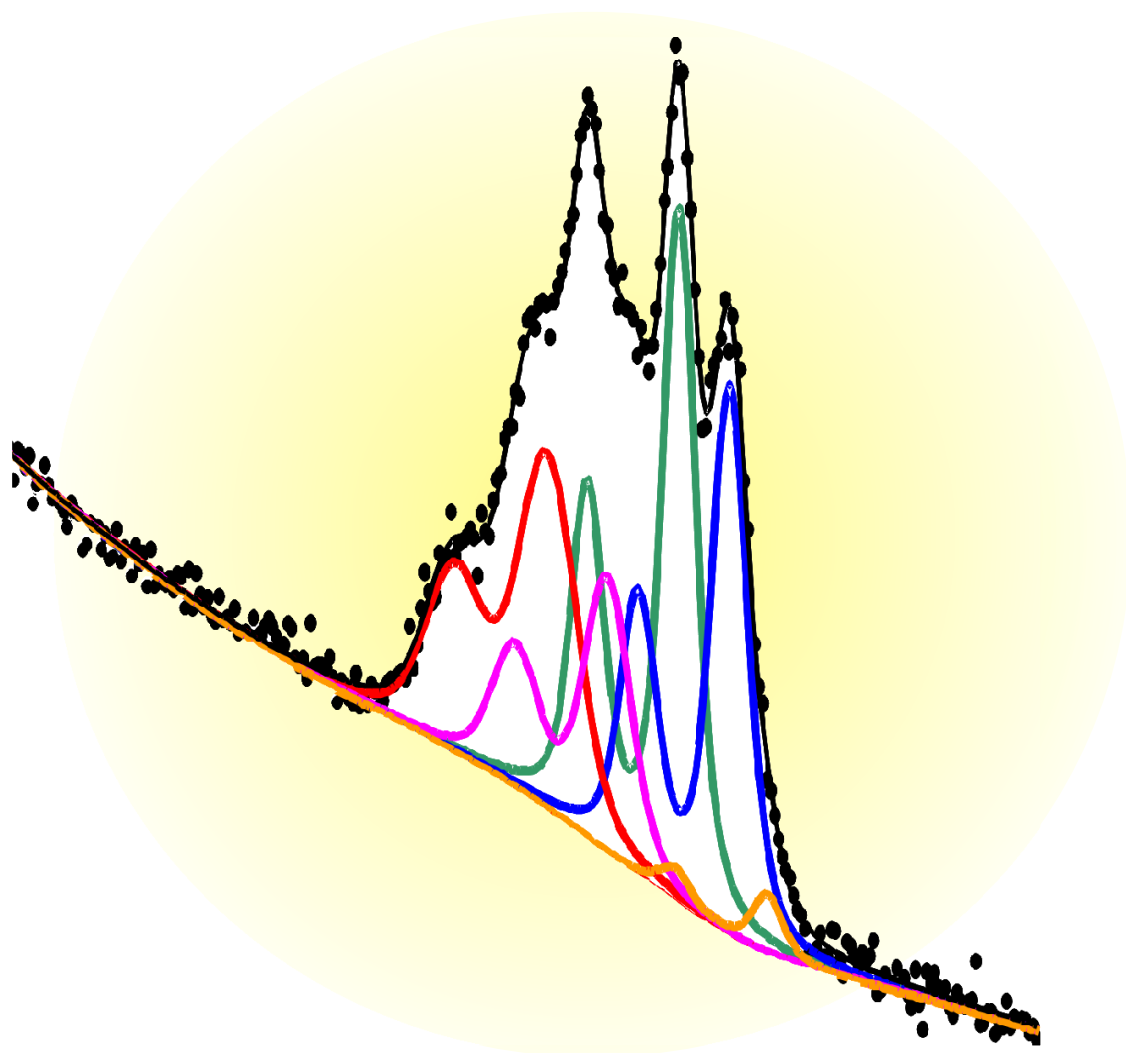


unifit

FOR WINDOWS



Spectrum Processing, Analysis and
Presentation Software for
XPS, XAS, AES and
RAMAN Spectroscopy

Version 2023

Ronald Hesse

Unifit for Windows

Spectrum Processing, Analysis and
Presentation Software for
XPS, XAS, AES and
RAMAN Spectroscopy

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Preface

The energy resolution and the sensitivity of photoelectron, Auger electron, X-ray absorption and RAMAN spectroscopy have been strongly improved since the development of the first spectrometers in the 1960s. Initially the resolution of the X-ray photoelectron spectra was restricted to a few eV by the width of the exciting X-ray lines. Nowadays energy resolutions as low as a few 10 meV may be obtained in favourable cases by both taking advantage of high-resolution electron analysers and employing monochromatized synchrotron radiation. However, an adequate modelling of the experimental spectra with several different components has remained a challenge all the time regardless of the achieved level of energy resolution, because higher resolution gives access to much more detailed information, which again has to be gained from the raw data. In particular, binding energies and intensities of components have to be derived to identify chemical species and quantify the chemical composition of investigated samples. In order to obtain the desired information from core level spectra several computer codes have been developed in the past that permit the numerical optimization of parameters from theoretical peak models.

However, practical application of this kind of data analysis software requires appropriate description of the spectra by adequate models, convenient data handling, excellent numerical performance for fast calculations, and versatile opportunities for data transfer and representation. The typical advantages of commercially available software are comfortable handling and extensive graphical design options. However, they often exhibit severe restrictions in data modelling. On the other hand, user-developed programme codes are very often tailor-made for single spectrometers and special applications. In many cases they were written by insiders for internal use only. In order to fill this gap, a programme for the peak shape analysis of core level photoelectron spectra has been developed, tested and used intensively by the author's group for years. The result is UNIFIT FOR WINDOWS, which solves several important problems in the evaluation of electron. X-ray and laser spectroscopy data and thus contributes to a more efficient usage of spectral information in XPS, XAS, AES and RAMAN spectroscopy.

The current version is executable on 32 bit and 64 bit Windows operating systems. Personal scientific studies in the field of spectroscopic processing methods in cooperation with international scientists secure the high theoretical and methodical level of this software.

In order to save a stable marketing, a continuous improvement of the software and a customer service the Unifit Scientific Software GmbH was found in August 2009.

Dr. rer. nat. Ronald Hesse

Leipzig, August 2016

Preface to versions 2022/2023

Main focus of the advancement to the **UNIFIT 2022** software was the improvement of the calculation procedure QPA (quantified-peak areas method) for the estimation of the spectrometer transmission function $T(E)$ (*IERF*). The functionality of the pop-up operation using the right mouse button was extended with design commands. A new input routine for the loading of SPECS Prodigy data was implemented. Two additional functions of the Min/Max value definition of the fit parameters were implemented. The input dialogue for the fit parameters has now a call for the increasing and decreasing of the number of peak-fit components. The spectra labelling and title functions were extended.

1. The sub-programme for the generation of the spectrometer transmission function using reference peak pairs was improved. The following tasks were realized:
 - a) Extending the $T(E)$ estimation from pure-element reference samples (Au, Ag, Cu, Ge) to well defined compounds (IL).
 - b) Plot of the input data and the $T(E)$ function in one sheet during the calculation and after loading the corresponding UNIFIT projects.

- c) Changing of the fixed value $E_0 = 1000$ eV to a variable adjustable fit parameter E_0 .
- d) Optimization of the fit procedure.
- e) Optionally setting of the number of cycles (more than one) and sweeps per cycle.
- f) Saving and reloading as UNIFIT project.
- g) Improved saving and reloading of the estimated $T(E)$ functions.

The characterization of the new feature is:

- a) Extending the $T(E)$ estimation from pure-element reference samples (Au, Ag, Cu, Ge) to well defined compounds (IL).
- b) The calculation time is:
Time = Number of cycles · Number of sweeps · $11^{\text{number of free fit parameters}}$
- c) The typical acquisition parameters of a measurement function are saved additionally with the estimated parameters of the $T(E)$ function (*.dat). After a reloading the $T(E)$ function is displayed like after the calculation.
- d) The separation between:
 1. 'Calculation Transmission Function Al/Mg Excitation' and
 2. 'Calculation Transmission Function Synchrotron Excitation'
 is cancelled.
- e) The $T(E)$ approach can be saved and reloaded as UNIFIT project.
- f) After a reload the calculation can be continued and the input data can be displayed.
- g) $T(E) > 0$ at the displayed energy range.
- h) After pressing 'Calculate' the normalized intensities of the peak pairs and the curve of the $T(E)$ function are displayed in one plot. The dialogue for the definition of the fit parameters of the $T(E)$ function will be opened.
Additionally, the fit conditions can be defined with:
 1. Number of sweeps per cycle.
 2. Number of cycles.
 3. Break condition (The iteration stops if the error (SSD) lower a defined value (e.g. 0.05).
 4. The function $T(E)$ can be normalized ($T(E_0) = 1$).
- i) The following information are displayed (also after a iteration):
 1. Error of the iteration.
 2. Calculation time (zero before the iteration was started).

The fit parameters can be saved and reloaded.

2. A new input routine for the SPECS Prodigy data format was implemented. The input of XPS, REXPS and XAS data are supported:
 - a) Four loading options are offered:
 1. Spectrum
 2. Ring Current
 3. Mirror Current
 4. TYR-Data
 5. Free data block name, edit field
 - b) One normalization option: normalizing to Ring Current.
 - c) Option: Create sum curve of scans (slices).
 - d) Incorrect input data are identified and changed to readable data.
 - e) XAS;
 1. Energy scale is calibrated to the external true excitation energy values.
 2. Energy scale is converted to equidistant steps using linear interpolation of the intensities.
 3. Minimum of the step width: 0.02 eV.

f) XPS:

Data of a RESXPS measurement are identified automatically.

3. Two new options for the definition of the Min/Max values of the fit parameters were implemented. The Min/Max values of the positions of all defined peak-fit components may be defined using the position of the peak-fit component.
The Min/Max values can be defined:
 1. All maxima and minima: positions of peak-fit component +0.2 eV and -0.2 eV.
 2. All maxima and minima: positions of peak-fit component +0.4 eV and -0.4 eV.
4. The number of the peak-fit components can be increased or decreased using a separate control implemented into the dialogue for the definition of the start parameters of the peak fit. The controls are titled with 'PN+' and '-PN'.
5. New functions were implemented into the dialogue 'Spectrum Labelling 1' and 'Spectrum Title 1'.
 - a) The x- and y position of the labelling of the spectra can be defined.
 - b) The mouse operation for the positioning after a definition of a spectrum label was removed.
 - c) An additional label is placed with a short shift of the x and y position.
 - d) The new command 'OK Plus New Labelling' or 'OK Plus New Title' allows the definition of more than one label or title with a short closing and reopening of the dialogue 'Spectrum Labelling 1' or 'Spectrum Title 1'.
 - e) The commands '-DS' and 'DS+' permits the simultaneous decreasing and increasing of the text size without closing the dialogue. The changed text size is saved automatically and is used for a new activation of a dialogue.
6. New functions were implemented into the dialogues 'Spectrum Labelling 2' and 'Spectrum Title 2'. These programme features allow an integration of a formatted text, figures or pictures into the spectra windows. The position and the site of the generated edit field may be defined.
7. The functionality of the popup menu of standard-spectra windows using the right mouse button was extended by:
 - a) Spectrum Labelling 2
 - b) Spectrum Title 2
 - c) Activate Resizing ,Spectrum Labelling 2'
 - d) Activate Resizing ,Spectrum Title 2'.
8. In order to increase the secure use of the program UNIFIT, open dialogues are closed in two cases:
 - a) Automatic without an information message on changing the active window.
 - b) With an information message in case of saving a Unifit project, export of data, export of images and printing out operations.
9. The internal used spectra names can be modified manually. Five options are offered:
 - a) Spectrum name without extension (multi region measurement),
 - b) Spectrum name plus batch parameter (SDP, ARXPS),
 - c) Spectrum name plus x-Axis (line scan),
 - d) Spectrum name plus y-Axis (line scan),
 - e) Spectrum name plus x-axis and plus y-axis (multipoint measurement, mapping),
 - f) Spectrum name plus batch parameter plus x-axis and plus y-axis (SDP mapping).

Main focus of the advancement to the **UNIFIT 2023** software was the optimization of the saving and loading procedure of Unifit projects and the bath processing sub-routine. The definition of the general programme parameters was improved. Additional design elements of 3D-plots were implemented. For a better and faster operation of the software the common Windows shortcuts were

integrated. The undo function was completely reworked. Some sub-routines were optimized and the functionality was extended.

1. The setting of the general programme parameters was extended. The definition of the maximal numbers of presentable processing steps inside the parameter plot was implemented. The call 'Typical Values' is new option.
2. In order to reduce the storage space of Unifit projects the sub-routines 'Save Projects', 'Save Projects as...' and 'Load Projects' were completely reworked and optimized. The storage space was reduced up to five with respect to the version UNIFIT 2022. Now, the saving and loading of Unifit projects with more than 50,000 spectra are well possible and practicable.
3. Because a file-copy operation of the measurement data files is now implemented into the saving procedure of Unifit projects, the generation and saving of backup-files can take a lot of processing time. Therefore, the generation of backup files of the Unifit projects can now activated or deactivated. The pull-down call is: [Preferences – Create and Save Unifit-Project Backup Files]. If the generation and saving of backup files is activated and the number of standard windows is larger than 1000, an additional message box will be opened.
4. The procedure 'Marker Lines' was reworked. Now, the position and length of marker lines are correct displayed and plotted after a resize-windows operation.
5. New fill colour and colour of the lines of 3D plots can be generated automatically. The calculation is carried out using a randomize operation.
6. The common Windows shortcuts were implemented into the software Unifit. Five ways to activate a call are available (not for all sub-routine):
 - a. Pull-down commands
 - b. Shortcut with 'Alt-Charcter'
 - c. Pop-up commands
 - d. Shortcut with 'Ctrl-Charcter'
 - e. Icons (The number, the functionality and the size of the icons can be defined by the user.)

| | |
|----------|--|
| ▪ Ctrl-a | Programme-Internal Copying |
| ▪ Ctrl-b | Fit Background |
| ▪ Ctrl-c | Charge Correction |
| ▪ Ctrl-d | Differentiation |
| ▪ Ctrl-e | Expansion |
| ▪ Ctrl-f | Fit-Parameter Table |
| ▪ Ctrl-g | Calculate Background (previous call) |
| ▪ Ctrl-h | Subtract Background |
| ▪ Ctrl-i | Iteration |
| ▪ Ctrl-j | Edit Acquisition Parameters |
| ▪ Ctrl-k | Subtract Satellite |
| ▪ Ctrl-l | Fit-Parameter Limits Table |
| ▪ Ctrl-m | Spectrum Manipulation – Intensity Correction |
| ▪ Ctrl-n | Normalization |
| ▪ Ctrl-o | Spectrum Operation (previous call) |
| ▪ Ctrl-p | Print-Out |
| ▪ Ctrl-q | Quantification |
| ▪ Ctrl-r | Reduction |
| ▪ Ctrl-s | Save Project |
| ▪ Ctrl-t | Correction with $T(E)$ |
| ▪ Ctrl-u | Copy Image |
| ▪ Ctrl-v | Programme-Internal Insertion |
| ▪ Ctrl-w | z-Axis |
| ▪ Ctrl-x | x-Axis |
| ▪ Ctrl-y | y-Axis |
| ▪ Ctrl-z | Undo |

7. The 'Undo' function was reworked and improved. Up to 100 processing steps are saved for undo operations. All processing and design operations are supported. In former Unifit versions, one processing operation was supported only. The 'Undo' function is deactivated at the following two processes:
 - Operations at Wagner-Plot Windows
 - Batch processing operations
 - Operations at the estimation of transmission functions
 - Windows operations (close, cascade,...).
8. In order to increase the processing speed, the software code was reworked and optimized. Now, batch-processing operations using more than 50,000 spectra are well possible and practicable.
9. Now, the calculation of the normalization factor can have carried out using a defined numbers of average points (with exception the option 'Norm. to a Fixed Value'). The sub-menu 'Points to Average' can be opened directly form that menu point.
10. The sub-routines 'Calculate Background' were reworked. The background calculation can be applied to all standard windows directly activated from the menus 'Constant', 'Linear', 'Shirley', 'Tougaard' and 'Polynom+Shirley'. The additional call 'Batch Processing' is not necessary. The sub-menu 'Points to Average' can be opened directly form that menu point.
11. The sub-menu 'Information – Processing Steps' was optimized.

Leipzig, den 01.06.2022

Dr. rer. nat. Ronald Hesse

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1 General Characteristics

UNIFIT FOR WINDOWS is an universal processing, analysis and presentation software for photoelectron spectroscopy (XPS, SXPS, RESXPS and ARXPS), X-ray absorption spectroscopy (XAS XANES, NEXAFS, and XMCD), Auger electron spectroscopy (AES, SAM) and RAMAN spectroscopy based on Windows XP, Windows Vista, Windows 7, Windows 8 and Windows 10 (32-bit and 64-bit). Personal computer systems with 1 GHz processor or higher are recommended. The layout of the controls has the common Windows design. Additional design features were implemented. The usage of a SSD hard disk and the definition of the programme Unifit2023.exe as exclusion process in the used anti-virus software (e.g. Windows Defender (Win 10), Windows Security Essentials (Win 7)) may considerably reduce the loading and processing time of projects with a large number of spectra. The software can be ten times executed simultaneously.

Tab. 1. File size of UNIFIT projects of UNIFIT 2023 with respect to the former version UNIFIT 2022, SW = standard window, 3DW = 3D window, PW = parameter window

| UNIFIT project | Saved spectra windows | Storage space UNIFIT 2022 (MByte) | Storage space UNIFIT 2023 (MByte) |
|---|-----------------------|-----------------------------------|-----------------------------------|
| SAM-Mapping-256x256-PHI700.ufp | 65536 SW, 1 3DW | 275 | 149 |
| SAM-O-Ti-Si-64x64-PHI700.ufp | 4096 SW, 6 3DW | 15 | 8 |
| RAMAN-Si-Mapping-101x101.ufp | 10201 SW, 2 3DW | 133 | 26 |
| RAMAN-After-Spike-Correction.ufp | 86 SW | 1.2 | 0.2 |
| Cu2p-14300-Spectra-with-BackgroundSubtraction.ufp | 14300 SW, 1 PW | 73 | 32 |
| Si2p_AreaScan_26x26_AfterSputtering.ufp | 676 SW, 9 3DW, 1 PW | 2.6 | 1.9 |

The dynamic memory management allows the execution of UNIFIT (version 2014 or higher) using older computer systems, too, but with significant increase in computing time, especially when using the convolution of several components. The installation could be incomplete using an operation system older than Windows XP. The necessary main memory depends on the number of simultaneously processable spectra and displayed spectra windows. Table 1 gives an indication of the storage space of the UNIFIT projects. Table 2 illustrates the processing time of different processing steps of UNIFIT 2022 and UNIFI 2023 of a large number of spectra.

The programme permits the simultaneous handling of up to 75600 windows with spectra or other presentations (see Fig. 1, presentation of four standard windows). The standard windows may be generated hidden or visible. All generated standard windows (visible or hidden) may be used for the following operations (e.g. batch processing, 3D presentation, quantification, parameter plot). The number of the first standard window can be defined between 1 and 101. The parameter-plot windows, 3D windows, Wagner-plot windows and image windows can be displayed only using windows with the numbers 1 - 100 (see 3.10.3). The title line of the parent window shows the name of the project currently loaded. The X-axis of XP spectra in standard spectra windows is drawn with increasing kinetic energy or decreasing binding energy from the left to the right. The title bar includes significant information for the user (see Fig. 1). The X-axis of XA spectra is always presented with increasing photon energy, the X-axis of AES spectra is always presented with

increasing kinetic energy and the X-axis of RAMAN spectra is always presented with increasing wave number. The annotation of the energy/wave number, intensity or parameter axis will be adjusted to the chosen presentation mode. The annotation, the start and end energy/wave number, the number of increments and the number of decimal places of all axes may be changed manually by the user.

