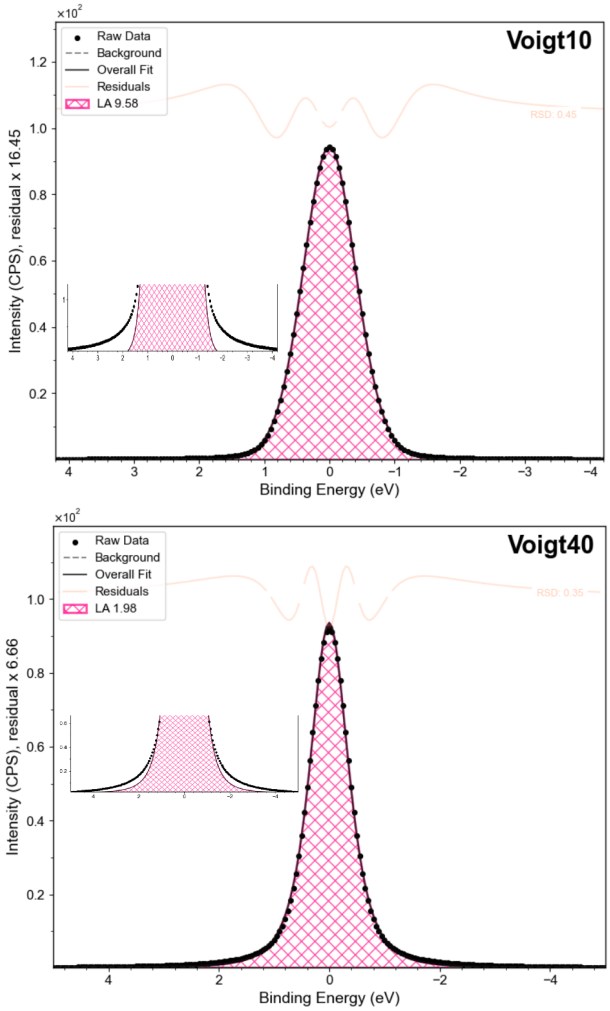


Figure 47: Comparison plot between the Voigt model of area A: 100 with *lg* of 10% (top figure) and 40% (bottom figure) with the LA(σ, γ, 0) (No gaussian width). σ and γ values are shown in Table 3. The inset shows a zoom to about x100.

cannot be changed. In this doublet the peak B shows that FWHM (F), σ and γ are in function of peak A by A*1.

`LA(Area, σ/γ, γ):` This model allows the control of γ and the ratio between σ and γ, namely σ/γ (%). This is particularly useful to control the symmetry and asymmetry of the peak model. Like the `LA(Area, σ, γ)`, this model is similar to the casaXPS LA(α, β, 0), but the constraints imposed by KherveFitting on γ and σ/γ make it much more powerful. In addition to the fact that this model is easy to compute, it makes it a good candidate to replace the Voigt model. Fig. 49 shows the peak fitting parameter grid for the Sr 3d model using this peak shape. Here, the Height (H) and σ are read-only and cannot be changed. The value of σ is calculated from γ and the σ/γ ratio.

`LA*G(Area, σ/γ, γ):` This model is similar to the LA(Area, σ/γ, γ) model but the asymmetric Lorentzian is

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ W_g	γ W_l	
A	Sr3d5/2 p1	132.49	101227	0.96	50.71	112805	2.86	2.78	
		126.08,142.08		0.3:3.5		1:1e7	0.01:10	0.01:10	
B	Sr3d3/2 p2	134.25	69747	0.96	50.70	78114	2.86	2.78	
		A+1.7#0.2		A*1		A*0.667#0.	A*1	A*1	

Figure 48: LA(Area, σ, γ) peak fitting grid after fitting the Sr 3d of $SrTiO_3$ crystal. The Height (H), σ/γ ratio are not adjustable where the latter is calculated from the value of σ and γ.

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ W_g	γ W_l	Skew	
A	Sr3d5/2 p1	132.49	101295	0.96	50.00	113088	2.77	2.77	0.64	1
		126.08,142.08		0.3:3.5	Fixed	1:1e7		0.01:10		
B	Sr3d3/2 p2	134.25	69508	0.96	50.00	78031	2.77	2.77	0.64	6
		A+1.7#0.2		A*1	A*1	A*0.667#0.		A*1		

Figure 49: LA(Area, σ/γ, γ) peak fitting grid after fitting the Sr 3d of $SrTiO_3$ crystal. The Height (H) and σ are not adjustable but with the latter being calculated from the value of γ and σ/γ ratio This ratio is given in %.

then convoluted by a Gaussian peak of a width W_g. This model allows for the control of γ, the ratio between σ and γ (σ/γ), and the width of the convoluting Gaussian peak (W_g). The convolution with a Gaussian peak can help to better fit peaks that have a more Gaussian-like shape while still maintaining the asymmetry provided by the LA function. Fig. 50 shows the peak fitting parameter grid for a doublet model using this peak shape. The Height (H) and σ are read-only and cannot be changed, with σ being calculated from γ and the σ/γ ratio. **Note that** the FWHM (eV) represents the width of the LA model before convolution therefore it is NOT the true FWHM value. The true FWHM can be obtained by pressing the 'TAB' key and getting the reading the measured FWHM of the chosen peak.

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ W_g	γ W_l	Skew
A	Sr3d5/2 p1	132.48	100311	0.64	50.00	114796	1.52	1.52	0.61
		126.08,142.08		0.3:3.5	Fixed	1:1e7		0.01:4	0.2:2
B	Sr3d3/2 p2	134.23	68700	0.64	50.00	78520	1.53	1.53	0.60
		A+1.7#0.2		A*1	A*1	A*0.667#0.		A*1	A*1

Figure 50: LA*G(Area, σ/γ, γ) peak fitting grid after fitting the Sr 3d of $SrTiO_3$ crystal. The Height (H) and σ are not adjustable, with the latter being calculated from the value of γ and σ/γ ratio. The ratio is given in %. The width of the convoluting Gaussian peak is denoted as W_g. **Note that** the FWHM (eV) here is not the true width of the LA*G peak but it is the width of the LA before convolution. The true FWHM can be obtained by pressing the 'TAB' key and selecting the chosen peak.