Tab. 2. Comparison of the processing time of different processing steps of UNIFIT 2022 and UNIFIT 2023, operating software: Win 10, hard disk: SSD, anti-virus software: Microsoft defender, SW = standard window, DSW = displayed standard windows, 3DW = 3D window, PW = parameter window

| UNIFIT project | Spectra windows, operation | Processing time UNIFIT 2022 | Processing time UNIFIT 2023 |
|---|--|-----------------------------|-----------------------------|
| SAM-Mapping-256x256-PHI700.ufp | 65536 SW, 1 3DW Background subtraction | 2 min 19 sec | 1 min 14 sec |
| SAM-Mapping-256x256-PHI700.ufp | 65536 SW, 1 3DW Differentiation | 1 min 51 sec | 0 min 37 sec |
| SAM-Mapping-256x256-PHI700.ufp | 65536 SW, 1 3DW Peak fit, 1 Comp., Sum, Fittable Backg. | 13 min 18 sec | 12 min 36 sec |
| RAMAN-MicroAnalysis.ufp | 2601 SW, 12 3DW, 1 PW Reduction, Peak fit, 1 Comp., Sum, Fittable Backg. | 2 min 12 sec | 2 min 05 sec |
| Cu2p-14300-Spectra-with-BackgroundSubtraction.ufp | 14300 SW, 1 PW Background subtraction | 0 min 31 sec | 0 min 13 sec |

Fifteen presentations are available:

1. **Standard:** presentation of spectra (see Fig 1), saved transmission or loss functions (see Fig 20, left),
2. **Wagner Plot:** presentation of Auger parameters (see Fig. 7).
3. **3D Waterfall 0°:** presentation of spectra, background functions, modified spectra, sum curves (after peak fit) or chemical components (after peak fit) of parameter dependent measurements in one window without x-shift (see Fig. 27).
4. **3D Waterfall 0° Plus:** presentation of fitted spectra of parameter dependent measurements without x-shift in one window (see Fig. 28).
5. **3D Waterfall 45°:** presentation of spectra, background functions, modified spectra, sum curves (after peak fit) or chemical components (after peak fit) of parameter dependent measurements in one window with x-shift to right (see Fig. 29).
6. **3D Waterfall -45°:** presentation of spectra, background functions, modified spectra, sum curves (after peak fit) or chemical components (after peak fit) of parameter dependent measurements in one window with x-shift to left (see Fig. 30).
7. **3D Colour Profile:** presentation of the intensities of spectra, background functions, modified spectra, sum curves (after peak fit) or chemical components (after peak fit) as brightness of different colours of parameter dependent measurements in one window (see Fig. 31).
8. **XY 3D Plot 45°:** presentation of
 - i) the maximum or minimum of the intensities of spectra or
 - ii) the positions of the maxima or minima or
 - iii) the areas of background free spectra or
 - v) the areas of sum curves (after peak fit) or

- v) all peak-fit results of the components (after peak fit) with respect to the x and y coordinates of multipoint (area) measurements in one window with x-shift to right (see Fig. 32),
- 9. **XY 3D Plot -45°:** presentation of
 - i) the maximum or minimum of the intensities of spectra or
 - ii) the positions of the maxima or minima or
 - iii) the areas of background free spectra or
 - v) the areas of sum curves (after peak fit) or
 - v) all peak-fit results of the components (after peak fit) with respect to the x and y coordinates of multipoint (area) measurements in one window with x-shift to left (see Fig. 33),
- 10. **XY 3D Colour Profile:** presentation of
 - i) the maximum or minimum of the intensities of spectra or
 - ii) the positions of the maxima or minima or
 - iii) the areas of background free spectra or
 - v) the areas of sum curves (after peak fit) or
 - v) all peak-fit results of the components (after peak fit) with respect to the x and y coordinates of multipoint (area) measurements as brightness in one window (see Fig. 34),
- 11. **XY 3D 45° Colour Profile:** presentation of
 - i) the maximum or minimum of the intensities of spectra or
 - ii) the positions of the maxima or minima or
 - iii) the areas of background free spectra or
 - iv) the areas of sum curves (after peak fit) or
 - v) all peak-fit results of the components (after peak fit) with respect to the x and y coordinates of multipoint (area) measurements in one window with x-shift to right (see Fig. 36),
- 12. **XY 3D -45° Colour Profile:** presentation of
 - i) the maximum or minimum of the intensities of spectra or
 - ii) the positions of the maxima or minima or
 - iii) the areas of background free spectra or
 - iv) the areas of sum curves (after peak fit) or
 - v) all peak-fit results of the components (after peak fit) with respect to the x and y coordinates of multipoint (area) measurements as brightness of different colours in one window with x-shift to left (see Fig. 37),
- 13. **Parameter Plot:** presentation of fit parameters (peak height, line position ...) or the results of quantification (peak areas, normalized peak areas ...) with respect to the parameters (sputter time, emission angle ..., see Fig. 26),
- 14. **Image:** presentation of images (e.g. corresponding SEM image to an analysed SAM measurement),
- 15. **Show Windows Video Sequence:** presentation of a short windows video sequence of standard, 3D or parameter plot windows (maximal 75600 frames using standard windows, maximal 100 frames using 3D or parameter plot windows). Only visible windows can be included into this presentation (project: Unifit_2023_User_Files\Examples\XPS\As2p3-SDP-MultiPointMeasurement-AllWindowsVideoSequence.ufp).

With the menu point **Preferences** (see 3.10) the operator can define, store and load (*.set) all setting parameters of the programme handling (see 3.10.1 and 3.10.2). In order to optimize the using of the main memory the dimension of the five general programme parameters (see 3.10.3) and the number of the first standard window (1 - 101) may be aligned to the current analysis. The toolbar can be modified and switched on or off. The size of the icons is variable (see 3.10.4 and 3.10.5). The size,

form and colour of the menu text (see 3.10.6) and table export (fit parameters, fit-parameter errors, quantification results, and XAS background parameters) may be modified independently of the spectra windows setting (see 3.10.7). The programme language is German or English (see 3.10.8). The general programme parameters, the toolbar and the language can only be changed if no window is opened. Independent from the language setting the decimal character point or comma can be used for the monitor presentation; the printout and the table export (see 3.10.9). The user can activate an automatic restore function of the UNIFIT projects and define the cyclic saving time (see 3.10.10). The layout of the printout can be equal to the monitor setting or defined separately. The loading of projects with or without the showing of saved quantification and film thickness tables is offered (see 3.10.11). The decimal character and delimiter of the exported data can be defined (see 3.10.12). Four options for the VAMAS and one option for the ScientaSES input are available (see 3.10.13). The resolution of the exported images may be changed in six levels up to 1200 dpi (see 3.10.14). The number of average points for the smoothing, differentiation and background calculation is variable (see 3.10.13.3). For the automatic spike correction the threshold multiplier and the maximal number of spikes (in %) can be defined manually (see 3.10.16). The presentation of the XP spectra may be done in kinetic energy or binding energy (see 3.10.17), the intensities in counts or cps (see 3.10.18). XA spectra are displayed invariably in photon energy, AES spectra in kinetic energy and RAMAN spectra in wave number. The form, size and colour of the curves as well as the fill colours of the fitted component areas may be selected (see 3.10.19). Additionally, the form, size and colour of the coordinate axes and all other lines are adjustable. The form, size and colour of the symbols of the parameter plot may be defined, too. The design of the printing out can be defined separately (see 3.10.20) or adapted to the display design (see 3.10.21). The presetting of the printer offers five options for the printing out of the spectra windows (see 3.10.22). In a special menu the excitation satellites for $MgK\alpha$ and $AlK\alpha$ and for two other user defined sources can be corrected and saved in up to five sets of data (see 3.10.23). The transmission function $IERF$ (or also $T(E)$) can be loaded and defined manually (see 3.10.25). UNIFIT offers different mathematical backgrounds of the model function (product, sum or convolution of Lorentzian and Gaussian functions) and fit parameters (see 3.10.26), XAS background parameters, and the XPS background parameters of inhomogeneous samples (absolute or relative) to realise the peak and background fit (see 3.10.27). The calculation of the spectral background can be selected between one background for all peak-fit components (homogeneous sample) or separate defined background functions for each peak-fit component (inhomogeneous sample, the number of peak-fit components and background functions has to be the same) (see 3.10.28). The option 'Batch Processing - Load Original Spectra' can be activated or deactivated. In case of a spike correction before the batch processing this option should be deactivated (typical for RAMAN spectra). With the option [Batch Processing - Input Number of Iterations] the number of iterations of the peak fit during the batch processing can be defined (see 3.10.29). Additionally, the user can choose from two different methods for the calculation of the fit-parameter errors (see 3.10.30).

The menu point **File** (see 3.2) includes an extended input routine (see 3.2.1). This input routine allows the direct reading of measurement data of different kinds (see book: Line Positions and Data Formats UNIFIT 2023, saved on USB-memory card). All processing steps, the window sizes, positions and design elements of all windows (hidden or shown), the quantification table as well as the film thickness estimation may be stored as one project (see 3.2.2, 3.2.10 and 3.2.11). The original measurement data are saved in a separate directory using the project name. The optionally saved backups of the projects can be opened (see 3.2.3). Additionally, templates of the processing steps and design features can be generated, saved and reloaded (see 3.2.4 and 3.2.12). The integrated test spectra and the well chosen examples enable the user to test the different functions of the programme without measured data (3.2.5). Auger parameters can be easily plotted as Wagner plot (see 3.2.6). Images (all typical data formats: wmf, tif, jpg,...) can be loaded (e.g. corresponding SEM images of a SAM measurement) (see 3.2.7). A closing function for all windows (see 3.2.8) or

all standard windows (3.2.9) is available. The presentation of the active window (see 3.2.13) all windows (see 3.2.14) or selected windows (3.2.15) can be exported as image taking a commonly used format (jpg, bmp, gif, wmf, etc.) or transferred to the clipboard via the copy–paste function (see 3.2.16). The resolution may be selected stepwise from the monitor resolution to 1200 dpi in six steps (see 3.10.14). The data achieved with the spectra analysis of the active window (see 3.2.17), of all standard windows (see 3.2.18) and before selected standard windows (3.2.19) can be quickly transferred to the standard spreadsheet software (e.g. Excel[®], Origin[®]) with an export routine. All important information is clearly shown on the direct printouts of the active window, all displayed windows or windows selected before (see 3.2.20). The menu [File – Presetting Printer...] defines the individual setting of the printing out using five options. The menus [File - Select Spectra] (see 3.2.24) and [File - Select Blocks] (see 3.2.25) allow the individual displaying of spectra from the loaded data file. The format of programme-internal spectrum name can be defined. The menu point [File - Original/Accept Preferences] allows undoing all processing steps, the reloading of the original measurement data and the refreshing of the display of the active window (see 3.2.26). With [File - Exit] the programme can be closed (see 3.2.27).

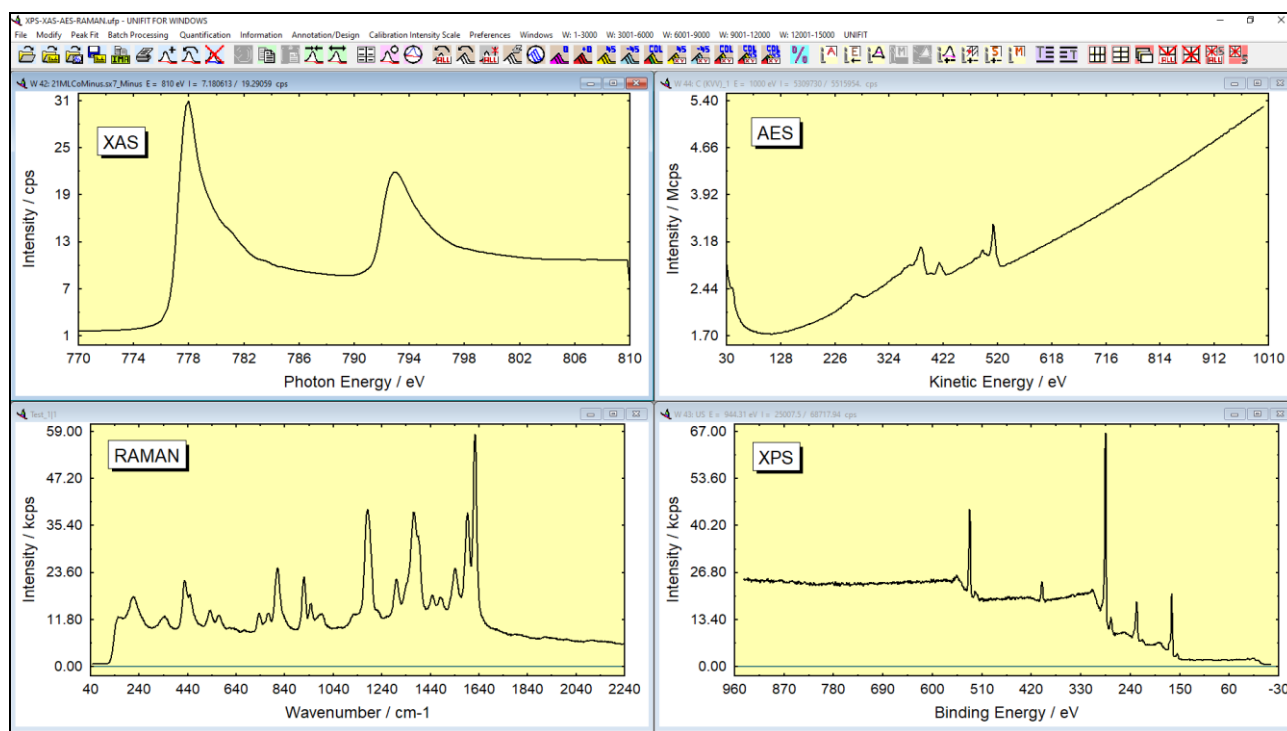


Fig. 1. Presentation of the four supported spectroscopic methods (XAS, AES, RAMAN and XPS) in four windows, project: Unifit_2023_User_Files\examples\Specials\XPS-XAS-AES-RAMAN.ufp

For the spectra **Modification** (see 3.3) menu there is an undo function for one processing step (see 3.3.1), an programme-internal copy (see 3.3.2) and programme-internal inseration function (see 3.3.3) for the duplication of a standard window with all processing steps and design features, the charge correction of the active window (see 3.3.4), a correction with the *IERF* (see 3.3.5), several procedures for the background calculation and subtraction before the peak fit (see 3.3.6), the subtraction of the spectral background (3.3.7), a satellite subtraction (see 3.3.8), reduction (see 3.3.9), expansion (see 3.3.10), differentiation (see 3.3.11), integration (see 3.3.12), mirroring (see 3.3.13), smoothing (see 3.3.14), and a manual spike correction (see 3.3.15) as well as the possibility for spectra manipulation (see 3.3.16) and operation (see 3.3.17). Additionally, a normalization routine with four different methods is available (see 3.3.18).

The **Peak Fit** (see 3.4) is based on the non-linear least squares curve-fitting algorithm of Marquardt and Levenberg. The programme allows choosing product, sum or convolution of Gaussian and Lorentzian functions for the calculation of the model function (see 3.10.26). All peak parameters may be varied independently, varied within a chosen interval or fixed at certain values. Moreover, parameters may be determined on absolute scales or they may be treated as relative parameters i.e. related to the leading peak of a doublet or to a defined master peak of a group of peaks (see 3.10.27). Different options are available, enabling the user to hold constant e.g. energy distances, peak widths or relative intensities of peaks during iteration. A very helpful option of the fit-parameter table is the labelling of the components with the corresponding names of the chemical species (e.g. for the C 1s components: -C-C-, -CH₂-, -CO-, -COOH ...). The advantage of this option is the automatic transfer of the component annotations to the following processing steps (export, batch processing, parameter plot, quantification table) providing an easy way for a correct labelling of the chemical components with both the region name and the name of the chemical component (C1s_-CH₂-, C1s_-CO- ...). Additionally, the fit-parameter table can be transferred to the clipboard with the 'Copy – Paste' functions or exported as image. Furthermore, it is possible to include the background parameters in the fit routine. Alternatively, the background can be simulated by five different methods (or combinations of them) and subtracted from the experimental curve before initiating the peak fit. Additionally, the error of the fit parameters can be calculated. Three separate sub-programmes permit the estimation of valence-band edges (see 3.4.10 and 3.4.10) or Fermi levels (see 3.4.10). The curve-fit results can be printed including fit parameters, acquisition parameters, and additional comments, or exported for further treatment and presentation.

The **Batch-processing** (see 3.5) submenu was implemented for fast analysis and presentation of parameter-dependent series of spectra (e.g. depth profiles, angle dependent measurements, multipoint (area) measurements). All options for spectra modification and the peak fit can be included in batch processing. After the batch-processing the fit-parameter results may be presented with respect to given batch parameters, X- and Y-coordinates of the measuring points, the window numbers or on a fixed parameter point. The fit parameters and fit-parameter errors of all fitted spectra can be exported and printed out. Five different presentations for parameter-dependent measurements (see 0, 3.5.13, 3.5.13, 3.5.15 and 3.5.16) and five presentations for multipoint measurements (see 3.5.16, 3.5.16, 3.5.18, 3.5.20 and 3.5.20) are available. A charge correction for all windows (see 3.5.1) or before selected windows (see 3.5.2) and a reload of the original measurement data for all (see 3.5.3) or specific selected standard windows (see 3.5.4) is available. An automatic spike correction for a large series of spectra is available (see 3.5.5). With a parameter plot the fit parameters, the background-free areas, the minima or maxima of the spectra can be plotted (3.5.8).

A **Quantitative Analysis** (see 3.6) is possible from survey or single spectra using ionization cross-sections as given by Scofield, empirical sensitivity factors by Wagner for XPS and PHI for AES or defined individually by the user. The quantification table may be transferred to the clipboard via the copy-paste function or exported as image (800 dpi) using a typical image format (jpg, wmf, gif, tif, etc.). A parameter-plot function allows the presentation of the peak areas or atom percentages with respect to the window numbers, series parameters or manually chosen values. The film thickness can be estimated by two different methods (see 0 and 3.6.3).

The **Information** (see 3.7) about the acquisition parameters (see 3.7.1) or the processing steps (see 0) of the activated standard window may be displayed any time. The charge correction (see 3.7.3), the quantities of the peak fit (see 3.7.4) and the correction of the magnetic field (see 3.7.7) (important for XMCD measurements) can be displayed of maximal 100 windows. The minimum and maximum of the intensity (see 3.7.5) of the activated standard window can be shown. The *FWHM* (see 3.7.6) of the spectrum, the modified spectrum or the peak-fit components can be displayed of the active window. The information about the path of the loaded measurement (see 3.7.8) and the project comment (see 3.7.9) is available. Identification and labelling of the XPS and

AES peaks (see 3.7.7) may be realized with the integrated data base of photoelectron lines. An additional data base of Auger parameters (see 3.7.12) can be presented as chemical state plot (Wagner plot). The data banks integrated in UNIFIT (sensitivity factors (see 3.7.14), XPS and AES line positions (see 3.7.11), Auger parameters (see 3.7.13), doublet data (see 3.7.15) and AES target atom subshells (see 3.7.19)) can be shown, edited and extended directly with special sub-programmes. The calculated inelastic electron cross-section (see 3.7.16) can be plotted. A special tool for the calculation of AES sensitivity factors (see 3.7.18) is available. Additionally, the main memory (see 3.7.17) usable and currently used by UNIFIT can be displayed.

The subroutine **Annotation/Design (see 3.8)** gives the user the manual control over the scaling and labelling of the energy/wave number (see 3.8.10), intensity (see 3.8.11), parameter axis (see 3.8.12) as well as the x and y recording position. The design setting, the spectrum title and the complete labelling of the active window, selected or all windows can be stored and reloaded (*.dsg) (see 3.8.1, 3.8.2, 3.8.3 and 3.8.4). Grid lines can be plotted optionally. Additionally, the spectrum may be entitled and labelled with formatted or unformatted text (see 3.8.5, 3.8.5, 3.8.7 and 3.8.8). The number of decimal places of the values on all axes (energy/wave number, intensity, parameter axis, X-axis and Y-axis) can be fixed. A zero line can be displayed optionally. For all window types a legend (see 3.8.9) for specifying the plotted curves can be shown. Important remarks, comments and a title may be inserted into the plot. The displaying of the intensity-energy wall, intensity-parameter wall or energy-parameter wall in the 3D waterfall 45° Plot, 3D waterfall -45° Plot, XY 3D Plot 45°, XY 3D Plot -45°, XY 3D 45° Colour Profile and XY 3D -45° Colour Profile is optionally. The acquisition parameter (see 3.8.11) (spectrum name, comment, batch parameter, pass energy, analyser mode, lens mode, x position, y position, dwell time, start and end energy, and number of accumulations) may be edited in a special sub-routine for all opened standard windows. Additionally, the batch parameters (polar angle, sputter time ...) can be changed and sorted after a generation of a 3D plot. A paste and export function allows the transfer of modified data from other software (e.g. Origin, Excel, etc.) via the clipboard. The subroutines of annotation and design can be activated using the pull down menu or by pressing the right mouse button at the appropriate mouse position. Fifteen marker lines (see 3.8.14) can be displayed using different forms.