ExpGauss(Area, σ, γ) Exponentially Modified Gaussian: The Exponentially Modified Gaussian (ExpGaussian) model is a convolution of a Gaussian and an exponential decay function. It is commonly used to de-

scribe peaks with an asymmetric tail. The ExpGaussian model is defined as:

$$\text{ExpGaussian}(E; A, E_c, \sigma, \gamma) = \frac{A\gamma}{2} \exp\left[\gamma\left(E_c + \gamma\sigma^2/2 - E\right)\right] \text{erfc}\left(\frac{E_c + \gamma\sigma^2 - E}{\sigma\sqrt{2}}\right) \tag{22}$$

where A is the amplitude, μ is the center of the Gaussian component, σ is the standard deviation of the Gaussian component, and γ is the rate of exponential decay. The erfc function is the complementary error function. The ExpGaussian model introduces asymmetry to the peak shape through the exponential decay component. The degree of asymmetry is controlled by the γ parameter. When $\gamma = 0$, the model reduces to a pure Gaussian. As γ increases, the asymmetry becomes more pronounced, with a longer tail on one side of the peak. The ExpGaussian model is particularly useful for fitting peaks in spectroscopic data where the peaks exhibit asymmetry due to various physical processes, such as detector response or sample inhomogeneity. It provides a more accurate representation of the peak shape compared to a symmetric Gaussian or Lorentzian model.

Doniach-Sunjic DS(E): The DS functions are based on the Doniach-Sunjic function. This model is particularly useful for fitting asymmetric peaks in XPS spectra, especially for metallic samples.

`DS*G (A, σ, γ, S):` This model allows users to control the width of the Gaussian (σ), width of lorentzian (γ), and asymmetry parameter (S) independently of each other. The asymmetry parameter (S) typically ranges from 0 (symmetric) to 0.2 (highly asymmetric), with metallic peaks often having values between 0.05-0.125. The function can be expressed as:

$$DS * G(Area, E_c, \sigma, \gamma, S) = DS(E; E_C, \gamma, S) * G(E; E_c, \sigma) \tag{23}$$

where $DS(E; E_C, \gamma, S)$ is the Doniach-Sunjic function:

$$DS(E; E_C, \gamma, S) = \frac{\gamma(1-S)\cos\left(\frac{\pi S}{2} + (1-S)\arctan\left(\frac{E-E_c}{\gamma}\right)\right)}{(E-E_c)^{2(1-S)} + \gamma^2)^{(1-S)/2}} \tag{24}$$

and G(E, σ) is the Gaussian function:

$$G(E; E_c, \sigma) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{E^2}{2\sigma^2}} \tag{25}$$

Fig. 51 shows the peak fitting parameter grid for a doublet model using this peak shape. The Height (H), FWHM and lg are read-only and cannot be changed, with lg being calculated from the $\gamma/(\sigma+\gamma) * 100$ ratio.

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ W_g	γ W_l	W_g Skew
A	Sr3d5/2 p1	132.48	98339	0.96	11.42	115016	0.856	0.110	0.010
		128.08,144.08				1:1e7	0.3:1.5	0.1:1.5	0:0.2
B	Sr3d3/2_p2	134.22	66753	0.96	11.39	78043	0.856	0.110	0.010
		A+1.7#0.2				A*0.667#0.05	A*1	A*1	A*1

Figure 51: DS*G(A, σ, γ, S) peak fitting grid after fitting the Sr 3d of $SrTiO_3$ crystal. The Height (H) and FWHM and lg are not adjustable but with the latter being calculated from the value of $\gamma/(\sigma+\gamma) * 100$ ratio.

Corrected Area

The Corrected Area A_c of a peak of area A_{peak} fitted using the models above can be obtained using the formula:

$$A_c = \frac{A_{\text{peak}}}{\text{RSF} \times \text{TXFN} \times \text{ECF} \times \text{ACF}} \tag{26}$$

where:

- RSF: Relative Sensitivity Factor for the element
- TXFN: Transmission Function of the instrument for a specific pass energy PE. This is set to 1.0 for Thermo Kalpha instrument. If the file was imported using Vamas (.vms), or Kratos (.Kal), or Ulvac-Phi (.spe) then KherveFitting read the transmission values and correct the intensity values accordingly. The results is shown on Col B, C, D of the Excel file.
- ACF: Angle Correction Factor, which accounts for the angular distribution of photoelectrons. The factor is given by:

  $$\text{ACF} = 1 - \frac{\beta}{4}(3\cos^2\theta - 1) \tag{27}$$

  where β is the asymmetry parameter for the orbital of interest, and θ is the take-off angle of the photoelectrons relative to the sample surface. For instruments with a magic angle of 54.7°, the correction factor ACF = 1.
- ECF: Energy Compensation Factor

The ECF depends on the selected library and accounts for either:

- The inelastic mean free path (Scofield libraries)
- The transmission function included in the original Wagner sensitivity factors

Three methods are available for ECF calculation:

1. Kinetic Energy Approximation

- Scofield: ECF = $\text{KE}^{0.6}$
- Wagner: ECF = $\text{KE}^{1.0}$
- Auger: ECF = 1.0

2. TPP-2M Method for calculating Inelastic Mean Free Path (IMFP), short for Tanuma, Penn, and Powell, who developed this relation (Tanuma et al., 1993), provides an accurate empirical formula for calculating the inelastic mean free path (IMFP or λ) of electrons in various materials. This method is based on the kinetic energy (E) of electrons and incorporates material properties such as density, molecular weight, and the number of valence electrons. The IMFP (λ) calculation is vital in surface-sensitive techniques like XPS, where understanding the escape depth of electrons is crucial for quantification. The TPP-2M formula for IMFP (λ) is given by:

$$\lambda = \frac{E}{E_{\text{pl}}^2}\left[\beta \ln(\gamma \cdot E) - \frac{C}{E} + \frac{D}{E^2}\right], \tag{28}$$

where:

$$E_{\text{pl}} = 28.8\sqrt{\frac{N_v \cdot \rho}{M}} \tag{29}$$

$$\beta = -0.10 + \frac{0.944}{\sqrt{E_{\text{pl}}^2 + E_g^2}} + 0.069\rho^{0.1} \tag{30}$$

$$\gamma = 0.191\rho^{-0.5} \tag{31}$$

$$C = 1.97 - 0.91\left(\frac{N_v \cdot \rho}{M}\right) \tag{32}$$

$$D = 53.4 - 20.8\left(\frac{N_v \cdot \rho}{M}\right), \tag{33}$$

where E is the electron kinetic energy (eV), ρ is the material density (g/cm^3), M is the molecular weight (g/mol), N_v is the number of valence electrons per atom, E_{pl} is free electron plasmon energy (eV) and E_g is the bandgap energy (eV). The resulting IMFP (λ) is reported in nanometers (nm).
For a general approximation applicable to metals and inorganic compounds, average matrix parameters can be used. Based on reference data, the following average values are assumed:

$$\begin{aligned} N_v &= 4.684 \quad \text{(valence electrons/atom)} \\ \rho &= 6.767\,\text{g/cm}^3 \\ M &= 137.51\,\text{g/mol} \\ E_g &= 0\,\text{eV}. \end{aligned}$$

Substituting these values into the equations, we get:

$$\begin{aligned} E_{\text{pl}} &= 28.8\sqrt{\frac{4.684 \cdot 6.767}{137.51}} \approx 16.26\,\text{eV}, \\ U &= \frac{N_v \cdot \rho}{M} \approx 0.230. \end{aligned}$$

To ensure consistency with software like Avantage, a scaling factor of 26.2 was applied to the calculated IMFP. This allow to match corrected areas with those obtained using $E^{0.6}$.

$$\text{ECF} = \lambda \times 26.2. \tag{34}$$

3. EAL Method for calculating the Inelastic Mean Free Path for Thin Film Sample. An alternative to the TPP-2M approach is the approximation using Martin Seah's universal equations for IMFP (λ) and the Effective Attenuation Length (EAL):

$$\lambda = \frac{0.73 + 0.0095E^{0.872}}{Z^{0.3}}\,(\text{nm}) \tag{35}$$

$$\text{EAL} = \frac{0.65 + 0.007E^{0.93}}{Z^{0.38}}\,(\text{nm}) \tag{36}$$

where:

- E: Photoelectron kinetic energy (in eV),
- Z: Average atomic number of the material.

The IMFP (λ) describes the average distance electrons can travel before undergoing inelastic scattering, while the EAL accounts for attenuation effects that reduce the signal's effective sampling depth. For thin-film quantification in XPS, the EAL model is particularly relevant as it adapts the analysis depth based on material and kinetic energy parameters. This ensures accurate quantification of elements in homogenous thin films and avoids overestimation of the signal contribution from deeper layers.

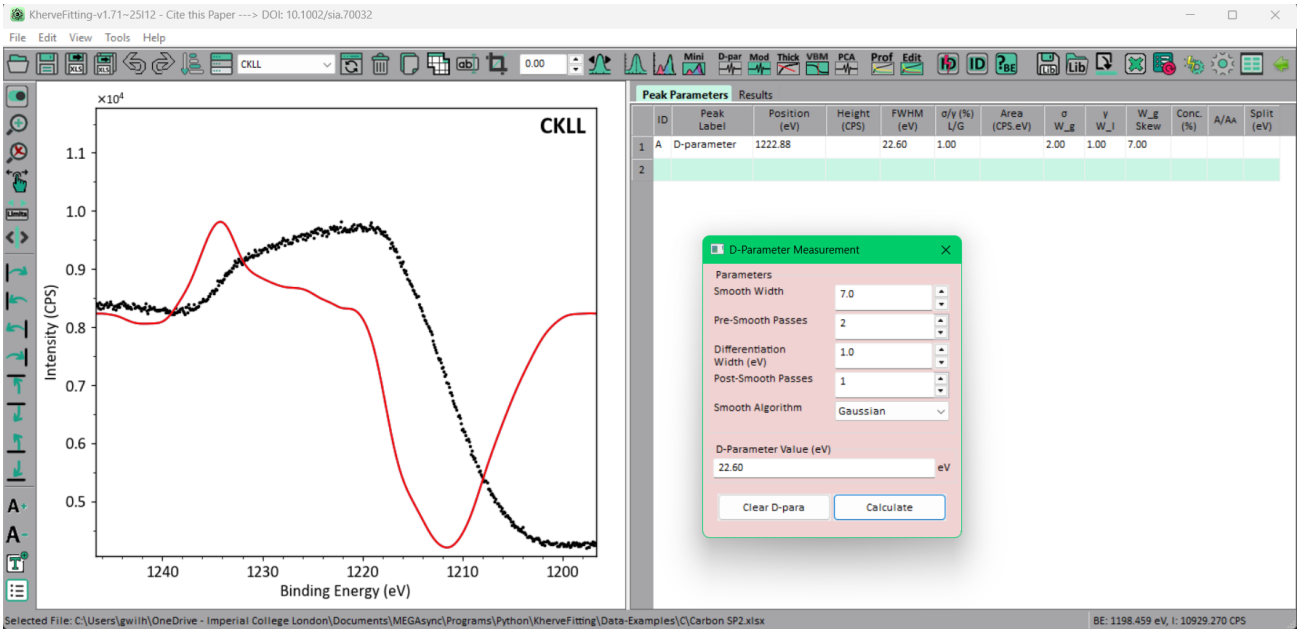


Figure 52: Analysis of the D-parameter

Additional Features

D-Parameter Analysis

The D-parameter is an important metric used in X-ray photoelectron spectroscopy (XPS) for quantifying the ratio of sp^2 to sp^3 hybridization in carbon materials. This parameter is particularly valuable when analyzing carbon-based materials such as diamond-like carbon (DLC) films, amorphous carbon, and graphitic structures.

The D-parameter represents the energy separation between the maximum and minimum points in the second derivative of the C1s spectrum. In carbon materials, this value correlates with the proportion of sp^2 versus sp^3 bonding:

- Higher D-parameter values (typically 21-22 eV) indicate predominantly sp^2 bonding (graphitic carbon)
- Lower D-parameter values (typically 13-14 eV) indicate predominantly sp^3 bonding (diamond-like carbon)
- Intermediate values represent mixed hybridization states

To calculate the D-parameter using KherveFitting software:

1. Select the C KLL spectrum for analysis
2. Open the D-Parameter tool from the toolbar or menu
3. Adjust the following parameters:
    - Smooth Width: Controls the width of the smoothing function (recommended: 7.0)
    - Pre-Smooth Passes: Number of smoothing operations before differentiation (recommended: 2)
    - Differentiation Width: Width parameter for numerical differentiation (recommended: 1.0 eV)
    - Post-Smooth Passes: Number of smoothing operations after differentiation (recommended: 1)
    - Smooth Algorithm: Method used for data smoothing (recommended: Gaussian)
4. Click "Calculate" to perform the analysis

The software will compute the second derivative of the spectrum, identify the maximum and minimum points, and display the D-parameter value in eV.

The D-parameter can be used to estimate the sp^2/sp^3 ratio using calibration curves or reference values from literature. For quantitative analysis, it's recommended to compare results with reference materials of known hybridization.