The menu **Calibrate Intensity Scale (see 3.9)** allows the determination of the transmission function of the spectrometer in two different ways. The calculated functions can be shown, saved and used for quantification.

The **Windows (see 3.11)** handling gives the following options:

- three different tile arrangements of the windows (see 3.11.1, 3.11.2 and 3.11.3, the automatic resizing of the windows can be deactivated optionally),
- direct selection and activation of the windows, particularly next or previous ones (see 3.11.6 and 3.11.7),
- hide standard windows (see 3.11.8),
- hide standard windows (manual) (see 3.11.9),
- changing manually the window size and position (see 3.11.10),
- changing of the windows number (see 3.11.11),
- four closing functions for windows and standard windows (see 3.11.13, 3.11.14, 3.11.15 and 3.11.16),
- show windows video sequence (see 3.11.12)
- two rize options (activated or deactivated) for all windows or image windows only.

The windows sizes and positions are saved in the UNIFIT projects.

The menu point **UNIFIT** (see 3.17) gives information of the version number, the revision code, the name and address of the owner of the licence, the used Windows version as well as the contact data of the developer of the UNIFIT **software**.

Opened dialogues while using Unifit are closed in two cases:

- a) Automatic closing without an information message by changing the active window,
- a) optional closing with an information message in case of saving a Unifit project, export of data, export of images and printing out operations.

2 Theoretical Base

2.1 Background Modelling and Treatment

The shape of the spectrum background or baseline is affected by inelastic energy loss processes, secondary electrons and nearby peaks. A reasonable approximation is essential for a qualitative and quantitative analysis of XPS data especially if several components interfere in one spectrum. The subtraction of the baseline before entering the fit iterations or the calculation of the peak area can be an acceptable approximation for simple analytical problems. In order to obtain chemical and physical parameters in detail, however, it is absolutely necessary to include the background function in the iterative peak fit procedure.

The primary function $F(E)$ results from the experimentally obtained function $M(E)$ and the background function $B(E)$ as

$$F(E) = M(E) - B(E). \quad (1)$$

The energy E (XPS: kinetic energy, XAS: photon energy) of the spectra can be described as

$$E = SE + SW \cdot (i - 1). \quad (2)$$

SE represents the start energy in eV, SW is the step width in eV and i the channel number ranging from 1 to N with N been the number of data points.

If the baseline is calculated before initiating the fit procedure, the background is set to the averaged experimental function $M(E)$ in a sector around the chosen start and end channels. With i_1 as left channel (E_1 : low energy side) and i_2 as right channel (E_2 : high energy side) the simulation of the baseline is obtained as

$$B(E_1) = \bar{M}(E_1) \quad (3)$$

and

$$B(E_2) = \bar{M}(E_2). \quad (4)$$

If NAP is the preset number of points used for averaging, the intensity of the averaged measuring function at the low energy side is calculated with

$$\bar{M}(i_1) = \frac{\sum_{i=0}^{NAP-1} M(i_1 + i)}{NAP} \quad (5)$$

and at the high energy side with

$$\bar{M}(i_2) = \frac{\sum_{i=0}^{NAP-1} M(i_2 + i)}{NAP} \quad (6)$$

2.1.1 XPS/AES/RAMAN

2.1.1.1 Constant Background

The simplest possibility for background correction is the subtraction of a constant from the measured spectrum:

$$B_c(E) = c, \quad (7)$$

with

$$c = \overline{M}(E_2). \quad (8)$$

2.1.1.2 Linear Background

The linear background may be applied for spectra with small intensity differences between the low and high-energy side of the peak, e.g. for peaks derived from surface species, which are hardly affected by inelastic losses. It is calculated with

$$B_L(E) = a(E_2 - E) + c \quad (9)$$

where a results from the following equation

$$a = \frac{\overline{M}(E_1) - \overline{M}(E_2)}{E_2 - E_1}. \quad (10)$$

2.1.1.3 Polynomial Background

An additional model for the background consists of a third order polynomial B_p . The polynomial function allows the description of the contribution of secondary electrons at low kinetic energies.

$$B_p(E) = a' + b'(i_2 - i) + c'(i_2 - i)^2 + d'(i_2 - i)^3. \quad (11)$$

2.1.1.4 Shirley Background

In many cases the Shirley model [1] turned out to be a successful approximation for the inelastic background of core level peaks of buried species, which suffered significantly from inelastic losses of the emitted photoelectrons. The calculation of the baseline is an iterative procedure. The number of iteration cycles should be chosen high enough so that the shape of the obtained background function does not change anymore. The analytical expression for the Shirley background is

$$B_S(E) = \int_E^\infty F(E')dE' + c. \quad (12)$$

The algorithm of Proctor and Sherwood [2] applied in the programme UNIFIT is based on the assumption that for every point of the spectrum the background intensity generated by a photoelectron line is proportional to the number of all photoelectrons with higher kinetic energy. The intensity of the background $B_S(i)$ in channel i is given by

$$B_S(i) = \frac{(a-b)Q(i)}{P(i)+Q(i)} + b, \quad (13)$$

where a and b are the measured intensities in channel i_1 and i_2 , respectively, and $P(i)$ and $Q(i)$ represent the effective peak areas to lower and higher kinetic energies relative to the channel under consideration. An iterative procedure is necessary because P and Q are unknown. In first approximation $B_S(i) = b$ is used.

2.1.1.5 Tougaard Background

The Tougaard background model [3, 4] has originally been developed as an alternative to the Shirley background for transition metals and is therefore especially suited for asymmetrical signals like metal 4f lines. Recording a larger energy window towards lower kinetic energies or larger energy losses is recommended if this background model is intended to be applied.

The calculation is a non-iterative procedure. It integrates the experimental function while weighting it with a universal energy loss function $K(E)$ and the inelastic mean free path of the electrons λ . The background $B_{TH}(E)$ for homogeneous samples results from

$$B_{TH}(E) = \lambda \int_E^{\infty} K(E'-E) M^*(E') dE'. \quad (14)$$

and $M^*(E') = M(E') - c$ (see eqn. (8)). With the energy loss $T = E' - E$ we get the Two-parameter inelastic electron scattering cross section

$$\lambda(E) \cdot K(E, T) = \frac{BT}{(C + T^2)^2}. \quad (15)$$

or the Three-parameter inelastic electron scattering cross section

$$\lambda(E) \cdot K(E, T) = \frac{BT}{(C - T^2)^2 + DT^2}. \quad (16)$$

In order to use both loss functions [5, 6] with UNIFIT the Five-parameter inelastic electron scattering cross section with the additional parameter C' and the gap-energy parameter T_0 for a better simulation of the loss structure of insulators was created. With $C' = 1$ or $C' = -1$ and $T_0 = 0$ the inelastic electron scattering cross-sections recommended by Tougaard can be written as:

$$\lambda(E) \cdot K(E, T) = \Theta(T - T_0) \frac{B(T - T_0)}{(C + C'(T - T_0)^2)^2 + D(T - T_0)^2} \quad (17)$$

with $\Theta = 0$ for $T - T_0 \leq 0$ and $\Theta = 1$ for $T - T_0 > 0$. It is assumed that $B(E) = M^*(E)$ for a loss energy of approximately 100 eV. The values for B , C , C' , D and T_0 in the universal loss function are empirically estimated by Tougaard to be 2866 (eV)^2 , 1643 (eV)^2 , $+1$, 0 and 0 eV respectively. B , C , C' , D and T_0 can be defined manually. The parameters C , C' , D and T_0 can be adjusted manually as well as fitted using the fittable background.

The Tougaard-background method gives also the possibility to subtract the background from survey spectra. We recommend the using of the Tougaard background in case of lines with an intrinsic asymmetry (e.g. 4f-metal lines).

2.1.1.6 Polynomial + Shirley Background

The superposition of the polynomial background B_P (see eqn. (11)) and the Shirley background $B_S(E)$ generates the background B_{PS} :

$$B_{PS}(E) = B_P + e' B_S(E). \quad (18)$$

The parameter a' is fixed at the minimum of the experimental function $Min(M(E))$ while b' , c' , d' , and e' can be varied manually by the user.

2.1.1.7 Fittable Background XPS/AES/RAMAN

2.1.1.7.1 Homogeneous Samples

A rather general approach for the characterization of the background in core level photoelectron spectra takes into account all previously described contributions, weighted by the background shape parameters from a , b , c , d , e , B , C , C' , D and T_0 (with $B_S(E)$ = Shirley background and $B_{TH}(E,B,C,C',D,T_0)$ = Tougaard background for homogeneous samples):

$$B_H(E, i, \bar{p}_B) = B_P(i, a, b, c, d) + B_S(E, e) + B_{TH}(E, B, C, C', D, T_0). \quad (19)$$

The parameters a , b , c , d defines the polynomial background and e the Shirley contribution. The parameters B , C , C' , D and T_0 (17) define the inelastic electron scattering cross-section (loss function) of the Tougaard background. The Tougaard background B_{TH} in eqn. (19) and defined in eqn. (14) is calculated using a different $M^*(E') = M(E') - B_P(i, a, b, c, d)$. All parameters can be fitted parallel to the peak fit. An iterative calculation of the background in the fit procedure by including its parameters, or at least a part of them, is recommended especially for fitting photoelectron lines with a strong Lorentzian contribution.

Tab. 3. Parameters of loss function (equation (17)) by Tougaard [3] and estimated by Hesse

| Tougaard | | | | | |
|--|-------------------|-------------------|-------|-------------------|-----------------|
| Material Class | $B/(\text{eV})^2$ | $C/(\text{eV})^2$ | C' | $D/(\text{eV})^2$ | T_0/eV |
| Metal and Metal Oxides | 2866 | 1643 | +1 | 0 | 0 |
| Polymers | 434 | 551 | -1 | 436 | 0 |
| Silicon Oxides | 325 | 542 | -1 | 275 | 0 |
| Silicon | 132 | 325 | -1 | 96 | 0 |
| Germanium | 73 | 260 | -1 | 62 | 0 |
| Aluminium | 16.5 | 230 | -1 | 4.5 | 0 |
| Hesse | | | | | |
| Silicon Oxide SiO ₂ | 448 | 376 | -1.25 | 687 | 7.2 |
| Aluminium Oxide Al ₂ O ₃ | 626 | 532 | -1.67 | 1018 | 6.9 |

2.1.1.7.2 Inhomogeneous Samples

An advanced Tougaard background method for XPS measurements of laterally inhomogeneous samples requires [7] a separate background calculation for each peak-fit component SC_i . In that case $M^*(E')$ in eqn. (14) is substituted by the peak-fit components SC . The number and the sequence of peak-fit components and Tougaard-background functions have to be the same. The generation of the advanced Tougaard background is a ten steps series calculation.

The Tougaard background B_{TI} for inhomogeneous samples with k different chemical compounds or elements (k different peak-fit components) of the sample can be defined by

$$B_{TI}(E, B, C, C', D, T_0) = \lambda(E) \sum_{j=1}^k \int_E^{\infty} K_j(E, T) M_j^*(E') dE'. \quad (20)$$

with the partial spectra $M_j^*(E') = M_j(E') - B_P(i, a, b, c, d)$.

$$M^*(E) = \sum_j^k M_j^*(E). \quad (21)$$

By using of equation (14) we can also write:

$$B_{TI}(E, \vec{p}_{BT}) = \sum_{j=1}^k B_{THj}. \quad (22)$$

The number of elements of the parameter vector \vec{p}_{BT} is $5 \cdot k$. Because we have no information about the partial spectra $M_j^*(E)$ a substitution of the measured spectrum by the fit component SC_j in equation (14) is necessary.

$$B_{THj}^*(E, B_j, C_j, C'_j, D_j, T_{0j}) = \lambda(E) \int_E^\infty K_j(E, T) SC_j(E') dE'. \quad (23)$$

Because the fit components SC_j in equation (23) can generate one loss structure only, a series calculation of the advanced Tougaard background is required. With the recursion formula for the component j and the recursion steps m we can write:

$$B_{THj(1)}^*(E, B_j, C_j, C'_j, D_j, T_{0j}) = \lambda(E) \int_E^\infty K_j(E, T) SC_j(E') dE', \quad m=1 \quad (24)$$

and

$$B_{THj(m)}^*(E, B_j, C_j, C'_j, D_j, T_{0j}) = \lambda(E) \int_E^\infty K_j(E, T) [SC_j(E') + B_{THj(m-1)}^*] dE', \quad m \geq 2. \quad (25)$$

At $m = 10$ a well convergence is achieved. For one component ($j = 1$) or a homogeneous sample we can write

$$B_{TH}(E, B, C, C', D, T_0) \cong B_{TH1(10)}^*(E, B, C, C', D, T_0). \quad (26)$$

For inhomogeneous samples the Tougaard background for homogeneous samples B_{TH} is replaced by the Tougaard background for inhomogeneous samples B_{TI} and gives the universal background for inhomogeneous samples B_I

$$B_I(E, i, \vec{p}_B) = B_p(i, a, b, c, d) + B_s(E, e) + B_{TI}(E, \vec{p}_{BT}). \quad (27)$$

with the background-parameter vector \vec{p}_B and the parameters of the Tougaard background \vec{p}_{BT} . The e parameter should be settled to zero.

2.1.2 XAS

2.1.2.1 Constant Background

The simplest possibility for background correction is the subtraction of a constant from the measured spectrum:

$$B_C(E) = c, \quad (28)$$

with

$$c = \overline{M}(E_1). \quad (29)$$

2.1.2.2 Linear Background

The linear background may be applied for spectra with small intensity differences between the low and high-energy side of the peak, e.g. for peaks derived from surface species, which are hardly affected by inelastic losses. It is calculated with

$$B_L(i) = a(i - i_1) + c \quad (30)$$

where a results from the following equation

$$a = \frac{\overline{M}(i_2) - \overline{M}(i_1)}{i_2 - i_1} \quad (31)$$

2.1.2.3 Shirley Background

Although the Shirley model cannot describe the spectral background of XA spectra optimally, this simple approach is also offered for XA spectra. However, the calculation of the integral occurs in the direction of lower photon energy. The analytic formula for the Shirley background for XA spectra is

$$B_S(E) = \int_E^{E_1} F(E') dE' + c. \quad (32)$$

2.1.2.4 Tougaard-Background

The spectral background of XA spectra are not optimally described by the Tougaard model. However, this background has a similar shape as the so-called Giant function. That's why this model function also is usable with XA spectra. As for the Shirley background the calculation of the integral must also be calculated in the direction of lower photon energy. The measuring function is weighted with a universal loss function $K(T)$ and the inelastic mean free path of the electrons. $B_T(E)$ is given by

$$B_T(E) = \lambda \int_E^{E_1} K(E' - E) M^*(E') dE'. \quad (33)$$

with $M^*(E') = M(E') - c$ (see eqn. (29)).

2.1.2.5 Polynomial + Shirley Background

$B_S(E)$ is the Shirley background and b' , c' , d' and e' are manually adjustable parameters. The calculation for XA spectra is as follows with $B_S(E)$ as Shirley background

$$B_{pS}(E) = a' + b'(i - i_1) + c'(i - i_1)^2 + d'(i - i_1)^3 + e'B_S(E) \quad (34)$$

The parameter a' is the value $M(i_1)$.

2.1.2.6 Fittable Background XAS

The fittable background for XAS strongly differs from the background models for XP spectra. The background combines a 3rd order polynomial with the Shirley background or with a special step background $B'''(E)$ consisting of a sum of the error function and the Arc tangent function. The model suggested by Outka, Stöhr et al. [8] was improved and inserted in the software UNIFIT.

2.1.2.6.1 Step Background

The error function is the antiderivative of the Gaussian function. The Arc tangent function is the antiderivative of the Lorentzian function. The analytical form of the error function is given by

$$erf(E) = \frac{2}{\sqrt{\pi}} \int_0^E e^{-\tau^2} d\tau. \quad (35)$$

In the programme UNIFIT the following approximations are used. With $E_{erf} = \frac{E - E_{0S}}{1.2 \cdot \beta_S}$ and the step position E_{0S} , the *FWHM* of the step $2 \cdot \beta_S$ and the normalization factor $1.2 \cong \sqrt{\ln 4}$ we can calculate $erf(E)$ for small E_{erf} with the series expansion:

$$erf(E) = \frac{2}{\sqrt{\pi}} \left(E_{erf} - \frac{E_{erf}^3}{3} + \frac{E_{erf}^5}{10} - \frac{E_{erf}^7}{42} \right), \quad 0 \leq E_{erf} < 1 \quad (36)$$

For large values of E_{erf} the continuous fraction series expansion is used:

$$erf(E) = 1 - \frac{e^{-E_{erf}^2}}{\sqrt{\pi} \left(E_{erf} + \frac{1}{2E_{erf} + \frac{2}{E_{erf} + \frac{3}{2E_{erf}}}} \right)}, \quad E_{erf} \geq 1. \quad (37)$$

For negative values of E_{erf} we use

$$erf(E) = -erf(-E), \quad E_{erf} < 0. \quad (38)$$

The Arc tangent function will be calculated with

$$Arc \tan(E) = Arc \tan \left(\frac{E - E_{0S}}{\beta_S} \right). \quad (39)$$

The error function $erf(E)$ and the Arc tangent function $Arctan(E)$ (Fig. 2) are combined by a sum. With $M_{VS} = 0$ a pure error function is generated and $M_{VS} = 1$ results in an Arc tangent function. With the additional summand $h_S/2$ only positive function values are received. h_S is the step height.

$$B'''(E) = \frac{h_S}{2} + h_S \left(\frac{1}{2} (1 - M_{VS}) \cdot erf(E) + M_{VS} \cdot \frac{1}{\pi} Arc \tan(E) \right) \quad (40)$$

The calculation of the XAS background can be made using two different ways:

- Step number = 0: Polynomial plus Shirley background
- Step number > 0: Polynomial plus step background.

2.1.2.6.2 Step Number = 0

The background is calculated by a sum of a polynomial function and the Shirley background. The parameters a , b , c , d and e may be optimized parallel with the peak fit or fixed at a certain value. The equation

$$B(E) = a + b(i - i_1) + c(i - i_1)^2 + d(i - i_1)^3 + eB_s(E) \quad (41)$$

describes the background (B_s - Shirley background).

2.1.2.6.3 Step Number > 0

The step background to describe the spectral background of XA spectra is the generally used method. The software UNIFIT the maximal number of steps SN can be chosen freely. The maximum of SN is ten (doublets: twenty). The resulting step background is the sum of all defined step functions:

$$B'''(i) = \sum_{j=1}^{SN} B_j'''(i, \vec{p}_{Sj}). \quad (42)$$

The parameter vector \vec{p}_{Sj} includes four parameters for defining each step function j : step height h_{Sj} , mixing of error and Arc tangent function M_{VSj} , step position E_{0Sj} and the $FWHM$ of the step $2\beta_{Sj}$. The polynomial background is added to the step function in the following way: If i_{1j} is the channel number of the step function j at the photon energy $E_{0Sj} + 2\beta_{Sj}$ then we can define the following equations for the calculation of the XAS background:

$$B'''(i) = a + \sum_{j=1}^{SN} B_j'''(i, \vec{p}_{Sj}) \quad , \quad i < i_{1j} \quad (43)$$

$$B'''(i) = a + \sum_{j=1}^{SN} B_j'''(i, \vec{p}_{Sj}) + b(i - i_{1j}) + c(i - i_{1j})^2 + d(i - i_{1j})^3 \quad , \quad i \geq i_{1j} \quad (44)$$

The number of background fit parameters is twelve in case of two steps (Fig.2).

2.2 Subtraction of Satellites

A subtraction of satellites caused by non-monochromatic X-ray excitation is possible after a first approximation of the background if the main signal that is responsible for the satellites is part of the spectrum under investigation. The intensity in the spectrum produced by the $K\alpha$ satellites of the excitation source is obtained assuming energy differences and intensities as given in table 4 [9].

For a correct satellite correction, it is necessary that the main signal causing the satellites is shown in the measured spectra. The values for the satellite subtraction of the Mg and Al excitation (relative intensity, energetic position) are saved in the file 'satellite.set'. These values can be easily edited by the user in the menu Preferences - Satellite and saved in up to five separate sets of data. Additionally, two excitation sources can be defined by users. These data are saved in 'satellite1.set'.

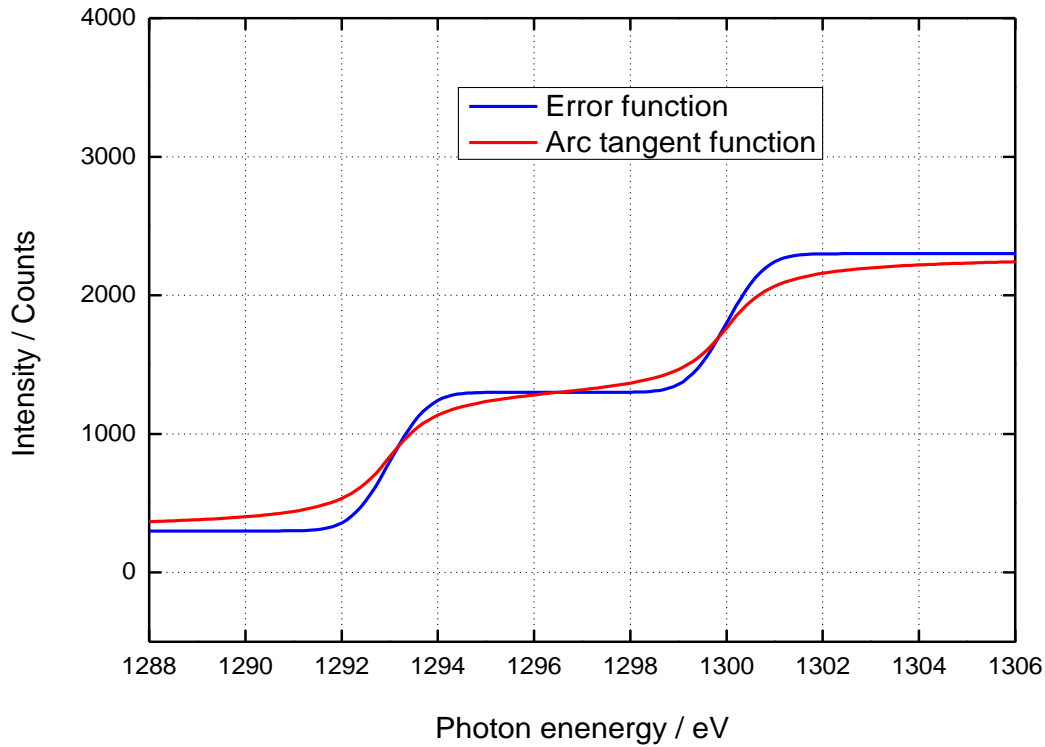


Fig. 2. Comparison of error and Arc tangent step functions for two steps (height: 1000 counts, positions: 1293 and 1300 eV, $M_{VS} = 0$ for error function and $M_{VS} = 1$ for Arc tangent function, FWHM = 1.5 eV)

Tab. 4. Intensity ratio and energy differences of Mg K α und Al K α (Set 1, see 0)

| Set 1 | $\alpha_{1,2}$ | α_3 | α_4 | α_5 | α_6 | β |
|---|----------------|------------|------------|------------|------------|---------|
| Mg excitation: Energy (eV) rel. main line | 0 | 8.4 | 10.2 | 17.5 | 20.0 | 48.5 |
| Relative Intensity | 100 | 8.0 | 4.1 | 0.55 | 0.45 | 0.5 |
| Al excitation: Energy (eV) rel. main line | 0 | 9.8 | 11.8 | 20.1 | 23.4 | 69.7 |
| Relative Intensity | 100 | 6.4 | 3.2 | 0.4 | 0.3 | 0.55 |

2.3 Differentiation

The possibility for differentiating spectra following a procedure of Proctor and Sherwood [10] represents an efficient tool for spectrum processing. This procedure allows to include the start and end channel of the spectrum and to select the width of the interval independently (optimal: $0.7 \cdot FWHM$; number of average points $NAP =$ half width of interval). The determination of peak energies and the choice of fit procedure start parameters are facilitated for spectra consisting of complex overlapping lines by using the even derivatives of the spectra [11]. With m as the half width of the interval, L is calculated by

$$L = \frac{m(4m^2 - 1)(2m + 3)(m + 1)}{3} \quad \text{mit} \quad -m < j < -m. \quad (45)$$

The derivative $dM(E)/d(E)$ results as

$$\frac{dM(j+i)}{d(i)} = \sum_{t=-m}^{t=m} \frac{(10(3t^2 - m(m+1))j + (2m-1)(2m+3)t)M(i+t)}{L}. \quad (46)$$

2.4 Smoothing

The procedure of Pavlath and Millard [11] allows to include the start and end channel of the spectrum and to select the width of the interval independently (optimal: $0.7 \cdot FWHM$; number of average points $NAP =$ half width of interval). With m as the half width of the interval, L is calculated by

$$L = \frac{m(4m^2 - 1)(2m + 3)(m + 1)}{3} \quad \text{mit} \quad m < j < -m. \quad (47)$$

The smoothed spectrum $M^*(E)$ results as

$$M^*(j+i) = \sum_{t=-m}^{t=m} \frac{((5(3t^2 - m(m+1))j^2 + (2m-1)(2m+3)tj) + m(m+1)(3m(m+1) - 1 - 5t))}{L} M(j+i). \quad (48)$$

2.5 Modelling the Peak Shape

Basically, comparing the experimental spectra with a theoretical model curve requires the analysis of core level contributions of several species as well as a background or baseline curve. Energy distribution curves in photoelectron and X-ray absorption spectroscopy may be theoretically characterized by spectral functions, which take into account all the possible excitation processes in the sample. In most cases these spectral functions may be described by a set of peaks, e.g. main line and satellites, multiplets, doublets or even single lines. The peak shapes are typically given by a Lorentzian contribution due to the limited lifetime of the core hole state and a Gaussian broadening mostly due to the measurement accuracy of the analyser. Gaussian contributions may also be related to thermal broadening. Chemical, structural, and electronic inhomogeneities in the surrounding of the emitting atom often contribute to Gaussian broadening, too.

Both the height-normalized Lorentzian function $L(E)$ (Fig. 3)

$$L(E) = \left\{ 1 + \left[\frac{(E - E_0)}{\beta} \right]^2 \right\}^{-1} \quad (49)$$

and the Gaussian function $G(E)$ (Fig. 3)

$$G(E) = \exp \left\{ - \ln 2 \frac{(E - E_0)^2}{\beta^2} \right\} \quad (50)$$

are completely characterized by the peak parameters β , i.e. half of the full width at half maximum (FWHM), and E_0 , the peak position.

2.5.1 Product and Sum Function

A frequently used approach to describe XPS core level lines or XAS line has been the product or sum of Gaussian and Lorentzian functions of the same width [12, 13]. In order to include asymmetrical lines, the peak width parameter β may be substituted by $[\beta + \alpha(E - E_0)]$ [14].

Product:

$$f(E) = h \cdot \left\{ 1 + M_V \cdot \left[\frac{E - E_0}{\beta + \alpha(E - E_0)} \right]^2 \right\}^{-1} \cdot \exp \left\{ - (1 - M_V) \cdot \ln 2 \cdot \left[\frac{E - E_0}{\beta + \alpha(E - E_0)} \right]^2 \right\}. \quad (51)$$

Sum:

$$f(E) = h \cdot M_V \cdot \left\{ 1 + \left[\frac{E - E_0}{\beta + \alpha(E - E_0)} \right]^2 \right\}^{-1} + h \cdot (1 - M_V) \cdot \exp \left\{ -\ln 2 \cdot \left[\frac{E - E_0}{\beta + \alpha(E - E_0)} \right]^2 \right\} . \quad (52)$$

Besides E_0 and β , the peak height h , the asymmetry parameter α , and the Lorentzian-Gaussian mixing ratio M_V have to be specified in this product or sum function.

The advantages of applying this product or sum peak shape model are the availability of analytical expressions for the partial derivatives of $f(E)$ with respect to the parameters, the correspondence of experimental $FWHM$ values and the analytical value of 2β , and finally a faster convergence of the iterative process as observed frequently.

2.5.2 Convolution

A more adequate description of the photoelectron- or X-ray absorption spectra line shape may be obtained by convoluting Gaussian and Lorentzian (or Doniach-Sunjic (DS) type (54)) contributions rather than by simply multiplying them [15]. This convolution, the so-called Voigt profile, is defined as follows:

$$f(E) = f(L * G) = \int_{-\infty}^{\infty} L(E') G(E - E') dE' . \quad (53)$$

Application of this peak shape model is highly recommended if the resolution is sufficient to derive physically meaningful peak shape parameters, e.g. different characteristic peak widths of Gaussian and Lorentzian. This profile function and the corresponding derivatives with respect to the parameters have to be evaluated numerically, which makes the minimization process a bit more time-consuming.

Due to a more complex photo excitation process most metal signals exhibit inherently asymmetric peak shapes, which may be taken into account by substituting the Lorentzian by the Doniach-Sunjic (DS) peak shape. It may describe the low-energy tail of the peak and is determined by the value of the so-called asymmetry parameter α . $DS(E)$ is given here as

$$DS(E) = h \cdot \frac{\cos \left\{ \pi \frac{\alpha}{2} + (1 - \alpha) \arctan \left[\frac{(E - E_0)}{\beta} \right] \right\}}{[(E - E_0)^2 + \beta^2]^{\frac{1-\alpha}{2}}} . \quad (54)$$

Notice that the Doniach-Sunjic peak shape converges into a Lorentzian in the limit of $\alpha \Rightarrow 0$.

2.5.3 Valence-Band Edge Calculation

2.5.3.1 Convolution of Square Root and Gaussian Functions

The density of states of electrons of the valence band close to the edge is approximated by a square root function. In the programme UNIFIT for modelling these edges the convolution of the square root $W(E)$ and Gaussian functions (50) is used. With

$$W(E) = \sqrt{E} \quad (55)$$

one gets equation (56) of the model function as the following

$$f(E) = f(W * G) = \int_{-\infty}^{\infty} W(E')G(E - E')dE'. \quad (56)$$

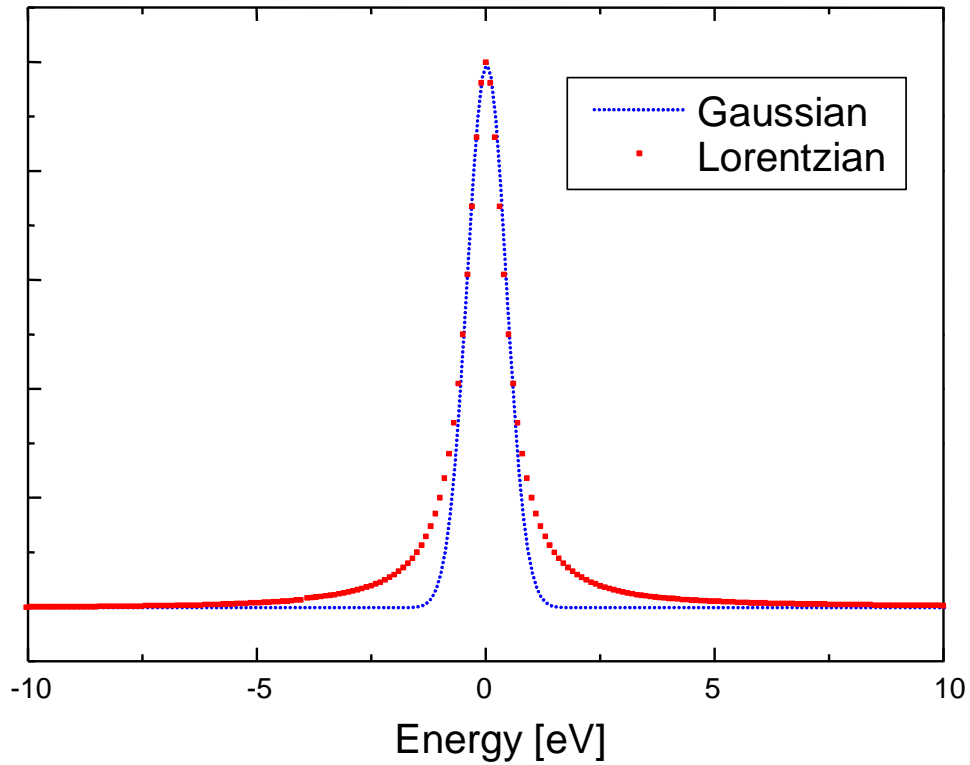


Fig. 3. Comparison of Gaussian and Lorentzian function (FWHM = 1 eV)

2.5.3.2 Convolution of Linear and Gaussian Functions

The density of states of electrons of the valence band close to the edge is also approximated by a linear function. The programme UNIFIT offers the convolution of the linear function $L_V(E)$ and Gaussian function additionally for modelling these edges. With

$$L_V(E) = mE + n \quad (57)$$

we get equation (58) of the model function as the following

$$f(E) = f(L_V * G) = \int_{-\infty}^{\infty} L_V(E')G(E - E')dE'. \quad (58)$$

2.5.4 Fermi Edge Calculation

The Fermi edge can be approached by a Theta function $\Theta(E)$. The programme UNIFIT uses the convolution of the Theta and Gaussian functions for modelling this edge. With

$$\Theta(E) = \begin{cases} I_0 & : E < E_0 \\ 0 & : E \geq E_0 \end{cases} \quad (59)$$

one gets equation (60) of the model function as the following

$$f(E) = f(\Theta * G) = \int_{-\infty}^{\infty} \Theta(E')G(E - E')dE'. \quad (60)$$

2.5.5 Chi-square

The results of the least-square method used for minimization of χ^2 are reliable if the differences between the experimental spectrum $M(i)$ and the calculated spectrum are independent and distributed homogeneously. In that case only statistical measuring errors remain.

The sum curve is given for homogeneous samples by

$$S(i, \vec{p}) = \sum_{j=1}^k SC_j(i) + B(i), \quad (61)$$

and for inhomogeneous samples by

$$S(i, \vec{p}) = \sum_{j=1}^k [SC_j(i, \vec{p}_j) + B_j(i, \vec{p}_{Bj})] + B_p, \quad (62)$$

with the functions of the components $SC_j(i)$, the background function $B(i)$ and the number of component functions k . Describing the averaged error of the experimental data $M(i)$ by the square root of $M(i)$, the sum of square errors χ^2 results in

$$\chi^2(\vec{p}) = \sum_{i=1}^N \frac{(S(i, \vec{p}) - M(i))^2}{M(i)}, \quad (63)$$

with \vec{p} the parameter vector and N the number of channels. In order to obtain the weighted sum of square errors which is minimized in UNIFIT, χ^2 is divided by the total number of degrees of freedom, i.e. by the difference between the number of channels and the total number of fit parameters F . The reduced Chi-square χ^{2*} can then be obtained as

$$\chi^{2*}(\vec{p}) = \frac{\chi^2}{N - F - 1}. \quad (64)$$

The expected value of χ^{2*} is about 1.

2.5.6 Abbe Criterion

Already small systematic deviations between the experimental data and the model can result in strong inaccuracies for the fit parameters. The *Abbe* criterion is a mean to estimate the extent of systematic errors. If the deviation of the sum curve from the spectrum under treatment is

$$R'(i) = S(i, \vec{p}) - M(i), \quad (65)$$

the *Abbe* criterion is given by

$$Abbe = \frac{1}{2} \frac{\sum_{i=1}^N (R'(i+1) - R'(i))^2}{\sum_{i=1}^N (R'(i))^2}. \quad (66)$$

The value of the *Abbe* criterion indicates the existence of correlated residuals and therefore of systematic deviations between experiment and model function. A value of 0 pinpoints systematically correlated deviations; a value of 1 indicates statistical deviations and a value of 2 is obtained in case of systematically anti-correlated deviations.

The expected value of *Abbe* is 1.

2.5.7 Residual Function

The residual R expresses the deviation between sum curve and experimental data. In the programme a normalized residual is used:

$$R(i) = \frac{S(i, \vec{p}) - M(i)}{\sqrt{M(i)}}. \quad (67)$$

The normalization with the square root of intensity was introduced in order to obtain the same weight of errors for the complete spectrum.

2.5.8 Non-linear Optimization using the Marquardt Algorithm

The criterion of an optimal description of spectra with a parameterized model function is the finding of the minimum of χ^2 (63) or χ^{2*} (64) using a defined set of parameters. χ^2 and χ^{2*} are square functions of the residuals $R(i)$ (67) to the channels i of the measurement spectrum $M(i)$.

The model function (or sum curve) $S(i, \vec{p})$ is calculated using a parameter vector \vec{p} with the P parameters. The components of the model function are described by five parameters:

Product and sum: peak height h , Lorentzian-Gaussian mixing ratio M_V , energy E_0 , full width half maximum $FWHM = 2 \cdot \beta$, asymmetry α ;

Convolution: peak height h , full width half maximum of the Gaussian peak $GP-FWHM$, energy E_0 , full width half maximum of the Lorentzian peak $LP-FWHM$, asymmetry α .

The approaching of Q components results in $5 \cdot Q$ optimizing parameters. A fit of the background (19) parallel to the fit of the component parameters increases the number of the optimizing parameters by six: $P \rightarrow P + 6$. In case of linear parameters (e.g. peak height or background parameters) χ^2 is a square function of the parameters. Then χ^2 may be minimized in one step. Otherwise a Gaussian-Newton iteration process is necessary to find the minimum of χ^2 .

Based on a start-parameter vector \vec{p} a vector of residuals $\vec{\delta p}$ is determined. This means that a step width and a step direction for the parameter optimizing are calculated by minimizing of χ^2 . The gradient of χ^2 with respect to the parameter vector \vec{p} is given by

$$\frac{\partial \chi^2}{\partial \vec{p}} = 2\mathbf{J}^T \vec{R} \quad (68)$$

with the Jacobi matrix \mathbf{J} ($i \times j$ elements)

$$\mathbf{J}(i, j) = \frac{\partial R(i)}{\partial p(j)}, \quad (69)$$

the normalized residual $R(i)$ (67) of the channel i ($i = 1 \dots N$), and the model parameters $p(j)$ ($j = 1 \dots P$).

A Taylor expansion of the model function to the first order at the starting point of the iteration step gives the following equation for estimation of $\delta\vec{p}(j)$

$$\mathbf{J}^T \mathbf{J} \cdot \delta\vec{p} = -\mathbf{J}^T \vec{R}. \quad (70)$$

This linear system of equations may be calculated directly by appropriate methods. The new improved set of parameters to describe the model function is given by $\vec{p} + \delta\vec{p}$.

In case the starting point is inside the convergence range of the χ^2 minimum then the Gaussian-Newton algorithm converges quadratic to the searched minimum. Otherwise or in case of numerical problems (a negative definite matrix $\mathbf{J}^T \mathbf{J}$) the finding of a global minimum is uncertain.

A global convergence may be obtained by using a modified Gaussian-Newton algorithm, the so-called Marquardt-Levenberg algorithm [16]. This algorithm has been chosen to minimise χ^2 , because it is well documented and is known to be very successful even for a suboptimal guess for the initial peak parameter set. The following equation is used

$$(\mathbf{J}^T \mathbf{J} + \kappa \mathbf{D}(\mathbf{J}^T \mathbf{J})) \delta\vec{p} = -\mathbf{J}^T \vec{R} \quad (71)$$

with the diagonal matrix $\mathbf{D}(\mathbf{J}^T \mathbf{J})$. $\mathbf{J}^T \mathbf{J}$ are the diagonal terms of the matrix \mathbf{D} and κ is the Marquardt parameter.

The idea of the introduction of the κ parameter is the different weighting of both the Gaussian-Newton algorithm and gradient methods. A very small κ favours the Gaussian-Newton algorithm. In contrast a large κ gives a solution close-by the gradient method.