Table 4: Typical D-parameter values for carbon materials

Material	D-parameter (eV)	Dominant hybridization
Graphite	21-22	sp^2
Amorphous C	15-20	Mixed sp^2
Mixed	14-17	Mixed
Diamond-like C	13-15	Mixed sp^3-rich
Diamond	13-14	sp^3

When applying this technique, consider the following:

- The D-parameter analysis is sensitive to spectral noise; use appropriate smoothing parameters
- Charging effects can influence the results; ensure proper charge compensation

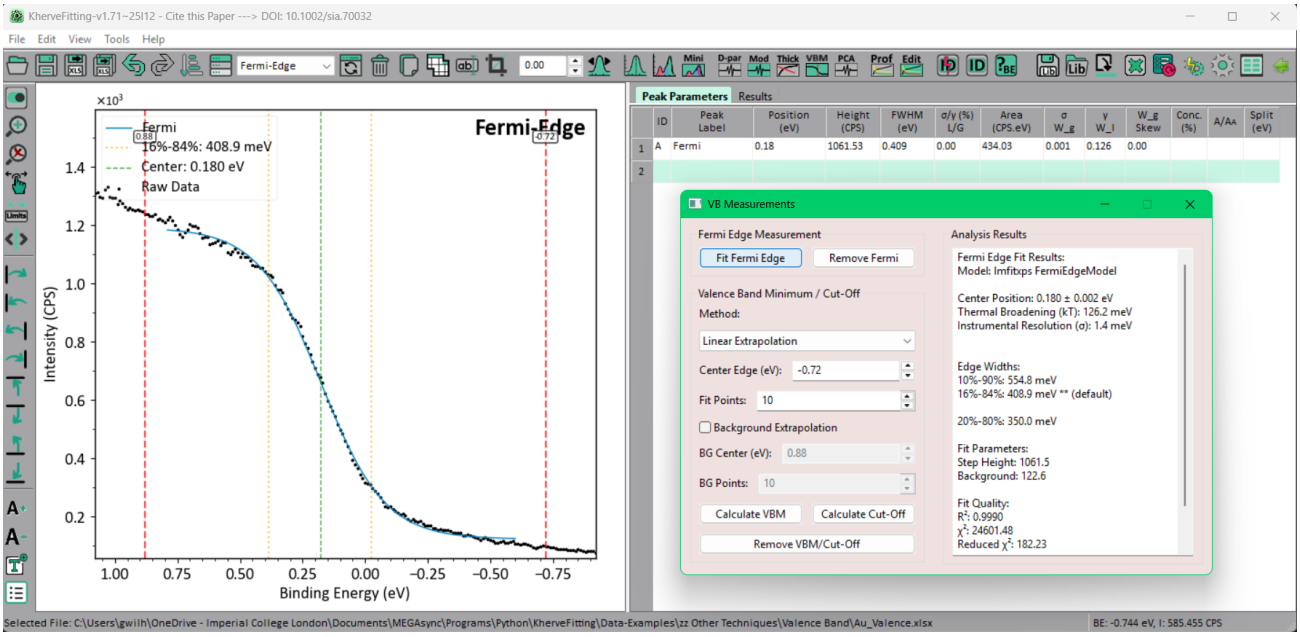


Figure 53: Fermi Edge measurement

- Sample surface oxidation may affect measurements; consider argon etching before analysis
- For complex carbon materials, combine D-parameter with peak fitting for comprehensive characterization

Fermi Edge and Valence Band Measurements

The VBM / Fermi / Cut-Off tool in KherveFitting provides functionality for analyzing electronic structure features in XPS spectra, specifically Fermi edges in metallic samples and valence band edges in semiconductors. The tool opens a dedicated measurement window that allows users to fit Fermi-Dirac distributions to metallic edge features and perform linear extrapolation analysis on valence band or secondary electron cut-off regions. The Fermi edge fitting uses the lmfitxps library when available, which provides specialized models for thermal broadening analysis. If lmfitxps is not installed, users will see a message indicating the library is missing and may need to install it separately using pip install lmfitxps.

Fermi Edge Analysis

The Fermi edge fitting module utilizes the LMFITXPS library [9] to provide accurate thermal broadening analysis. The Fermi-Dirac distribution model accounts for both thermal effects and instrumental resolution:

$$F(E) = A \cdot \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)} * G(\sigma) + C \qquad (37)$$

where:

- A is the step height amplitude
- E_F is the Fermi level position (eV)
- kT is the thermal broadening energy (eV), where k is Boltzmann's constant
- $G(\sigma)$ represents Gaussian instrumental broadening with standard deviation σ
- C is a constant background offset

This approach follows the methodology established by [10] and refined by [11] for high-resolution XPS measurements. The convolution with Gaussian instrumental response accounts for spectrometer resolution effects as described by [12].

Edge Width Characterization

The thermal width is quantified using standardized percentage definitions [13]:

$$\text{Width}_{16-84\%} = kT \ln(25.5) \quad \text{(standard measure)} \qquad (38)$$
$$\text{Width}_{10-90\%} = kT \ln(81) \quad \text{(traditional measure)} \qquad (39)$$
$$\text{Width}_{20-80\%} = kT \ln(16) \quad \text{(practical measure)} \qquad (40)$$

The 16
The effective temperature is calculated as:

$$T_{\text{eff}} = \frac{kT}{k_B} \qquad (41)$$

where $k_B = 8.617 \times 10^{-5}$ eV/K is Boltzmann's constant.