If an iteration step is not successful then κ is increased by 10. With the same starting parameters and the larger κ a new solution $\delta\vec{p}$ is searched. If after a limited number of steps a decrease of χ^2 is found then κ is decreased and the iteration is continued up to the convergence. A decreasing step of κ by 0.4 is proved and tested in praxis.

2.5.9 Fit-Parameter Errors

The following definition [17, 18] is used in order to calculate the fit-parameter errors Δp_k : In the limit of the approximation that $\chi^2(p_k)$ has a parabolic form around the minimum, the uncertainty of one parameter shall increase χ^2 by 1. That is, if one parameter p_k is changed by an amount Δp_k and all other parameters $p_{j \neq k}$ are optimized for minimum χ^2 then the new value of χ^2 will be greater than the old value by one:

$$\chi^2(p_k + \Delta p_k) = \chi^2(p_k) + 1 \quad (72)$$

with the condition

$$\chi^{2*} \cong 1 \quad (73)$$

The calculation of Δp_k for independent parameters is shown in the following lines. We expand the left side of (72) to the second order in a Taylor series expansion.

$$\chi^2(p_k + \Delta p_k) = \chi^2(p_k) + \left. \frac{\partial \chi^2}{\partial p_k} \right|_{p_0} \Delta p_k + \frac{1}{2} \left. \frac{\partial^2 \chi^2}{\partial p_k^2} \right|_{p_0} (\Delta p_k)^2 \quad (74)$$

In the minimum of χ^2 the first derivative equals zero. The right side of (74) and the right side of (72) give

$$\chi^2(p_k)+1 = \chi^2(p_k) + \frac{1}{2} \frac{\partial^2 \chi^2}{\partial p_k^2} (\Delta p_k)^2 \quad (75)$$

and one finds for Δp_k

$$\Delta p_k = \sqrt{\frac{2}{\left(\frac{\partial^2 \chi^2}{\partial p_k^2}\right)}} \quad (76)$$

In the regular case of the calculation of fit parameters the parameters p_k are not independent and so the values $\frac{\partial^2 \chi^2}{\partial p_k^2}$ are calculated with the matrix \mathbf{H} .

$$\mathbf{H} = \begin{pmatrix} \frac{\partial^2 \chi^2}{\partial p_1^2} & \frac{\partial^2 \chi^2}{\partial p_1 \partial p_2} & \cdots & \frac{\partial^2 \chi^2}{\partial p_1 \partial p_P} \\ \frac{\partial^2 \chi^2}{\partial p_2 \partial p_1} & \frac{\partial^2 \chi^2}{\partial p_2^2} & \cdots & \frac{\partial^2 \chi^2}{\partial p_2 \partial p_P} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 \chi^2}{\partial p_P \partial p_1} & \frac{\partial^2 \chi^2}{\partial p_P \partial p_2} & \cdots & \frac{\partial^2 \chi^2}{\partial p_P^2} \end{pmatrix} \quad (77)$$

In the programme UNIFIT we use two methods for the calculation of the fit-parameter errors Δp_k .

2.5.9.1 Inverse of the Matrix \mathbf{H}

The calculation of Δp_k is made as an inversion of the matrix \mathbf{H} (77).

$$\mathbf{B} = \mathbf{H}^{-1} \quad (78)$$

The fit-parameter errors Δp_k are the square-root of twice the values of the diagonal terms b_{kk} of matrix \mathbf{B} .

$$\Delta p_k = \sqrt{2 \cdot b_{kk}} \quad (79)$$

2.5.9.2 Iterative Calculation

The idea of the iterative calculation of Δp_k is to increase Δp_k stepwise to form a new parameter $p_k = p_k + \Delta p_k$. The first values are the fit-parameter errors of independent parameters Δp_k . These values are given by the diagonal terms h_{kk} of the matrix \mathbf{H} (77).

$$\Delta p_k = \sqrt{\frac{2}{h_{kk}}} \quad (80)$$

During the new iteration to find χ_{new}^2 , p_k is fixed and all other parameters $p_{l \neq k}$ are free. When a new χ_{new}^2 is found it is compared to χ^2 . If $\chi_{new}^2 < \chi^2 + 1$ then a new p_k is calculated using an increased Δp_k , and a new iteration is started. Is the condition $\chi_{new}^2 \geq \chi^2 + 1$ true, then the first fit-parameter error Δp_{k1} is found.

Since the function χ^2 is not always exactly symmetric, the behaviour of Δp_k is also tested for negative values and Δp_{k2} calculated. The parameter Δp_k is the larger one of both Δp_{k1} and Δp_{k2} .

This procedure is made for all free parameters p_k to estimate the error Δp_k . The parameter is calculated in regards to the min/max-values as follows:

Case 1: If $p_k - p_{k,\min} \leq p_{k,\max} - p_k$ and $\Delta p_k \geq p_{k,\max} - p_k$ then $\Delta p_k = p_{k,\max} - p_k$,

Case 2: If $p_k - p_{k,\min} > p_{k,\max} - p_k$ and $\Delta p_k \geq p_k - p_{k,\min}$ then $\Delta p_k = p_k - p_{k,\min}$.

Step 1: Calculation of χ^2 and the fit-parameter errors of independent parameters of the parameter k , set $n = 1$:

$$\Delta p_{\min,k} = \sqrt{2 \cdot \left(\frac{\partial^2 \chi^2}{\partial p_k^2} \right)^{-1}}$$

Step 2: Set $p_k = p_k + \Delta p_k$, parameter k is fixed and all other free parameters are optimized to find a new χ_{new}^2 .

Step 3: $\chi_{new}^2 < \chi^2 + 1$: $n = n + 1$ go to step 2 or $\chi_{new}^2 \geq \chi^2 + 1$, $\Delta p_{k1} = n \Delta p_k$

Step 4: Repeat the procedure with $p_k = p_k - \Delta p_k$ and find the value Δp_{k2}

Step 5: $\Delta p_k = \Delta p_{k1}$,

Step 6: If $\Delta p_{k2} > \Delta p_k$ then $\Delta p_k = \Delta p_{k2}$

Step 7: Repeat the procedure with all other free fit parameters p_l .

2.5.10 Calculation of Peak-Areas Uncertainties

In the programme UNIFIT the areas $A_j(\vec{p})$ of the components j are not fit parameters. Therefore the errors of the areas of the components cannot be estimated directly from the calculation of the fit-parameter errors. In this case we calculate the errors of the areas with the following formula

$$\Delta A_j(\vec{p}) = A_j(\vec{p} + \Delta \vec{p}) - A_j(\vec{p}) \quad (81)$$

If the background $B(\vec{p}_B)$ was fitted together with the fit parameters, the error of the background $\Delta B(\vec{p}_B)$ is given by

$$\Delta B(\vec{p}_B) = B(\vec{p}_B - \Delta \vec{p}_B) - B(\vec{p}_B) \quad (82)$$

with \vec{p}_U = fit parameters of background function (a to B in (19)).

If the area of the spectrum $A_G = SW \cdot \sum_{i=1}^N [M(i) - B(i)]$, then the error of the area of the total spectrum ΔA_G is

$$\Delta A_G = SW \cdot \sum_{i=1}^N \{M(i) - [B(i) - \Delta B(i)]\} - [M(i) - B(i)] = SW \cdot \sum_{i=1}^N \Delta B(i) \quad (83)$$

with i = measurement channel, N = number of measurement points and SW is the step width in eV. The error of the component area $\Delta A_j^G(\vec{p})$ is increased with the error of the background according to the part of its component relative to the total area of the spectrum.

$$\Delta A_j^G = \Delta A_j + \frac{A_j}{A_G} \cdot \Delta A_G \quad (84)$$

For calculation of the error of relative areas $\Delta A_{R,j}^G(\vec{p})$ from component j we use

$$\Delta A_{R,j}^G = \frac{A_j}{A_G^2} \cdot \Delta A_G + \frac{1}{A_j} \cdot \Delta A_j^G. \quad (85)$$

A detailed description of the fit-parameter error calculation was published [18].

2.5.11 Calculation of FWHM Uncertainties

At the peak fit procedure using the convolution of Gaussian and Lorentzian functions the $FWHM_j(\vec{p})$ of the components j are not fit parameters. Therefore the uncertainties of the $FWHM$ of the components cannot be estimated directly from the calculation of the fit-parameter errors. In this case we calculate the errors of the $FWHM_j$ with the following formula

$$\Delta FWHM_j(\vec{p}) = FWHM_j(\vec{p} + \Delta\vec{p}) - FWHM_j(\vec{p}) \quad (86)$$

2.6 Determination of the Transmission Function

The exact knowledge of the transmission function of the spectrometer or the different spectrometer set-up may drastically improve the quantification of the measured data [19, 20]. For the calculation of the transmission function measured data of Au, Ag, Cu and Ge are used for calibration. The model of the transmission function is given by:

$$T(E) = a_0 + a_1\varepsilon + a_2\varepsilon^2 + a_3\varepsilon^3 + a_4\varepsilon^4 + b_1E^{b_2} \quad (87)$$

with E as the kinetic energy and

$$\varepsilon = \frac{(E - E_0)}{E_0}. \quad (88)$$

The fitting parameter $a_0, a_1, a_2, a_3, a_4, b_1, b_2$ and E_0 (If E_0 is zero or negative, then the default value 1000 eV is used.) are optimized during the calculation of the transmission function. Each fitting parameter can also be set to a special value and fixed. The determination of the transmission function can be done in two different procedures.

2.6.1 Fitting of Au-, Ag-, and Cu Survey Spectra

This procedure (SSA method) for the determination corresponds exactly to the fitting of reference spectra with measured spectra using the algorithm of Marquardt described in chap. 2.5. In this case, however, “true” survey spectra $S(E)$ with $T(E) = 1$, taken at the reference spectrometer [21] are fitted to the measured survey spectra $M(E)$. This fitting is done by multiplication with a transmission function having variable parameters.

$$\chi^2(a_0, a_1, a_2, a_3, a_4, b_1, b_2, E_0) = \sum \frac{[S(E)T(E, a_0, a_1, a_2, a_3, a_4, b_1, b_2, E_0) - M(E)]^2}{M(E)} \quad (89)$$

The function $T(E)$ is fitted to optimum, when χ^2 is in a minimum. The “true” survey spectra of Au, Ag, and Cu are provided with the programme UNIFIT. It is recommended to try the first fit using only the variables a_0 , b_1 and b_2 fixing all other parameters at zero and E_0 at 1000 eV.

2.6.2 Fitting of the Peak Areas

Another procedure (QPA method) for the determination of the transmission function uses the peak areas of the reference lines. The QPA method was built up from Au 4f, Au 4d, Au 4p_{3/2}, Ag 3d, Ag 3p_{3/2}, Cu 3p, Cu 2p_{3/2}, Ge 3p and Ge 2p_{3/2} standard peak areas applying adequate ionisation cross sections $\sigma(E, h\nu)$ and mean free path length $\lambda(E)$.

In order to expand the estimation of $T(E)$ using variable excitation energies, different kinetic energies of the reference peaks or different reference compounds the QPA method was improved.

With the known values of the inelastic mean free path $\lambda(E)$, the ionization cross section $\sigma(E, h\nu)$ and the peak area A under the selected photoemission signals of the reference compound the corrected peak area A' is given by

$$A' = \frac{A}{\lambda(E)\sigma(E, h\nu)T(E)} \quad (90)$$

With the known values of the inelastic mean free path $\lambda(E)$, the ionization cross section $\sigma(E, h\nu)$ and the peak area A under the selected photoemission signals of the reference compound the corrected peak area A' is given by

$$\frac{A'_1}{A'_2} \cong \frac{X_1}{X_2} \quad (91)$$

Provided that the relative quantification of two photoelectron lines 1 and 2 of a reference compound with a well-known number of atoms X_1 and X_2 using known values for cross section and mean free path and exactly estimated peak areas A gives the ratio X_1/X_2 , we can determine the transmission function $T(E)$. Using Eqn. (1) we can write

$$\frac{A'_1}{A'_2} = \frac{\frac{A_1}{\sigma_1(E, h\nu)\lambda_1(E_1)T(E_1)}}{\frac{A_2}{\sigma_2(E, h\nu)\lambda_2(E_2)T(E_2)}} = \frac{X_1}{X_2} \quad (92)$$

and the separation of $T(E_1)/T(E_2)$ gives

$$\frac{X_2 \frac{A_1}{\sigma_1(E, h\nu)\lambda_1(E_1)}}{X_1 \frac{A_2}{\sigma_2(E, h\nu)\lambda_2(E_2)}} = \frac{T(E_1)}{T(E_2)} \quad (93)$$

Introducing the normalised reference value r_i of a photoelectron peak i

$$r_i = \frac{A_i}{X_i\sigma_i(E, h\nu)\lambda_i(E_i)} \quad (94)$$

we can write for the photoelectron peak pair of peak 1 and 2

$$\frac{T(E_2) \cdot r_1}{T(E_1) \cdot r_2} = 1 \quad (95)$$

In case of photoelectron lines of the same element (e.g. pure reference samples Au, Ag, Cu or different kinetic energies of one core level) the X values are unity.

The model function for describing $T(E)$ is given by

$$T(E) = a_0 + a_1\varepsilon + a_2\varepsilon^2 + a_3\varepsilon^3 + a_4\varepsilon^4 + b_1E_0^{b_2} \quad (96)$$

with the fit parameters $a_0, a_1, a_2, a_3, a_4, b_1, b_2, E_0$ and $\varepsilon = (E_0 - 1000\text{eV})/1000\text{eV}$. The calculation of the reference values r_i for the photoelectron peaks of the reference compound the transmission function $T(E)$ may be approximated by minimisation of the sum of the squared deviations SSD varying the parameters of the chosen model function $T(E)$:

$$SSD = \sum_{n=1}^k \left(\frac{T(E_{2n}) \cdot r_{2n-1}(E_{2n-1})}{T(E_{2n-1}) \cdot r_{2n}(E_{2n})} - 1 \right)^2 \quad (97)$$

with k = number of pairs of photoelectron lines (max. 10).

For a better comparison of the estimated transmission functions the software UNIFIT allows the normalization at the energy E_0 :

$$T_N(E) = \frac{T(E)}{T(E_0)} \quad (98)$$

The defined limits of the parameters are: $-100 \leq a_0 \leq 100$, $-50 \leq a_1 \leq 50$, $-20 \leq a_2 \leq 20$, $-20 \leq a_3 \leq 20$, $-20 \leq a_4 \leq 20$, $200 \leq b_1 \leq 200$, $-2 \leq b_2 \leq 2$, $E_0 \geq 10 \text{ eV}$.

An essential feature of the QPA method is the plot of the input data (normalized reference peak areas) and the $T(E)$ function in one frame. Because the intensities of the input data (from 0% to 100%) and the $T(E)$ function (unlimited intensity, in the plotted energy range $T(E) > 0$) a special normalization of the input data is necessary. If Sum_1 the sum the intensities of $T(E)$ at two corresponding energies

$$Sum_1 = T(E_{2n}) + T(E_{2n-1}) \quad (99)$$

and the Sum_2 the sum of a pair of the input data

$$Sum_2 = r_{2n}(E_{2n}) + r_{2n-1}(E_{2n-1}) \quad (100)$$

then the two normalised plot values of the reference-input data r are given by

$$r_{2n,plot} = \frac{Sum_1 \cdot r_{2n}(E_{2n})}{Sum_2} \quad (101)$$

$$r_{2n-1,plot} = \frac{Sum_1 \cdot r_{2n-1}(E_{2n-1})}{Sum_2} \quad (102)$$

If E_0 is zero or negative, then the default value 1000 eV is used.

2.7 Determination of the Film Thickness

Two methods are applied for the determination of the film thickness [22]. The normalized intensities and the inelastic mean free path (*IMFP*) or alternatively the effective attenuation length (*EAL*) of the film are used.

2.7.1 Method 1 (ERXPS)

This method (ERXPS – Energy Resolved XPS) uses the different *IMFPs* of electrons at different kinetic energies if the electrons pass the film ($\lambda = \text{IMFP}$ film). For the thickness d determination the different attenuation of normalized intensities I' of the substrate in different films will be analysed.

$$d = \cos\theta \cdot \frac{\lambda(E_1)\lambda(E_2)}{\lambda(E_1) - \lambda(E_2)} \cdot \ln\left(\frac{I'(E_1)}{I'(E_2)}\right) \quad (103)$$

2.7.2 Method 2 (ARXPS)

Method 2 is the traditional angle resolved analysis (ARXPS). For determining the thickness d of the film the substrate intensities with film I and without film I_∞ at different angles θ° are used (λ is the *IMFP* or *EAL* of the film).

$$d = \lambda \cdot \cos\theta \cdot \ln\left(\frac{I_\infty(\theta)}{I(\theta)}\right) \quad (104)$$

2.8 Determination of Auger Sensitivity Factors

A pseudo-first principle technique for Auger quantification is used to calculate relative Auger yields [23].

The Auger transition probability γ is given

$$\gamma = 1 - \frac{Z^4}{Z^4 + a} \quad (105)$$

where Z is the atomic number, $a = 1.12 \cdot 10^6$ for K electrons, $6.4 \cdot 10^7$ for L electrons, $5.9 \cdot 10^8$ for M electrons and $6 \cdot 10^9$ for N electrons. The ionization cross section σ of a subshell u is given by

$$\sigma_u = \left(\frac{n_u \sigma_0}{E_C^2 U}\right) \left(\frac{U-1}{U+1}\right)^{3/2} \left\{1 + \frac{2}{3} \left(1 - \frac{1}{2U}\right) \cdot \ln\left[2.7 + (U-1)^{1/2}\right]\right\} \quad (106)$$

where σ_u is the ionization cross section of the u th level (in cm^2), n_u the electron population in the target atom subshell, $\sigma_0 = 6.56 \cdot 10^{-14}$ and $U = E_P/E_C$ ($E_P =$ excitation energy, E_C energy of the target atom subshell). The ionization cross section values were not adjusted for the effect of Coster-Kronig transitions.

The backscatter correction factors are calculated from the empirical equation

$$r_i = 1 + 2.8 \left(1 - 0.9 \frac{E_C}{E_P}\right) \cdot \eta \quad (107)$$

where

$$\eta = -0.0254 + 0.016Z - 0.000186Z^2 + 8.3 \cdot 10^{-7} Z^3 \quad (108)$$

The Auger electron emission yield σ_{AES} of the element i and transition u is calculated by

$$\sigma_{AES,i} = \gamma_i \cdot \sigma_{u,i} \cdot r_i \quad (109)$$

The Auger sensitivity factor SF of an element i for a relative quantification is therefore given by

$$SF_i = \sigma_{AES,i} \cdot \lambda_i \cdot T(E) \quad (110)$$

2.9 Automatic Spike Correction

The theoretical basic of the automatic spike correction is a modified Laplace method [24]. The spikes are corrected using the intensity of the lower measurement channel at the same spectrum and the intensities of neighbouring spectra. The maximum number of spikes (in % with respect of all measuring points, 5%...30%) and the threshold multiplier (5...100) for the identification of the spikes has to be defined by the user. The general form of the Laplace operator is give by

$$L(i, j) = 4 \cdot M(i, j) - M(i-1, j) - M(i+1, j) - M(i, j-1) - M(i, j+1) \quad (111)$$

with the measured spectrum $M(i, j)$ recorded at N energy values corresponding to channels i and spectrum j . All spectra have the same number of energy channels N .