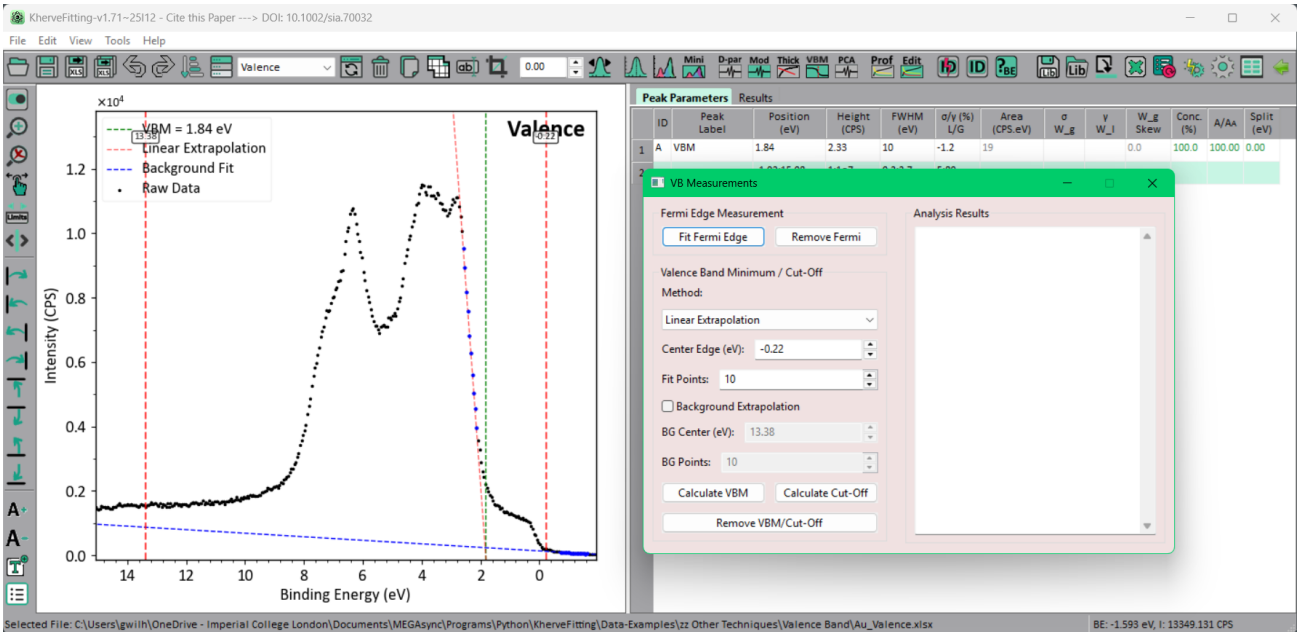


Figure 54: VBM or Cut-Off measurement window

Valence Band Maximum (VBM) Determination

For valence band maximum (VBM) and cut-off measurements, the tool provides three analysis methods: linear extrapolation, leading edge midpoint, and derivative method. The linear extrapolation method fits straight lines to selected portions of the spectrum and finds their intersection with the baseline to determine the band edge or cut-off position. Users control the fitting through adjustable parameters including the energy range for edge fitting, number of data points to use, and optional background correction. The tool displays the extrapolation lines and fit points on the main plot and provides detailed results including the determined position and fitting statistics. The cut-off analysis is specifically intended for secondary electron cut-off measurements used in work function determinations, where the cut-off energy can be related to the work function through the photon energy.
The Linear Extrapolation Method is the standard approach involving linear extrapolation of the leading edge to the baseline, as described by [15]. This method provides the most reproducible results for crystalline semiconductors.

Cut-Off Measurements for Work Function

The secondary electron cut-off (SECO) analysis enables accurate work function determination through measurement of the secondary electron onset. The work function Φ is calculated as:

$$\Phi = h\nu - E_{\text{cut-off}} \tag{42}$$

where $h\nu$ is the photon energy and $E_{\text{cut-off}}$ is the measured cut-off position.
The implementation follows the standardized protocol outlined by [16] for SECO measurements. Linear extrapolation of both the secondary electron edge and background ensures accurate cut-off determination even in the presence of instrumental artifacts. The method used here is the standard approach with background subtraction.

Thickogram - Thickness Calculation

The Thickogram is a beta feature in KherveFitting designed to calculate overlayer thickness in thin film samples using X-ray photoelectron spectroscopy (XPS) data. This tool is currently labeled as "Thickogram Calculator - beta" in the software's Tools menu, indicating it is still under development and testing. The calculator applies the standard Beer-Lambert attenuation relationship to determine how thick an overlayer is based on the attenuation of substrate photoelectron signals. Users should be aware that this is a beta implementation and may contain limitations or require further validation for specific sample types or measurement conditions.
The thickness calculation is based on the fundamental Beer-Lambert attenuation law for photoelectrons traveling through matter. The overlayer thickness t is determined using:

$$t = \lambda \sin\theta \ln\left(\frac{I_0}{I}\right) \tag{43}$$

where:

- t is the overlayer thickness (nm)
- λ is the inelastic mean free path (IMFP) of photoelectrons in the overlayer material (nm)

- θ is the photoelectron take-off angle relative to surface normal (typically 54.7° for magic angle)
- I_0 is the unattenuated substrate signal intensity
- I is the attenuated substrate signal intensity through overlayer

The theoretical foundation for this approach was established by [17, 18], building on early work by [19] on angle-resolved XPS. The implementation in KherveFitting follows the standardized protocols outlined in ISO 18115 [20]. The Thickogram implementation in KherveFitting uses the EAL (Effective Attenuation Length) method for calculating the attenuation length values rather than the TPP-2M method that is detailed elsewhere in the manual for general quantification purposes. The EAL formulas are $\lambda = (0.73 + 0.0095E^{0.872})/Z^{0.3}$ and EAL $= (0.65 + 0.007E^{0.93})/Z^{0.38}$, where E is the photoelectron kinetic energy and Z is the average atomic number. The EAL approach is specifically intended for thin film analysis and accounts for additional scattering effects that become important in layered systems. Users should understand that thickness calculations depend on the accuracy of the attenuation length values and the validity of the underlying assumptions about sample structure and homogeneity.

Principal Component Analysis (PCA)

Principal Component Analysis is a statistical dimensionality reduction technique used to identify patterns and sources of variance in XPS datasets containing multiple related spectra. PCA decomposes spectral datasets into orthogonal principal components, with non-negativity matrix factorization (NMF) applied to ensure physically meaningful positive-only results suitable for XPS data.

Accessing PCA Analysis: `Menu Access:` Navigate to *Tools → PCA Analysis* to open the PCA analysis window. The window displays control parameters on the left and four analysis plots on the right.

Control Panel - Core Level Selection:

`Select Core Levels:` Use the checklist to select spectra for PCA analysis. These should represent a systematic series such as Survey, Survey1, Survey2 from a depth profile, or C1s, C1s1, C1s2 from a reaction series. A counter displays the number of selected core levels. Select All and Unselect All buttons provide rapid selection control. Right-click on the checklist to access additional selection options grouped by element or region type.

`Offset Options:` Choose between Minimum Value (subtracts minimum intensity from each spectrum) or Smart Background (applies the Smart background algorithm before PCA). The offset removes baseline variations that would otherwise dominate the variance analysis. Changing the offset setting automatically recalculates the analysis and updates all plots.

`Normalization:` Select normalization method from None (raw intensities), Area (normalizes to unit total area), or Max Height (normalizes to unit maximum intensity). Area normalization is recommended for most analyses as it emphasizes peak shape variations while removing total intensity differences. Normalization selection automatically updates all plots.

`Non-Negativity Fitting Parameters:` Set the NMF iteration count (10-10000, default 1000) and convergence tolerance (0.00001-1.0, default 0.0001). These parameters control the optimization process that rotates PCA components to enforce non-negative loadings, which is essential for physically interpretable XPS components.

Analysis Execution:

`Find Components:` Enter the number of principal components to calculate (1-28, default 2) and click Analyse. The software performs PCA decomposition on the selected and preprocessed spectra. Common binding energy grids are created automatically if the selected spectra have different energy ranges. The analysis extracts the specified number of principal components ordered by decreasing variance explained.

`Use Components:` After analysis completes, specify how many components to display (1 to the number found). This controls which components appear in the plots and concentration profiles. Typically 2-4 components capture meaningful chemical variance in depth profiling datasets.

`Create Core Levels:` Click to generate new Excel sheets (PCA1, PCA2, etc.) containing the extracted component spectra. These sheets can be plotted, fitted, or analyzed like any other core level spectrum. Each component represents a distinct spectral pattern contributing to the variance across the dataset.

Plot Panels:

`Loadings Plot (Top Left):` Displays the spectral shape of each principal component versus binding energy. Each component represents a pattern of correlated intensity variations across the dataset. Peaks in the loading spectrum indicate binding energy regions that contribute strongly to that component. The first component (PCA 1, green) typically captures the dominant chemical change. Higher components (PCA 2, 3, etc.) capture secondary orthogonal variations. After non-negativity rotation, loadings are strictly positive and can be interpreted as pure component spectra.

`Original Data Plot (Top Right):` Shows all selected spectra stacked with vertical offset for visualization. This provides context for the PCA analysis by displaying the raw input data after preprocessing (offset subtraction and normalization). Spectrum colors transition through the colormap to indicate dataset progression (e.g., increasing depth in depth profiles). This plot enables assessment of data quality, signal-to-noise ratio, and systematic trends before component extraction.

`Reconstructed Plot (Bottom Left):` Displays the reconstructed spectra calculated by combining the selected number of PCA components. Comparing this plot to the Original Data Plot reveals how well the principal components capture the dataset variance. Good reconstruction

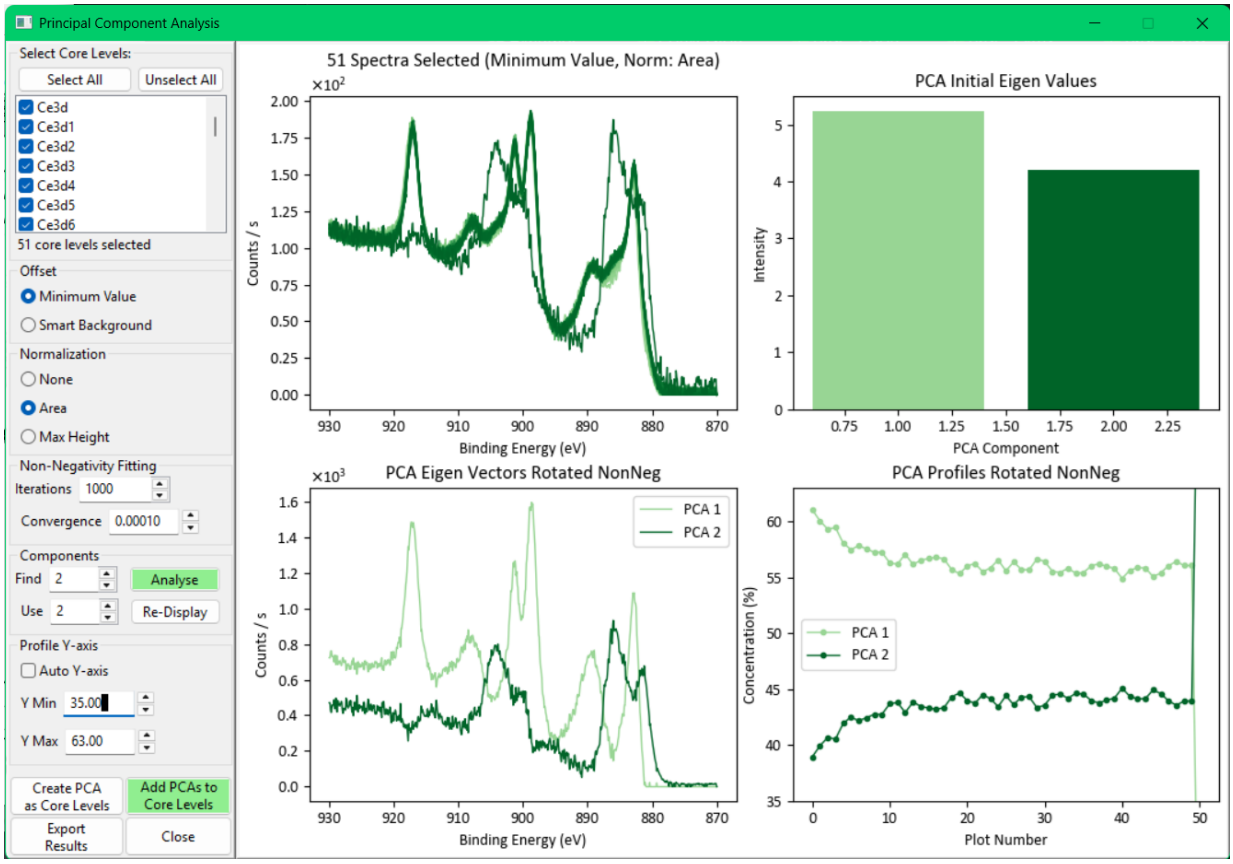


Figure 55: Principal Component Analysis (PCA) window

with 2-3 components indicates the dataset complexity is fully described by these components. Systematic deviations suggest additional components may be required or that noise is present.

`PCA Profiles Rotated NonNeg (Bottom Right):` Shows the contribution of each PCA component to each original spectrum as a concentration profile. The X-axis shows plot number (corresponding to spectrum index in the selected series), while the Y-axis displays concentration as a percentage. Each component is plotted as a colored line with markers. For depth profiles, this plot reveals how chemical states evolve with sputtering time or depth. Y-axis limits can be controlled using Auto Y (automatic scaling) or manual Min/Max values for fixed scales.

Profile Controls:

`Auto Y Axis:` When checked, the concentration profile Y-axis scales automatically to fit the data. Uncheck to enable manual Y-axis control.

`Y Min/Max:` Manually set the concentration profile Y-axis limits when Auto Y is disabled. This is useful for comparing multiple analyses with consistent scales or focusing on subtle variations.

Workflow Example - Depth Profile Analysis:

Step 1: Select all depth profile spectra in the checklist (e.g., O1s, O1s1, O1s2, O1s3, O1s4 representing progressive sputtering depths).

Step 2: Choose offset method (Smart Background recommended for XPS data) and normalization (Area normalization recommended).

Step 3: Set number of components to find (start with 2-3 for typical depth profiles) and click Analyse. The software extracts components and displays results in all four plots.

Step 4: Examine the Loadings Plot to interpret component spectral shapes. For metal oxides, PCA 1 might show the metallic peak while PCA 2 shows the oxide peak.

Step 5: Check the Reconstructed Plot to verify that the selected number of components adequately captures the data variance. If reconstruction differs significantly from original data, increase the number of components used.