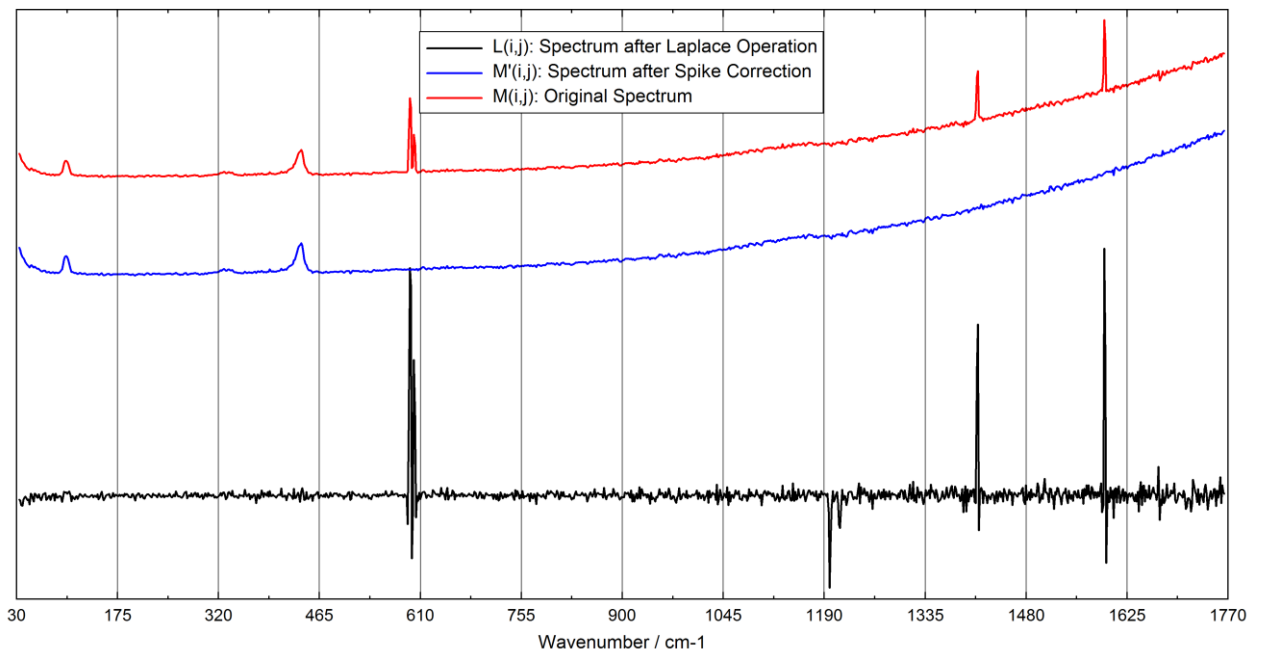


Fig. 4. Processing steps of the spike correction, red: original spectrum, black: spectrum after the Laplace operation, blue: spectrum after spike correction

The number of the recorded spectra is O . The spike correction is carried out in five steps:

1. **Definition of the threshold multiplier:** The definition of the threshold multiplier T (typically 20) and the maximal number of spikes N' (typically 5%, $N' = N \cdot 5\% / 100\%$).
2. **Generation of the Laplace spectra:** Generation of the modified spectra $L(i, j)$ using the Laplace operator for all nine possible cases is defined by (eqn. (112)):

$$L(i, j) = \begin{cases} 4 \cdot M(i, j) - M(i-1, j) - M(i+1, j) - M(i, j-1) - M(i, j+1) & 1 < i < N \quad 1 < j < O \\ 4 \cdot M(i, j) - M(i-1, j) - M(i+1, j) - 2 \cdot M(i, j+1) & 1 < i < N \quad j = 1 \\ 4 \cdot M(i, j) - M(i-1, j) - M(i+1, j) - 2 \cdot M(i, j-1) & 1 < i < N \quad j = O \\ 4 \cdot M(i, j) - 2 \cdot M(i+1, j) - M(i, j-1) - M(i, j+1) & i = 1 \quad 1 < j < O \\ 4 \cdot M(i, j) - 2 \cdot M(i-1, j) - M(i, j-1) - M(i, j+1) & i = N \quad 1 < j < O \\ 4 \cdot M(i, j) - 2 \cdot M(i+1, j) - 2 \cdot M(i, j+1) & i = 1 \quad j = 1 \\ 4 \cdot M(i, j) - 2 \cdot M(i+1, j) - 2 \cdot M(i, j-1) & i = 1 \quad j = O \\ 4 \cdot M(i, j) - 2 \cdot M(i-1, j) - 2 \cdot M(i, j+1) & i = N \quad j = 1 \\ 4 \cdot M(i, j) - 2 \cdot M(i-1, j) - 2 \cdot M(i, j-1) & i = N \quad j = O \end{cases}$$

3. **Determination of the average values $A(j)$:** The actual threshold value depends on the average intensity of the respective Laplace spectra $L(i, j)$ without the highest intensities, lowest intensities and negative values. The calculation of the reference-average values $A(j)$ of every Laplace spectrum $L(i, j)$ which is then multiplied with the defined threshold multiplier T for comparison with the Laplace spectra $L(i, j)$ is carried out using five steps:

- Determination of the channel numbers $P(k, l)$ ($k = 1 \dots N', l = 1 \dots O$) of the $N' \cdot O$ positions of the elements with the highest intensities of the two-dimensional field $L(i, j)$.
- Estimation of the channel numbers $Q(k, l)$ ($k = 1 \dots N', l = 1, \dots, O$) of the $N' \cdot O$ positions of the elements with the lowest intensities of the two-dimensional field $L(i, j)$.
- Estimation of the number of negative values $N_{neg}(j)$ of every spectrum j of the field $L(i, j)$ with exception of the elements $P(i, j)$ and $Q(i, j)$:

$$N_{neg}(j) = \sum_{i=1}^N \begin{cases} 1 & \text{for } L(i, j) < 0, \quad i \notin P(k, j), \quad i \notin Q(k, j) \\ 0 & \text{for } L(i, j) \geq 0, \quad i \in P(k, j), \quad i \in Q(k, j) \end{cases} \quad (113)$$

- Estimation of the number of channels $N_{ave}(j)$ for the calculation of $A(j)$:

$$N_{ave}(j) = N - 2 \cdot N' - N_{neg}(j) \quad (114)$$

- Calculation of $A(j)$ with exception of the channels $P(k, l)$, $Q(k, l)$ and the negative values of $L(i, j)$:

$$A(j) = \frac{1}{n_{ave}(j)} \sum_{i=1}^N L(i, j), \quad L(i, j) \geq 0, \quad i \notin P(k, j), \quad i \notin Q(k, j) \quad (115)$$

4. **Estimation of the spike positions:** Spike positions are found if the values of the Laplace spectra exceed the threshold set by the multiplication of the average value $A(j)$ and the threshold multiplier T . Thus, the definition of the positions of the spikes $P(k, j)$ of every spectrum j is defined by:

$$P(k, j) = \begin{cases} 0 & \text{for } L(P(k, j)) \leq T \cdot A(j), \quad k = 1 \dots N' \\ P(k, j) & \text{for } L(P(k, j), j) > T \cdot A(j), \quad k = 1 \dots N' \end{cases} \quad (116)$$

All channels $P(k, j) > 0$ define a spike position in the spectrum j .

5. **Spike correction:** Finally, the data points identified as spikes need to be corrected. If the channel i_s of the spectrum j is an element of $P(k, j)$ and therefore $M(i_s, j)$ is a spike, then the intensities of the five channels (if available) $M(i_s - 2, j)$, $M(i_s - 1, j)$, $M(i_s, j)$, $M(i_s + 1, j)$ and $M(i_s + 2, j)$ are changed. This is an important point because the spikes of the Laplace spectrum $L(i, j)$ are sharper with respect to the same spikes of the original spectrum $M(i, j)$. The correction is carried out consecutively (by stepping i for each spectrum j) from $M(1, 1)$, $M(2, 1)$, ... , $M(N, 1)$, $M(1, 2)$, ... , to $M(N, O)$. The actual calculation of the corrected points depends on two aspects: (i) the position of the spike and (ii) the possible presence of a neighbouring spike. In order to distinguish the latter, five different cases with adapted calculations have to be applied. The corrected spectra $M'(i, j)$ are calculated by:

Case I) The measuring points $i, i - 1$ and $i - 2$ of the spectrum $j + 1$ are **not** element of $P(k, j+1)$, $j < O$, ($k = 1...N'$) (eqn. (117)):

$$M'(i, j) = \begin{cases} (M(i-1, j) + M(i-1, j-1) + M(i-1, j+1) + M(i, j-1) + M(i, j+1))/5, & i > 1, \quad 1 < j < O \\ (M(i-1, 1) + M(i, 2) + M(i-1, 2))/3, & i > 1, \quad j = 1 \\ (M(1, j-1) + M(1, j+1))/2, & i = 1, \quad 1 < j < O \\ M(1, 2), & i = 1, \quad j = 1 \end{cases}$$

Case II) The measuring point $i, i - 1$ or $i - 2$ of the spectrum $j + 1$ is element of $P(k, j+1)$, $j < O$, ($k = 1...N'$) (eqn. (118)):

$$M'(i, j) = \begin{cases} (M(i-1, j) + M(i-1, j-1) + M(i, j-1))/3, & i > 1, \quad 1 < j < O \\ M(i-1, 1), & i > 1, \quad j = 1 \\ M(1, j-1), & i = 1, \quad 1 < j < O \\ M(1, 1), & i = 1, \quad j = 1 \end{cases}$$

Case III) The spectrum number $j = O$ (last spectrum of the series):

$$M'(i, O) = (M(i-1, O) + M(i, O-1) + M(i-1, O-1))/3, \quad i > 1, \quad j = O \quad (119)$$

$$M'(1, O) = M(1, O-1), \quad i = 1, \quad j = O \quad (120)$$

$$M'(i, j) = (M(i-1, j) + M(i, j-1) + M(i-1, j-1))/3, \quad i = N, \quad j = O \quad (121)$$

Case IV) The spectrum number $j = 1$ (first spectrum of the series) and the measuring point $i = N$ (last point in the spectrum):

$$M'(N, 1) = M(N-1, 1), \quad i = N, \quad j = 1 \quad (122)$$

Case V) The measuring points $i - 2, i - 1, i, i + 1$ and $i + 2$ of the spectrum j are **not** elements of $P(k, j)$, ($k = 1...N'$) and therefore the measuring point i is **not** a spike:

$$M'(i, j) = M(i, j) \quad (123)$$

6. Fig. 4 illustrates the different spike correction steps. Examples for a spike correction of Raman spectra are saved in the Unifit projects:

'Documents\Unifit_2023_User_Files\examples\RAMAN\RAMAN-Before-Spike-Correction.ufp' and 'Documents\Unifit_2023_User_Files\examples\RAMAN\RAMAN-After-Spike-Correction.ufp'.

3 Programme Handling

The handling of UNIFIT was designed according to common Windows[®] standards, while some details resulted from practical application. Five ways to activate a call are available (not for all sub-routine: calls are offered: **i**) Pull-down commands, **ii**) Shortcut with 'Alt-Character', **iii**) Pop-up commands, **iv**) Shortcut with 'Ctrl-Character', **v**) Icons (The number, the functionality and the size of the icons can be defined by the user). In the following terms in boxes (e.g.) refer to command buttons, while commands shown in square brackets represent pull-down or pop-up operations (e.g. [File - Open Spectra - XPS - VGX-900 (*.1)] or [Right-Mouse Button - Reduction]). A certain window can be activated by clicking the title bar with the left mouse button or by using the page-up and page-down keys. Hidden standard windows can be activated and displayed using the operation [Windows - Hide Standard Windows], [Windows - Hide Standard Windows (manual)], or with the direct activation pull-down operation (e.g. activation of window 120 with a N 1s spectrum: [W:1-3000 - W:1-200 - W 120: N 1s]). Only windows with a number lower than 150001 can be activated using the pull-down operation. Windows with a higher number (>15000) may be activated with the operation described in 3.11.8 and 3.11.9. By clicking the right mouse button at the appropriate position a pop-up menu or different sub-routines may be activated. The pop-up menu offers the following functionality:

A: All window types:

Output:

1. Save Project
2. Copy Image Active Window
3. Print Active Window

Design:

1. Marker Lines...
2. Marker of the Marker Lines (enabled if marker lines are displayed)
3. Spectrum Labelling 2...
4. Spectrum Title 2...
5. Activate Resizing Spectrum Labelling 2 (enabled if the formatted label is displayed)
6. Activate Resizing Spectrum Title 2 (enabled if the formatted title is displayed)

B: Standard Windows without defined reduction-marker lines:

Design:

1. Graph Standard Windows/Wagner Plot Display...
2. Axes/Lines/Text Display...
3. Plot Energy/Wavenumber Axis...
4. Plot Intensity Axis...

Modify:

5. Original/Accept Preferences
7. Undo
8. Programme-Internal Coping + Programme-Internal Insertion
9. Expansion

Edit:

10. Edit Spectra Names...

Peak ID:

11. Automatic Peak ID
 - with check of the main lines (not appropriated for narrow spectra)
 - Defined ΔE and ΔI are used from the Menu [Information - Identify Lines]

Quantification:

12. Use Peak for XPS Quantification (Mono) + Background (without satellite subtraction)

13. Use Peak for XPS Quantification (Twin) + Background (with satellite subtraction)
 - Background can be defined using background-subtraction routines.
 - If no annotation of the activated spectrum is available an Automatic Peak ID is carried out.

Peak Fit:

14. Fit Background XPS (HOM) (or INHOM)
15. Peak Fit Input Fit Parameters Singlet Peaks
16. Peak Fit Input Fit Parameters Doublet Peaks
17. Peak Fit Show Parameter Limits
18. Peak Fit Show Fit Parameters
19. Peak Fit Iteration

C: Standard Windows with defined and displayed reduction-marker lines:**Modify:**

1. Reduction
2. Reduction + Program-Internal Coping + Program-Internal Insertion
3. Remove Reduction Lines

Quantification:

4. Extract Peak for XPS Quantification (Mono) + Background
5. Extract Peak for XPS Quantification (Twin) + Background
 - Background can be defined using background-subtraction routines.
 - If no annotation of the activated spectrum is available an Automatic Peak ID is carried out.

D: Wagner Plot Windows:**Design:**

1. Graph Standard Windows/Wagner Plot Display...
2. Axes/Lines/Text Display...
3. Edit Window Names of the Same Type...

E: Parameter Plot Windows:**Design:**

1. Parameter Plot Display...
2. Axes/Lines/Text Display...
3. Plot Parameter Axis...
4. Plot Intensity Axis...
5. Edit Window Names of the Same Type...

G: Plot 3D Waterfall 0° Plus Windows:**Design:**

1. 3D-Plot Waterfall 0° Plus Display...
2. Axes/Lines/Text Display...
3. Plot Energy/Wavenumber Axis or Plot x-Axis
4. Plot Intensity Axis ...
5. Plot Parameter Axis...
6. Reverse Plot Parameter Axis
7. Edit Window Names of the Same Type...

H: Plot 3D Waterfall 0 Windows:**Design:**

1. 3D-Plot Waterfall/XY-3D Plot Waterfall/Color Profile Display ...
2. Axes/Lines/Text Display...
3. Plot Energy/Wavenumber Axis... or Plot X-Axis...
4. Plot Intensity Axis...
5. Plot Parameter Axis... or Plot Y-Axis...
6. Reverse Plot Parameter Axis
7. Edit Window Names of the Same Type...

8. Line of the Maxima

I: Plot 3D Waterfall 45°, Plot 3D Waterfall -45°, Plot 3D Colour Profile, XY 3D Plot 45°, XY 3D Plot -45°, XY 3D Colour Profile, XY 3D 45° Colour Profile, XY 3D -45° Colour Profile Windows:

Design:

1. 3D-Plot Waterfall/XY-3D Plot Waterfall/Color Profile Display ...
2. Axes/Lines/Text Display...
3. Plot Energy/Wavenumber Axis... or Plot X-Axis...
4. Plot Intensity Axis...
5. Parameter Plot Display... or Plot Y-Axis...
6. Reverse Plot Parameter Axis
7. Edit Window Names of the Same Type...

The direct activations of sub-routines are:

A: All window types:

1. Spectrum Title 1...
2. Spectrum Labelling 1...
3. Legend/Select Curves...
4. Axes/Lines/Text Display...

B: Standard Windows:

1. Plot Energy/Wavenumber Axis...
2. Plot Intensity Axis...

C: Parameter Plot Windows:

1. Plot Parameter Axis...
2. Plot Intensity Axis...

D: XY 3D Plot 45°, XY 3D Plot -45° Windows:

1. Plot X-Axis...
2. Plot Y-Axis...
3. Plot Intensity Axis...

E: XY 3D Colour Profile Windows:

1. Plot X-Axis...
2. Plot Y-Axis...

F: Plot 3D Waterfall 45°, Plot 3D Waterfall -45°, XY 3D 45° Colour Profile, XY 3D -45° Colour Profile Windows;

1. Plot Parameter Axis...
2. Plot Intensity Axis...
3. Plot Energy/Wavenumber Axis...

G: Plot 3D Colour Profile, Plot 3D Waterfall 0° Windows:

1. Plot Parameter Axis...
2. Plot Energy/Wavenumber Axis...

H: Plot 3D Waterfall 0° Plus Window:

1. Plot Parameter Axis...
2. Plot Energy/Wavenumber Axis...

Windows common shortcuts: The Unifit software supports the common Windows shortcuts:

- Ctrl-a Programme-Internal Copying
- Ctrl-b Fit Background
- Ctrl-c Charge Correction
- Ctrl-d Differentiation
- Ctrl-e Expansion
- Ctrl-f Fit-Parameter Table
- Ctrl-g Calculate Background (previous call)

- Ctrl-h Subtract Background
- Ctrl-i Iteration
- Ctrl-j Edit Acquisition Parameters
- Ctrl-k Subtract Satellite
- Ctrl-l Fit-Parameter Limits Table
- Ctrl-m Spectrum Manipulation – Intensity Correction
- Ctrl-n Normalization
- Ctrl-o Spectrum Operation (previous call)
- Ctrl-p Print-Out
- Ctrl-q Quantification
- Ctrl-r Reduction
- Ctrl-s Save Project
- Ctrl-t Correction with $T(E)$
- Ctrl-u Copy Image
- Ctrl-v Programme-Internal Insertion
- Ctrl-w z-Axis
- Ctrl-x x-Axis
- Ctrl-y y-Axis
- Ctrl-z Undo

In case of a window with a 3D-presentation the order of the spectra within this plot may be reversed by pressing the shift key and clicking the right mouse button or using the pop-up call. By clicking the middle button on a standard window, the acquisition parameters can be displayed. Two main types of title bars are used depending on the procedure carried out:

1. **Normal display:** In the title bar of each window the number of the window, the programme-internal peak name, the x-position of the mouse pointer i.e. the corresponding energy/wave number, the measured intensity for this energy/wave number (in case the background is displayed: difference between intensities of spectrum and background), and the intensity of the present y-position of the mouse pointer are shown simultaneously (see Fig. 1). The programme-internal peak names can be:
 - a. Spectrum name without extension (e.g. Si 2p, mux-achse
 - b. Iti region measurement),
 - c. Spectrum name plus _batch parameter (e.g. sputter time: Si 2p_80, SDP, ARXPS),
 - d. Spectrum name plus _x-axis (e.g. Si 2p_100, line scan regarding x-axis)
 - e. Spectrum name plus _y-axis (e.g. Si 2p_150, line scan regarding y-axis)
 - f. Spectrum name plus _x-axis plus |y-axis (e.g. Si 2p_100|150, multipoint measurement, mapping),
 - g. Spectrum name plus _batch parameter plus |x-axis plus |y-axis (e.g. Si 2p_80|100|150, SDP mapping).
2. **Display during peak fit:** The number of iterations, χ^{2*} , χ^2 and the *Abbe* criterion are provided in the title bar.

The name of the currently loaded project is displayed in the title bar of the parent window. When no project is loaded then the title bar shows 'New project'.

Note: The original spectra names of a measurement may not contain the characters ‘_’ and ‘|’.

3.1 Defining Ranges

Ranges for the reduction operation can be defined by placing markers on the window using the mouse. Place the mouse pointer at the desired left start position and click the left key once. This will cause a vertical reduction-marker line to appear. Now place the mouse at the end position (need to be right from the first marker) and click the left mouse key. A second marker will appear. The

marker lines can be shifted by placing the mouse over a marker line and hold the left mouse button. The reduction-marker lines may be cleared from the display by clicking the right mouse for displaying the pop-up menu and clicking the function 'Remove Reduction Lines'. A redraw of the window removes the marker lines, too. After a peak fit the marker-lines definition is deactivated.