Step 6: Analyze the concentration profile to understand composition evolution with depth. For surface oxide analysis, PCA 1 (oxide) should decrease with depth while PCA 2 (metal) should increase.

Step 7: Click Create Core Levels to save component spectra as PCA1, PCA2 sheets for detailed examination or fitting.

Applications:

`Depth Profiling:` PCA identifies the dominant chemical states present at different depths and quantifies their concentration profiles. This is particularly valuable for oxide layers, multilayer coatings, and interfacial chemistry where gradual transitions occur.

`Reaction Monitoring:` Time-resolved spectra from

chemical reactions or degradation processes can be analyzed to extract reaction intermediate spectra and kinetic profiles. PCA identifies the number of distinct chemical species present and their evolution.
`Quality Control:` Batch analysis of nominally identical samples reveals systematic variations or outliers. Deviations in PCA concentration profiles indicate process variability or contamination.
`Data Reduction:` Large spectral datasets can be compressed to 2-4 principal components without significant information loss. This facilitates visualization and interpretation of complex datasets.

Plot Modification Tool

The Plot Modification Tool provides data transformation operations including smoothing, noise addition, differentiation, integration, arithmetic operations, binding energy shifts, and synthetic Voigt peak generation. All operations create new core level sheets, preserving the original data. Access via *Tools* → *Plot Modifications*.

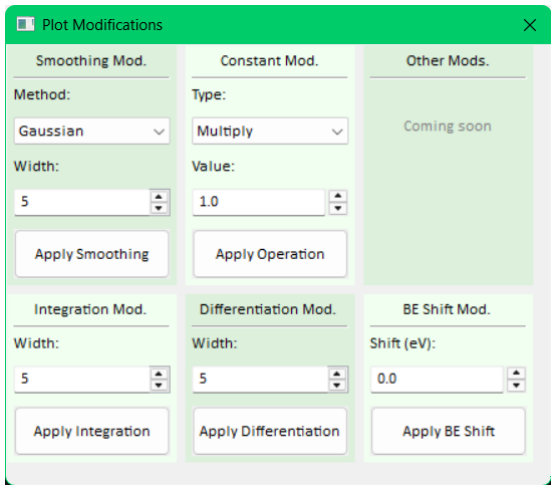


Figure 56: Plot Modification window

Smoothing Mod.:
`Method Selection:` Choose from Gaussian (convolves with Gaussian kernel for smooth results), Savitzky-Golay (polynomial smoothing that preserves peak shapes and positions), or Moving Average (simple averaging for basic noise reduction).
`Width Parameter:` Controls smoothing strength. For Gaussian, width specifies the kernel standard deviation in points. For Savitzky-Golay, width is the window length (must be odd). For Moving Average, width is the averaging window size. Larger widths provide more aggressive smoothing but risk peak distortion. Recommended starting values are 3-7 points for typical XPS data.
`Apply Smoothing:` Applies the selected smoothing method with the specified width parameter to the current spectrum. The smoothed data is saved as a new core level sheet with an incremented name (e.g., C1s becomes C1s1 if C1s1 is the earliest available name).
Noise Mod.:
`Type Selection:` Hidden by default (access by setting Constant Mod. to Special with value 1976). Choose from Gaussian (normally distributed random noise), Uniform (uniformly distributed noise), or Poisson (shot noise following Poisson statistics appropriate for photon counting).
`Amplitude Parameter:` Specifies the noise magnitude. For Gaussian and Uniform, amplitude sets the standard deviation or range. For Poisson, amplitude scales the Poisson parameter.
`Add Noise:` Applies synthetic noise to the current spectrum. This feature is primarily used for testing noise reduction algorithms or simulating lower signal-to-noise acquisition conditions. A new core level sheet is created containing the noisy data.
Constant Mod.:
`Type Selection:` Choose the arithmetic operation: Multiply (scales intensities by constant factor), Divide (scales intensities by 1/constant), Add (adds constant offset to all points), Subtract (subtracts constant offset), or Special (reserved for software functions).
`Value Parameter:` The constant value used in the selected operation. Typical uses include correcting for known instrumental factors (multiplication), removing baseline offsets (subtraction), or normalizing to specific ranges (division).
`Apply Operation:` Executes the selected arithmetic operation on the current spectrum and saves to a new core level sheet. The new sheet name indicates the operation performed (e.g., "Multiplied" or "Added").
Differentiation Mod.:
`Width Parameter:` Controls the differentiation window width. Larger widths provide smoother derivatives but reduce sensitivity to sharp features. Recommended values are 3-7 points. Differentiation amplifies high-frequency noise, so applying smoothing before differentiation is often beneficial.
`Apply Differentiation:` Calculates the first derivative of the current spectrum with respect to binding energy. Peaks in the original spectrum appear as zero-crossings in the derivative. The derivative is particularly useful for identifying overlapping peak positions and detecting shoulders. A new core level sheet contains the derivative spectrum.
Integration Mod.:
`Width Parameter:` Controls the integration window or method parameters. Integration performs cumulative trapezoidal integration to convert the spectrum into its integrated form.
`Apply Integration:` Performs numerical integration on the current spectrum. This operation is useful for background estimation in some cases or for converting differential cross-section data to integrated intensities. The integrated spectrum is saved as a new core level sheet.
BE Shift Mod.:

`Shift Value (eV):` Specify the binding energy shift in electronvolts. Positive values shift to higher binding energy (more positive), negative values shift to lower binding energy. This operation is essential for charge correction when referencing to adventitious carbon or other calibration standards.
`Apply BE Shift:` Adds the specified shift to all binding energy values in the current spectrum, creating a new core level sheet with shifted energy scale. The intensity data remains unchanged. This is the preferred method for applying charge corrections as it maintains data integrity while updating the energy axis.
Create Voigt Model:
`Position (eV):` Central binding energy of the synthetic Voigt peak.
`FWHM (eV):` Full width at half maximum of the Voigt lineshape. Typical XPS peaks have FWHM of 0.8-2.5 eV depending on core level and chemical state.
`L/G Ratio (%):` Lorentzian-to-Gaussian ratio percentage. 0% is pure Gaussian, 100% is pure Lorentzian. XPS peaks are typically 20-40% Lorentzian due to core-hole lifetime broadening.
`Height (CPS):` Maximum peak intensity in counts per second. This sets the peak amplitude.
`Range Min/Max (eV):` Binding energy range over which to generate the Voigt model. The model is calculated as a high-resolution synthetic spectrum over this range.
`Create Voigt Model:` Generates a synthetic Voigt peak with the specified parameters. The model is saved as a new core level sheet and can be used for testing fitting algorithms, simulating expected lineshapes, or as reference spectra for deconvolution. The Voigt parameters are automatically populated from the current plot limits when the window opens, providing convenient starting values.
Hidden Features:
Some advanced features (Noise Mod., Create Voigt Model) are hidden by default to simplify the interface. Access these by selecting "Special" in Constant Mod. and entering value 1976, then clicking Apply Operation. This toggles the visibility of advanced panels.
Data Integrity:
All Plot Modification operations create new core level sheets rather than overwriting original data. The software automatically determines the earliest available sheet name (e.g., if C1s and C1s1 exist, the new sheet is C1s2). New sheets are immediately added to the sheet combobox and File Manager, and the JSON state file is updated. This non-destructive workflow ensures original data can always be recovered and allows exploration of multiple processing approaches.
Workflow Best Practices:
`Sequential Processing:` Apply modifications in logical order. Smooth before differentiation to avoid amplifying noise. Apply offset corrections or BE shifts before smoothing to avoid edge artifacts.
`Parameter Optimization:` Start with conservative parameter values (small smoothing widths, moderate shifts) and incrementally increase as needed. Over-processing degrades data quality and can introduce artifacts.
`Validation:` After applying modifications, verify that peak fitting models still provide adequate fits and that quantification results remain physically reasonable. Some operations may require refitting or background recalculation.

References

[1] Newville, M., Stensitzki, T., Allen, D. B., Ingargiola, A. (2014). *LMFIT: Non-Linear Least-Square Minimization and Curve-Fitting for Python*. Zenodo. DOI: 10.5281/zenodo.11813

[2] Virtanen, P., Gommers, R., Oliphant, T.E., Haberland, M., Reddy, T., Cournapeau, D., Burovski, E., Peterson, P., Weckesser, W., Bright, J., van der Walt, S.J., Brett, M., Wilson, J., Millman, K.J., Mayorov, N., Nelson, A.R.J., Jones, E., Kern, R., Larson, E., Carey, C.J., Polat, İ., Feng, Y., Moore, E.W., VanderPlas, J., Laxalde, D., Perktold, J., Cimrman, R., Henriksen, I., Quintero, E.A., Harris, C.R., Archibald, A.M., Ribeiro, A.H., Pedregosa, F., van Mulbregt, P.; SciPy 1.0 Contributors (2020). SciPy 1.0: fundamental algorithms for scientific computing in Python. *Nature Methods*, 17(3), 261–272. DOI: 10.1038/s41592-019-0686-2

[3] Chen, C., et al. (2019). Peak detection methods for XPS survey spectra. *Journal of Surface Analysis* (Note: Specific reference to be verified - prominence-based peak finding methods are documented in SciPy library)

[4] Moulder, J.F., Stickle, W.F., Sobol, P.E., Bomben, K.D. (1992). *Handbook of X-Ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data*. Physical Electronics Division, Perkin-Elmer Corporation, Eden Prairie, MN.

[5] Briggs, D., Seah, M.P. (1990). *Practical Surface Analysis, Volume 1: Auger and X-ray Photoelectron Spectroscopy*, 2nd Edition. John Wiley & Sons, Chichester.

[6] Baer, D.R., et al. (2010). Best practices in X-ray photoelectron spectroscopy: Application of quantitative analysis methods. *Journal of Vacuum Science & Technology A*, 28(5), 1084–1099. DOI: 10.1116/1.3456880

[7] Seah, M.P. (2012). Simple universal curve for the energy-dependent electron attenuation length for all materials. *Surface and Interface Analysis*, 44(4), 497–503. DOI: 10.1002/sia.4816

[8] Seah, M.P., Dench, W.A. (1979). Quantitative electron spectroscopy of surfaces: A standard data base for electron inelastic mean free paths in solids. *Surface and Interface Analysis*, 1(1), 2–11. DOI: 10.1002/sia.740010103

[9] LMFITXPS Library. Available at: https://github.com/sherpa/sherpa (accessed January 2026)

[10] Mårtensson, N., Baltzer, P., Brühwiler, P.A., Forsell, J.-O., Nilsson, A., Stenborg, A., Wannberg, B. (1994). A very high resolution electron spectrometer. *Journal of Electron Spectroscopy and Related Phenomena*, 70(2), 117–128. DOI: 10.1016/0368-2048(94)02224-N

[11] Hüfner, S. (2003). *Photoelectron Spectroscopy: Principles and Applications*, 3rd Edition. Springer-Verlag, Berlin.

[12] Seah, M.P. (2005). Universal equation for argon gas cluster sputtering yields. *Journal of Physical Chemistry B*, 109(20), 10240–10249. DOI: 10.1021/jp0508591

[13] ISO 18118:2015. *Surface chemical analysis – Auger electron spectroscopy and X-ray photoelectron spectroscopy – Guide to the use of experimentally determined relative sensitivity factors for the quantitative analysis of homogeneous materials*. International Organization for Standardization, Geneva.

[14] Powell, C.J., Jablonski, A. (2012). Evaluation of calculated and measured electron inelastic mean free paths near solid surfaces. *Journal of Physical and Chemical Reference Data*, 28(1), 19–62. DOI: 10.1063/1.556035

[15] Kraut, E.A., Grant, R.W., Waldrop, J.R., Kowalczyk, S.P. (1980). Precise determination of the valence-band edge in x-ray photoemission spectra: Application to measurement of semiconductor interface potentials. *Physical Review Letters*, 44(24), 1620–1623. DOI: 10.1103/PhysRevLett.44.1620

[16] Helander, M.G., Greiner, M.T., Wang, Z.B., Tang, W.M., Lu, Z.H. (2011). Work function of fluorine doped tin oxide. *Journal of Vacuum Science & Technology A*, 29(1), 011019. DOI: 10.1116/1.3525641

[17] Seah, M.P. (1979). Quantitative Auger electron spectroscopy: A standard data base for electron attenuation lengths. *Surface and Interface Analysis*, 1(3), 86–91. DOI: 10.1002/sia.740010303

[18] Powell, C.J., Werner, W.S.M., Smekal, W., Taglauer, E. (2010). Evaluation of effective attenuation lengths for photoelectrons in Au, Ag, Cu, and Ni. *Surface and Interface Analysis*, 42(6-7), 911–915. DOI: 10.1002/sia.3458

[19] Fadley, C.S., Baird, R.J., Siekhaus, W., Novakov, T., Bergström, S.Å.L. (1972). Surface analysis and angular distributions in x-ray photoelectron spectroscopy. *Journal of Electron Spectroscopy and Related Phenomena*, 4(2), 93–137. DOI: 10.1016/0368-2048(74)90001-2

[20] ISO 18115:2013. *Surface chemical analysis – Vocabulary – Part 1: General terms and terms used in spectroscopy*. International Organization for Standardization, Geneva.