3.2 File

The programme offers several routines for file loading, because the different software applied for spectrum acquisition produces different data formats. The programme has to access the original spectrum from time to time. Therefore, the memory device with the experimental data should not be removed or changed during the processing. Single spectra, multi-region measurements, parameter dependent measurements, line scans and multipoint (area) scans can be loaded. The acquisition parameters peak name, comment, batch parameter, analyser mode (RAMAN: exposure mode), pass energy (RAMAN: Grating), lens mode (RAMAN: Slit), excitation energy (RAMAN: laser wavelength), start and end energy (RAMAN: start and end wave number), dwell time, number of accumulations, x-position and y-position can be corrected or changed after loading the spectra using a special sub-menu of UNIFIT.

Some Unifit-input routines support the automatically loading of a series of measurement files. That permits the loading of more than one single or multi-region measurement. The batch indicator is a number on the end of the file name (one to five digits, e.g. Test_00001.vms, Test_02156.vms). The loading procedure starts from the selected file. If a file is available with the same name and a batch indicator will be greater than the old value by one, then the file is loaded additionally and so on (e.g. Test_00001.vms, Test_00002.vms, Test_00003.vms, Test_00005.vms are saved, Test_00001.vms is selected, the files Test_00001.vms, Test_00002.vms and Test_00003.vms are loaded). The loaded regions get the batch parameter of the loaded measurement file (e.g. O1s_00001, O1s_00002, ...). The batch-file loading can be used with the following Unifit-input routines: 3.2.1.1.10, 3.2.1.1.17, 3.2.1.1.18, 3.2.1.4.7 and 3.2.1.4.8.

The batch-file loading of the input routine 3.2.1.1.9 is different from the described method above. Here the file extension (e.g. *.1, *.2, ...) is the file-batch parameter.

Examples of measurement data are saved on the install USB-memory card:

XPS: XPS_Measurement_Reference_Data,

XAS: XAS_Measurement_Reference_Data,

AES: AES_Measurement_Reference_Data,

RAMAN: RAMAN_Measurement_Reference_Data.

3.2.1 Open Spectra...



This menu contains all loading routines available at the moment created on different user demands. Several regions can be loaded for some of the data formats. The names of single regions (e.g. C 1s, S 2p, O 1s, etc.) should not be used twice. All region names should not include the character 'Underline _' or a 'Vertical Line |'. The examples for experimental data files are summarized in the book 'Line Positions and Data Formats – Version 2023'. The directory accessed the latest is selected automatically. Therefore, do not remove the memory device with the experimental data. The previously applied loading routine is opened if the icon is used. Measurement files with the same name cannot be opened simultaneously. In case of

1. **parameter dependent measurements** the batch parameters (sputter time, angle ...) will be added with an underline to the region name (e.g. Si 2p_0, Si 2p_5, Si 2p_10, etc.),
2. **line scan** (all regions have the same batch parameter but different x- or y-positions) the new batch parameters are created using the x- or y-positions, the region name displayed in the title lines of the windows will be modified with the batch parameter (e.g. region name: Si 2p, x-position: 10, region name: Si 2p_10),

3. **multipoint measurements** (all regions have the same batch parameter) the new batch parameters are created using the x- and y-positions, the region name displayed in the title lines of the windows will be modified with the batch parameter (e.g. region name: Si 2p, x-position: 10, y-position: 35, region name: Si 2p_10|35),
4. **parameter dependent multipoint measurements** the region name displayed in the title lines of the windows will be modified with the batch parameter, the x-position and the y-position (e.g. region name: Si 2p, batch parameter: -90, X-position: 10, Y-position: 35, region name: Si 2p_-90|10|35).

The decimal character of the data has to be a point. A maximum of 75600 spectra can be loaded simultaneously. In case of multipoint (area) scans (without batch parameters) the batch parameter will be generated by the x- and y-positions (e.g. x-position: 12, y-position: 25, resulting batch parameter: 12|25). The usage of a SSD hard disk may considerably reduce the loading and processing time of projects with a large number of spectra. All acquisition parameters may be modified at point 3.8.11.

Note: The usage of a SSD hard disk and the definition of Unifit2023.exe as exclusion in the used anti-virus software may considerably reduce the loading and processing time of projects with a large number of spectra.

3.2.1.1 XPS

The XPS measuring data (with the exception of snapshot scans) have equidistant step widths and a monotone increasing or decreasing energy scale.

3.2.1.1.1 ESCALAB Eclipse (*.TAP;*.TXT)

The sub-menu ESCALAB allows to load data from the Eclipse programme (ESCALAB220iXL), generated by the Eclipse sub-routine 'data export' in ASCII and saved with the extension *.tap (see book 'Line Positions and Data Formats – Version 2023' 3.1.1).

3.2.1.1.2 ESCALAB/K-ALPHA Avantage (*.AVG)

The sub-menu 'ESCALAB Avantage' allows to load data from the Avantage programme, generated by the data export programme C:\VGScientific\Software\bin\DataSpace BatchDump.exe in ASCII and saved with the extension *.avg (see book 'Line Positions and Data Formats – Version 2023' 3.1.2). This routine allows the data transfer of one single region (e.g. C 1s or O 1s...) but also the conversion of parameter dependent measurements (e.g. angle resolved measurement, seven regions, 0 – 60°: C 1s 0°, C 1s 10°, ..., C 1s 60°), the loading of line and multipoint (area) scans. The x and y positions of the recording points are available. In case of a multipoint scan the batch parameters are generated using the x and y position (x|y).

Additionally, parameter dependent multipoint measurements are loadable. Then the batch parameter includes the value of the batch parameter (e.g. sputter time), the x position and the y position (e.g. SDP multipoint measurement: batch parameter = sputter time|x position|y position).

3.2.1.1.3 ESCA3 (*.TAP)

This menu option initiates the loading routine for a data format provided by special software developed for a VG ESCA3 spectrometer at the University of Leipzig (see book 'Line Positions and Data Formats – Version 2023' 3.1.3).

3.2.1.1.4 BESSY/VSI/HHUD (*.*)

With the sub-menu BESSY/VSI/HHUD it is possible to load experimental data like those recorded with the EMP software from the synchrotron storage ring BESSY. A dialogue box asks for

excitation energy and region name, because they are not included in the data file (see book ‘Line Positions and Data Formats – Version 2023’ 3.1.4 – 3.1.6).

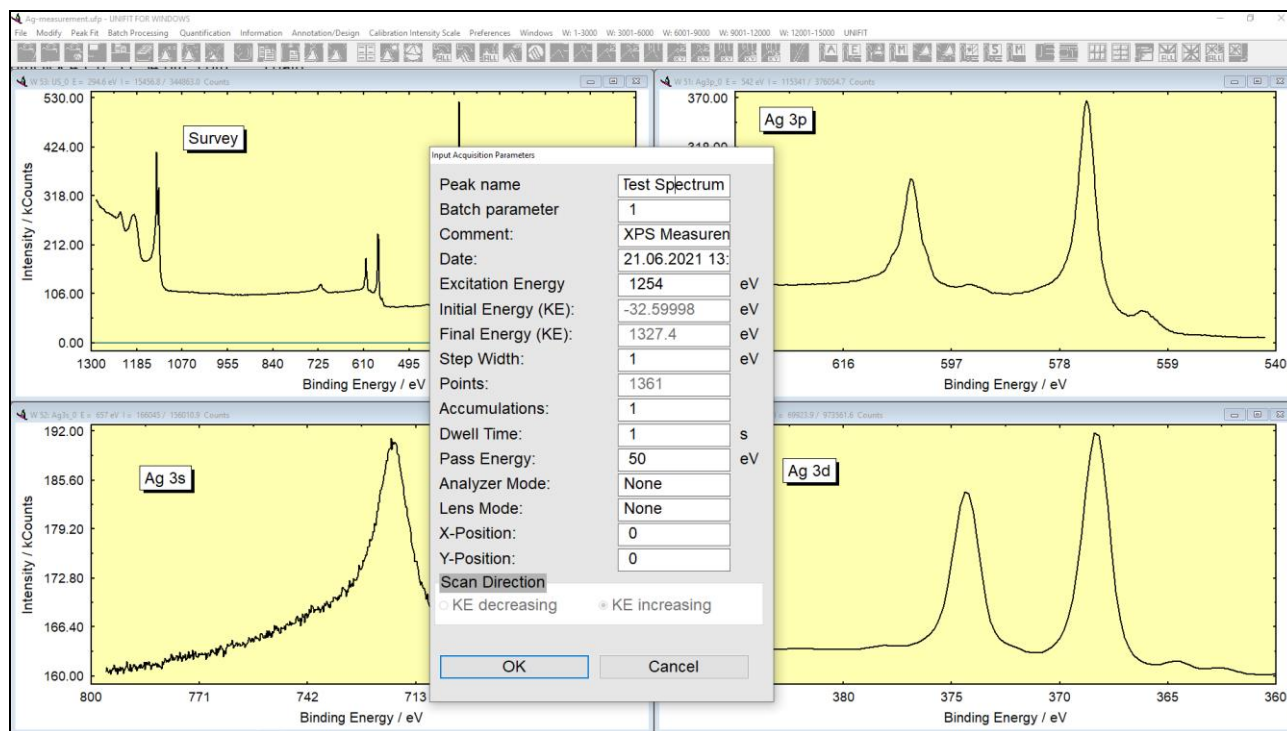


Fig. 5. Structure of the input dialogue for the manual definition of XPS acquisition parameters

3.2.1.1.5 CAF/KRATOS (*.*)

This menu item is developed for loading data in its simplest form with the energy in the first and the intensity in a second column. All remaining parameters are to be provided in a separate dialogue box (see Fig. 5). Start and end channel must be given as kinetic energies increasing from start to end. The start energy is used for controlling the data format (see book ‘Line Positions and Data Formats – Version 2023’ 3.1.7 – 3.1.8).

3.2.1.1.6 PHI-5400/5600 (*.INF + *.ASC)

The software used with PHI-5400 spectrometers provides the experimental spectrum (*.ASC) and the acquisition parameters (*.INF) in two separate files. After selection of this menu option, the *.INF file will be opened. The programme searches for the *.ASC file with the same name and opens it. The specific PHI peak names are converted into usual designations during the loading process (e.g. Ag1 to Ag 3d) (see book ‘Line Positions and Data Formats – Version 2023’ 3.1.9).

3.2.1.1.7 PHI-545/590 (*.TXT)

The software of the PHI-545/590 spectrometers permits the export of the spectra as txt-files. These created data files can be loaded with the programme UNIFIT. Three different measurement formats can be generated: single region, multi region and profile measurement format. For a correct handling of the data with UNIFIT the regions should have the usual designations (Ag 3d, Cu 2p3...) (see book ‘Line Positions and Data Formats – Version 2023’ 3.1.10).

3.2.1.1.8 PHI-1600/1600C (*.CSV)

The measurement data of the spectrometer PHI-1600/1600C can be exported as ASCII data. The acquisition parameters are saved at the top of the file. The intensities of the regions are saved at the end of the file. The CSV format allows the saving of standard spectra as well as parameter dependent measurements (see book 'Line Positions and Data Formats – Version 2023' 3.1.11).

3.2.1.1.9 VGX-900 (*.1)

The software VGX-900 supplied with VG spectrometers currently produces two files for one set of data. UNIFIT handles the measured data file in combination with a dialogue box asking for the excitation energy. The experiment name has to start with XPS (xps) or AES (aes), if the spectra were recorded with decreasing kinetic energy and with XPSREW (xpsrew) or AESREW (aesrew) in case of increasing kinetic energy. Up to ten regions can be loaded simultaneously. In case the experiment does not have the structure shown above, a dialogue is opened for specification of the scan direction (decreasing or increasing) and acquisition energy (BE or KE).

Parameter dependent (angle, sputter time) series of spectra collected with the VGX software can be loaded directly in the programme UNIFIT as well. Only files with the same name but consecutively numbered extensions are interpreted as batch. The extension is used by UNIFIT as batch parameter (see book 'Line Positions and Data Formats – Version 2023' 3.1.12).

Example 1: The files Test.1 and Test.2 and Test.5 are saved in the same directory. Loading Test.1, UNIFIT interprets only Test.1 and Test.2 as batch and loads all two spectra. The batch parameter is 1 and 2, e.g. the name of the O1s region of Test.2 appears as O1s_2, the name of the Si 2p region of Test.1 as Si2p_1.

3.2.1.1.10 VAMAS (*.VMS;*.NPL)

The VAMAS format is developed especially for chemical surface analysis with XPS. It allows transferring standard spectra, parameter-dependent measuring series (depth profiles, XPD's...), line scans, multipoint (area) scans as well for further treatment (see book 'Line Positions and Data Formats – Version 2023' 3.1.13). The x- and y-position of the recording point is available. Special options (normalization or sum operation) of the input may be selected in the menu point [Preferences – Import – VAMAS (*.VMS;*.NPL)] (3.10.13.1). In case of a multipoint scan the batch parameters are generated using the x- and y-position (x|y). This input routine supports the batch-file loading function (see 3.2).

3.2.1.1.11 VAMAS (*.VMS;*.NPL) Clipboard

Measurement data recorded in the VAMAS format and stored in the clipboard can be loaded using this menu point.

3.2.1.1.12 NPL (*.NPL)

The current VAMAS-format was developed from the NPL-data record type. Like VAMAS, the NPL-format also contains the most important measurement data, but it is less extended than VAMAS (see book 'Line Positions and Data Formats – Version 2023', 3.1.14).

3.2.1.1.13 SPECSLAB (*.EXP)

This input routine is able to read the measurement data recorded with the programme SPECSLAB especially used by the spectrometer of the SPECS brand. Data from normal as well as parameter dependent measurements are accepted. To enable UNIFIT to correctly interpret the data, it is essential that the correct name of each region (e.g. S 2p, Au 4f7...) is stated in the acquisition

parameter box “tag:” before the spectra are recorded. Intensities are read from the data set “original:” (see book ‘Line Positions and Data Formats – Version 2023’ 3.1.15).

3.2.1.1.14 VSW-Tübingen (*.DAT)

This special data format was implemented into UNIFIT for a spectrometer build by VSW for the University of Tübingen. The exact data structure is shown in the book ‘Line Positions and Data Formats – Version 2023’, 3.1.16.

3.2.1.1.15 VGS2000 (*.XPS)

This input routine reads a special data format of the University of Giessen. The excitation energy is specified using a separate dialogue box. The intensities are saved as cps (see book ‘Line Positions and Data Formats – Version 2023’ 3.1.17).

3.2.1.1.16 ScientaSES-Signals (*.TXT)

This special data format is used from the research centre of Karlsruhe (SES software). The energy values have to be stored as kinetic energy (see book ‘Line Positions and Data Formats – Version 2023’, 3.1.18).

3.2.1.1.17 ScientaSES-Spectra (*.TXT)

This special data format is generated by the Scienta spectrometer working with the SES software. The intensities split in small angle or y-axis regions (Number of slices) are saved in several columns. Two reading options are available;

1. The sum of all slices gives the intensities of the spectrum. Using this option, a series of files of a batch measurement can be loaded automatically (see 3.2).
2. The intensities of every slice are loaded in separate spectra (e.g. 3 regions, 100 slices, 300 spectra are generated, see 0),

(see book ‘Line Positions and Data Formats – Version 2023’, 3.1.19).

Multipoint measurements or line scans can be loaded if a third dimension is available (1. dimension: energy, 2. dimension: slice parameter, 3. dimension: stage position). In case the name of dimension 2 is 'y-Scale' then the slice parameters are loaded as y-position. The position of the stage defines the x-position.

3.2.1.1.18 PHI Spectrometers/Single Spectra (*.SPE)

This special different data formats (different software versions) are used from the PHI Spectrometers (e.g. VersaProbe, Quantera, ...). The acquisition parameters are saved from the line SOFH to line EOFH using the ASCII-text format. The intensity values are stored at the end of the file in single or double float format. The number of bytes of the saved intensities is four or eight times higher as the number of channels of all regions (book: ‘Line Positions and Data Formats – Version 2023’, 3.1.20.1). This input routine supports the batch-file loading (see 3.2).

3.2.1.1.19 PHI Spectrometers/SDP/ARXPS (*.PRO;*.ANG;*.MAP)

This special different data formats (different software versions) of profiles or mappings (SDP, angle-resolved measurements, etc.) is used from the PHI spectrometers (e.g. VersaProbe, Quantera, etc.). The acquisition parameters are saved from the line SOFH to line EOFH using the ASCII-text format. The intensity values are stored on the end of the file in single or double float format. The number of bytes of the saved intensities is four or eight times higher than the number of channels of all regions (book: ‘Line Positions and Data Formats – Version 2023’, 3.1.20.2 (*.PRO), 3.1.20.3 (*.ANG) and 3.1.20.4 (*.MAP)).

3.2.1.1.20 Focus CSA (*.DAT)

This special data format is used by the spectrometer Focus CSA (a special analyzer for high energies). Only one region will be saved. The header includes the recording parameters (e.g. start-, end- and excitation energy, step width, etc.). The data set with five columns includes the sum spectrum [DATA] and the single scans [DATA 1,...,[DATA 20]. The columns are: energy, intensity, three normalization values (book ,Line Positions and Data Formats – Version 2023’ 3.1.21).

The file name is used as spectrum name. Additionally, a batch parameter can be defined. The input routine allows the reading of the sum spectrum or the single scans. With the selected single scans, a new sum curve can be created. If single scans are loaded, the scan number expands the spectrum name. A spike test of the single scans and a preview can be made automatically. An optional normalization using the values of the column 3 – 5 can be carried out (see Fig. 6). The maximal number of loadable or presentable single scans is 100.

3.2.1.1.21 Croissant (*.PESP)

This special data format is used by the University Basel. Only one region will be saved. The header includes the recording parameters (e.g. start-, end- and excitation energy, step width, etc.). The data set with eight columns includes the binding energies, the kinetic energies, the sum intensities (is loaded) and the intensities of each channeltron (book ,Line Positions and Data Formats – Version 2023’ 3.1.22).

3.2.1.1.22 SSI XPS (*.MRS)

This special data format is used by the University Stanford. Only one region is saved. The header includes the recording parameters (e.g. start- end energy, step width, excitation energy, ...). Only the first data block is loaded (s. book ,Line Positions and Data Formats – Version 2023’ 3.1.23).

3.2.1.1.23 SPECS Phoibos225/Prodigy (*.XY)

This data was generated from a special converter of the spectra recording software SpecsLab/Prodigy. The SpecsLab/Prodigy software offers the following eight generation options:

1. Counts Per Second: yes/no, supported
2. Kinetic Energy Axis: yes/no, supported
3. Separate Scan Data: yes/no, supported
4. Separate Channel Data: yes/no,
5. External Channel Data: yes/no, ring current, mirror current, TEY are supported
6. Transmission Function: yes/no,
7. Asymmetry Recalculation: yes/no,
8. Error Bar: yes/no.

The acquisition parameters are stored in the header (s. book ,Line Positions and Data Formats – Version 2023’ 3.1.24). Multipoint (Area) scans include the x and y recording position of every region. Optionally the intensities, the ring current, the mirror current or the TEY data can be loaded. A normalization of the intensities with the ring current is possible. A sum curve of separate scans of the regions can be created. For the definition of the reading options see 3.10.13.3.

The step width of snapshot scans is not equidistant. Therefore, the energy values of the intensities are not used from the original data. The energy values and the step width are calculated using the initial and final energies and the number of the snapshot channels. The average energy values have uncertainties with respect to the original data of less than ± 0.02 eV.

3.2.1.1.24 HTW Berlin (*.DAT)

This special data format was implemented into UNIFIT for a spectrometer of the HTW Berlin. The exact data structure is shown in the book 'Line Positions and Data Formats – Version 2023', 3.1.26. The data comments are in German. The decimal delimiter is the comma. The first column is the energy axis in KE. The third column includes the intensities.

3.2.1.1.25 1. Column: BE decreasing/Following Columns: Intensity (*.*)

This input routine supports the simplest form of measurement data format. The 1st column includes the values of the decreasing binding energies and the following columns states the intensities. All comments without a preceding number before and after the measurement data are ignored. The characters of delimitation are arbitrary (no point!). The decimal character must be a point. The acquisition parameters:

- Excitation energy,
- Name of region,
- Comment
- Dwell time,
- Number of accumulations,
- Analyser mode,
- Pass energy,
- Lens mode,
- X position,
- Y position

are to be provided in a separate dialogue box (book 'Line Positions and Data Formats – Version 2023', 3.1.25).

3.2.1.1.26 1. Column: BE increasing/Following Columns: Intensity (*.*)

This input routine is the same as described in 3.2.1.1.25 but the binding energy is increasing (book 'Line Positions and Data Formats – Version 2023', 3.1.25).

3.2.1.1.27 1. Column: KE decreasing/Following Columns: Intensity (*.*)

This input routine is the same as described in 3.2.1.1.25 but the kinetic energy is decreasing (book 'Line Positions and Data Formats – Version 2023', 3.1.25).

3.2.1.1.28 1. Column: KE increasing/Following Columns: Intensity (*.*)

This input routine is the same as described in 3.2.1.1.25 but the kinetic energy is increasing (book 'Line Positions and Data Formats – Version 2023', 3.1.25).

3.2.1.2 XAS

XAS measuring data can be stored in non-equidistant step width and the energy scale not necessarily needs to be monotonously rising or falling. During reading data are converted into data with equidistant step width. Not available intensity values are calculated by linear interpolation. Before reading, the data are ordered according to the energy values and the step width. The smallest generated step width is 0.01 eV. The input of XAS data changes the labelling of the X-axis to 'Photon energy / eV'. All opened windows presenting an XA spectrum get an internal XAS sign for the special programme control XAS.

3.2.1.2.1 NEXAFS (*.DAT)

This special input routine reads data with non-equidistant step widths typical for NEXAFS measurements. Firstly, the smallest step width sw of the data set will be estimated. Secondly, the spectrum is converted to an equidistant form with the step width sw and a new number of data points. Not available intensity values are interpolated linearly. The X-axis will be annotated with 'Photon energy / eV'. All necessary recording parameters (pass energy, dwell time...) have to be inserted manually (book 'Line Positions and Data Formats – Version 2023', 3.2.1).

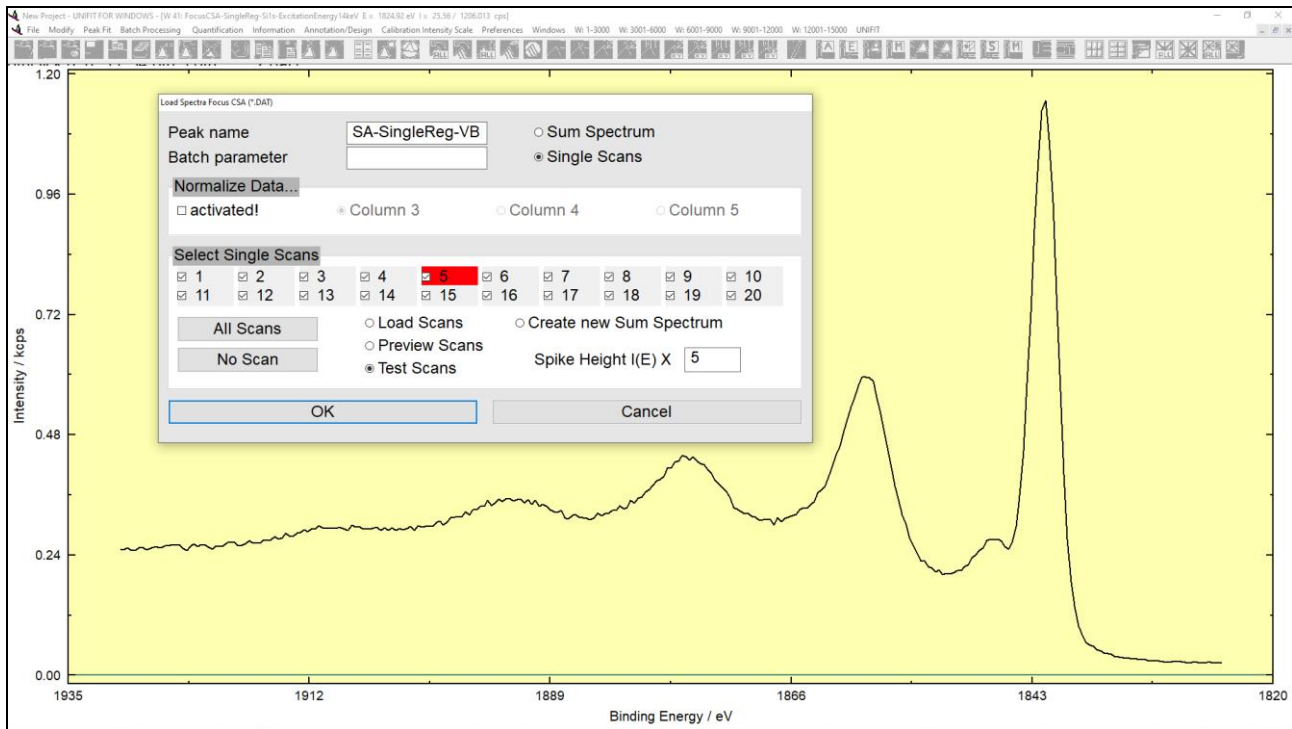


Fig. 6. Dialogue structure of the data input of the spectrometer Focus CSA

3.2.1.2.2 BESSY-EMP/2 (*.*)

The data are saved in a number of columns. (1. Column: Photon energy (increasing), next columns: intensity, reference data). The recording parameters are saved in the header (number of data points, dwell time...). A variable reading routine allows the allocation of the different columns to the correct data form. The intensities can be normalized optionally using reference data. (book 'Line Positions and Data Formats – Version 2023', 3.2.2). Start energy, end energy and step width of the input can be changed optionally.

3.2.1.2.3 MAXlab Scan Zeiss (*.SP7)

This data format is typical for the synchrotron in Lund. The data are saved in twelve columns with eleven characters. (1. Column: Photon energy (increasing), next columns: intensity, reference data). The recording parameters are saved in the header (number of data points, dwell time...). A variable reading routine allows the allocation of the different columns to the correct data form. The intensities can be normalized optionally using reference data (book 'Line Positions and Data Formats – Version 2023', 3.2.3). Start energy, end energy and step width of the input can be changed optionally.

3.2.1.2.4 Lausanne-NanoLab (*.*)

This data format is typical for the Lausanne Nanolab. The data are saved in columns with eleven characters. Every column has a title (e.g. MonoEnergy, Counter1...). A variable reading routine allows the allocation of the different columns to the correct data form. The intensities can be normalized optionally using reference data (book ‚Line Positions and Data Formats – Version 2023’, 3.2.4). Start energy, end energy and step width of the input can be changed optionally.

3.2.1.2.5 SPECS Prodigy (*.XY)

This data were generated from a special converter of the spectra recording software SpecsLab/Prodigy. The SpecsLab/Prodigy software offers the following eight-generation options:

1. Counts Per Second: yes/no, supported
2. Kinetic Energy Axis: yes/no, supported
3. Separate Scan Data: yes/no, supported
4. Separate Channel Data: yes/no,
5. External Channel Data: yes/no, ring current, mirror current, TEY are supported
6. Transmission Function: yes/no,
7. Asymmetry Recalculation: yes/no,
8. Error Bar: yes/no.

The acquisition parameters are stored in the header. The external channel data of the correct excitation energies are necessary. With the energy data sorted in the data block titled ‘# ColumnLabels: energy Excitation Energy [eV] (SISS PGM)’ a new start- and end energy, step width (minimum: 0.02 eV) and number of data points are generated. The new intensity values are extracted from the original one using linear interpolation. Optionally the intensities, the ring current, the mirror current or the TEY data can be loaded. A normalization of the intensities with the ring current is possible. A sum curve of separate scans of the regions can be created. For the definition of the reading options see 3.10.13.3 (book ‚Line Positions and Data Formats – Version 2023’, 3.2.6).

3.2.1.2.6 1. Column Photon Energy decreasing/2. Column Intensity (*.*)

This input routine supports the simplest form of measurement data format. The 1st column includes the values of the decreasing Photon energies and the 2nd column states the intensities. All comments without a preceding number before and after the measurement data are ignored. The characters of delimitation are arbitrary (no point!). The decimal character must be a point. The acquisition parameters:

- Name of region (comment),
- Dwell time,
- Number of accumulations,
- Pass energy

are to be provided in a separate dialogue box (book ‚Line Positions and Data Formats – Version 2023’, 3.2.5).

3.2.1.2.7 1. Column Photon Energy increasing/2. Column Intensity (*.*)

This input routine is the same as described in 3.2.1.2.6 but with increasing Photon energies (book ‚Line Positions and Data Formats – Version 2023’, 3.2.5).

3.2.1.3 AES

The AES measuring data have equidistant step widths and a monotone increasing or decreasing KE energy scale.

3.2.1.3.1 VAMAS (*.VMS;*.NPL)

The VAMAS format is developed especially for chemical surface analysis with XPS. It allows transferring standard spectra, parameter-dependent measuring series (depth profiles, XPD's...), line scans, multipoint (area) scans as well for further treatment (see book 'Line Positions and Data Formats – Version 2023' 3.3.1). The x and y position of the recording point is available. Special options (normalization or sum operation) of the input may be selected in the menu point [Preferences – Import – VAMAS (*.VMS;*.NPL)] (3.10.13.1). In case of a multipoint scan the batch parameters are generated using the x- and y-position (x|y)(book: 'Line Positions and Data Formats – Version 2023', 3.3.1).

3.2.1.3.2 PHI Spectrometers/Single Spectra (*.SPE)

This special different data formats (different software versions) are used from the PHI Spectrometers (e.g. PHI 700, PHI 680, ...). The acquisition parameters are saved from the line SOFH to line EOFH using the ASCII-text format. The intensity values are stored at the end of the file in single or double float format. The number of bytes of the saved intensities is four or eight times higher as the number of channels of all regions (book: 'Line Positions and Data Formats – Version 2023', 3.3.2.1).

3.2.1.3.3 PHI Spectrometers/SDP/SAM (*.PRO;*.ANG;*.MAP;*.LIN)

This special different data formats (different software versions) of profiles. Line scans or mappings (SDP, angle-resolved measurements, etc.) are used from the PHI spectrometers (e.g. PHI 700, PHI 680, etc.). The acquisition parameters are saved from the line SOFH to line EOFH using the ASCII-text format. The intensity values are stored on the end of the file in single or double float format. The number of bytes of the saved intensities is four or eight times higher than the number of channels of all regions (book: 'Line Positions and Data Formats – Version 2023', 3.3.2.2 (*.PRO) and 3.3.2.3 (*.MAP)).

If the x-y points at the energy E of a mapping have one intensity value I only, two additional points are generated during the input routine ($I(E - 1) = I(E)/100, I(E) = I(E), I(E + 1) = I(E)/100$).

3.2.1.3.4 1. Column: KE decreasing/Following Columns: Intensity (*.*)

This input routine is the same as described in 3.2.1.1.25 but the kinetic energy is decreasing.

3.2.1.3.5 1. Column: KE increasing/Following Columns: Intensity (*.*)

This input routine is the same as described in 3.2.1.1.25 but the kinetic energy is increasing.

3.2.1.4 RAMAN

RAMAN measuring data are stored in non-equidistant wave number-step width. The wave number scale is monotonously. During reading data are converted into data with equidistant step width. Not available intensity values are calculated by linear interpolation. Before reading the data are ordered according to the wave number values and the step width. The smallest generated step width is 0.01 eV. The input of RAMAN data changes the labelling of the X-axis to 'Wave number (cm-1)'. All opened windows presenting an RAMAN spectrum get an internal RAMAN sign for the special

programme control RAMAN. The acquisition parameters are adjusted to the RAMAN spectroscopy and can be checked and changed during the input procedure. The acquisition parameters are:

- Laser wavelength,
- Name of region,
- Comment
- Dwell time,
- Number of accumulations,
- Exposure mode,
- Grating,
- Slit entrance,
- Initial wave number,
- Final wave number
- X position,
- Y position.

3.2.1.4.1 S-I VistaControl (*.TVF)

This special format is created by the software VistaControl of the company S&I. The data format has a typical xml structure. All typical measurement types (single spectra, multi region spectra, batch-parameter measurement, XY mappings) can be saved. Many (not all) acquisition parameters are available (book: 'Line Positions and Data Formats – Version 2023', 3.4.1).

3.2.1.4.2 S-I VistaControl XY Multipoint/Batch Parameter Measurement (*.CSV)

This format is exported by the software VistaControl of the company S&I. The data format has a typical csv structure (1. column: wave numbers, 2. column: intensities). The header includes some acquisition parameters. In case of a multipoint measurement the number of x- and y-coordinates are the same (book: 'Line Positions and Data Formats – Version 2023', 3.4.2).

3.2.1.4.3 RRUFF (*.TXT)

This format has the RRUFF reference spectra (<http://rruff.info>). The header includes some acquisition parameters and chemical information about the reference material. The downloaded spectra are saved in a special folder: Documents\Unifit_2023_User_Files\RRUFF RAMAN spectra (book: 'Line Positions and Data Formats – Version 2023', 3.4.3).

3.2.1.4.4 EMCCD LabRam HR800 (*.TXT)

This format permits the loading of one spectrum of the spectrometer EMCCD LabRam HR800. The acquisition parameters must be defined manually. The wave number has to be decreasing (book: 'Line Positions and Data Formats – Version 2023', 3.4.4).

3.2.1.4.5 EMCCD LabRam HR800 Mapping WN Decreasing (*.TXT)

This format permits the loading of a large number of spectra of a multipoint measurement of the spectrometer EMCCD LabRam HR800. The values of the wave numbers are saved in the first line (decreasing). The positions of the recording points saved, too. The acquisition parameters must be defined manually (book: 'Line Positions and Data Formats – Version 2023', 3.4.5).

3.2.1.4.6 EMCCD LabRam HR800 Mapping WN Increasing (*.TXT)

This format permits the loading of a large number of spectra of a multipoint measurement of the spectrometer EMCCD LabRam HR800. The values of the wave numbers are saved in the first line

(increasing). The positions of the recording points saved, too. The acquisition parameters must be defined manually (book: 'Line Positions and Data Formats – Version 2023', 3.4.6).


3.2.1.4.7 1. Column: WN decreasing/Following Columns: Intensity (* .TXT;*.CSV;*.DAT)

This input routine is the same as described in 3.2.1.1.25 but the wave number is decreasing. A series of files of a batch measurement can be loaded automatically (see 3.2).

3.2.1.4.8 1. Column: WN increasing/Following Columns: Intensity (* .TXT;*.CSV;*.DAT)

This input routine is the same as described in 3.2.1.1.25 but the wave number is increasing. A series of files of a batch measurement can be loaded automatically (see 3.2).


3.2.2 Open Project...

 [File - Open Project...] realizes the input of previously saved projects. The original data files are not necessary. The preferences of fit procedure, fit parameters and all design elements for the newly opened windows are loaded together with the data. The charge correction is set for each window. The global charge correction is not changed (e.g. Unifit_2023_User_Files\examples\XPS*.ufp; Unifit_2023_User_Files\Exercises*.ufp). The windows are opened on the original size and position (before the project was saved, exception: image windows) and get the same windows number. If another window has already this number a new windows number is searched. In this case, a saved quantification table cannot be loaded. To avoid changes, close all windows before opening a project! Image windows are opened with the original X-Y pixel format of the saved image. (book 'Line Positions and Data Formats – Version 2023', 4.2).

3.2.3 Open Project Backup...

For the last five saved projects, a backup is created automatically (Project_backup_1.ufp ... Project_backup_5.ufp). The backup of the last project is named to Project_backup_5.ufp. This menu point allows the loading of the backup files.

3.2.4 Open Project Processing Steps/Design Standard Windows...

 This menu point allows the loading of previously saved processing steps (with exception of the charge correction and interpolation operations) and design features (with exception of formatted titles and annotations). This procedure is a combination of the Unifit-project procedure (see 3.2.2 and 3.2.10) and the batch-processing function (see 3.5.10). The loaded processing and design operations can be applied using all standard windows with the same name as the processing-step region (book 'Line Positions and Data Formats – Version 2023' 4.7).

Example 2: The processing steps (spectra: Unifit_2023_User_Files\test spectra\Test44-Processing-Design.ufp, processing steps/design: Test44.ppd) are saved of the regions Survey, S 2p, C 1s, N 1s and O 1s. Two multi-region measurements are loaded (maybe using the batch-file loading). Ten standard windows are opened (Survey_01, S 2p_01, C 1s_01, N-1s_01, O 1s_01, Survey_02, S 2p_02, C 1s_02, N-1s_02, O 1s_02).

1. Set the number of the first standard window to 30 with [Preferences - Setting of Programme Parameters].
2. Load the Unifit project **Test44-Processing-Design.ufp** with [File - Open Test Project...].

3. Charge correction 1.493 eV of all windows with [Batch processing - Charge Correction All Windows...].
4. Entitle of the windows with the sample numbers, the first five spectra with 'Sample 1' (batch parameter: 01) and the last five spectra with 'Sample 2' (batch parameter: 02) with:
 - 4.1 Activate the standard window 30.
 - 4.2 [Annotation/Design - Spectrum Title 1...) and the option 'Selected Windows of the Same Type'.
 - 4.3 Input of the spectrum title: Sample 1.
 - 4.4 Press A spectrum selection dialogue is opened. Select the windows 30 – 34, press The titles are displayed.
 - 4.5 Activate the standard window 35.
 - 4.6 [Annotation/Design - Spectrum Title 1...) and the option 'Selected Windows of the Same Type'.
 - 4.7 Input of the spectrum title: Sample 2.
 - 4.8 Press A spectrum selection dialogue is opened. Select the windows 35 - 39 and press . The titles are displayed.
5. Load the saved processing and design steps **Unifit_2023_User_Files\test spectra\Test44.ppd** with [File - Open Project Processing Steps/Design Standard Windows].
6. A windows-selection dialog will be displayed. Select all windows and activate the batch processing for all windows with .
7. A message box appears. The region names of the saved processing steps are shown. For a batch processing the name of the saved processing steps and the name of the loaded region has to be the same. Press for starting the batch processing of all ten regions.

3.2.5 Open Test Project...



With 'Test Spectra' it is possible to test different applications of UNIFIT and to practise the handling of the programme. 44 test spectra are integrated in the software package. All test spectra are saved as UNIFIT projects in the directory `Unifit_2023_User_Files\test spectra*.ufp`. Saved parameter sets are available for the test spectra from Test01 to Test12, Test15 and Test19, from Test01-Start.par, Test01-End.par to Test12-Start.par, Test12-End.par, from Test15-Start.par, Test15-End.par to Test17-Peak1.par, Test17-Peak2.par, Test17-Peak3.par, Test19-Start.par, Test19-End.par, Test20-Start.par, Test22-23-24-25-26-27-start.par, Test22-end.par, Test23.end.par, Test24-end.par, Test25-end.par, Test26-end, Test27-end, Test28-29-30-31-32-33-start.par, Test28-end.par, Test29-end.par, Test30-end.par, Test31-end.par, Test32-end.par, Test33-end.par, Test34-start.par, Test34-end.par, Test36-start.par, Test36-end.par, Test37-start.par, Test37-end.par, Test38-start.par, Test38-end.par, Test39-start.par, Test39-end.par, Test40-start.par, Test40-end.par, Test41-start.par, Test41-end.par, Test42-start.par, Test42-end.par, Test43-start.par, Test43-end.par (directory: `Unifit_2023_User_Files\test spectra`). The projects with '_Result' at the end of the name show the correct processing.

Test01: Voigt function (for testing convolution)

- Intensity 1000, Lorentzian line width 1 eV, peak position 190 eV, Gaussian line width 1 eV, asymmetry 0

Test02: Voigt function (for testing convolution)

- Intensity 1000, Lorentzian line width 1.7 eV, peak position 190 eV, Gaussian line width 0.3 eV, asymmetry 0

Test03: Voigt function (for testing convolution)

- Intensity 1000, Lorentzian line width 0.3 eV, peak position 190 eV, Gaussian line width 1.7 eV, asymmetry 0

Test04: Voigt function with Polynomial background (for testing the polynomial background)

- Intensity 10000, Lorentzian line width 1.7 eV, peak position 190 eV, Gaussian line width 0.3 eV, asymmetry 0, background: $105+1E+0.25E^2$

Test05: two Voigt functions + background + noise [25] (for testing the convergence behaviour)

- Peak1: Intensity 10000, Lorentzian line width 1.7 eV, peak position 192 eV, Gaussian line width 0.3 eV, asymmetry 0,
- Peak2: Intensity 50000, Lorentzian line width 0.3 eV, peak position 190 eV, Gaussian line width 1.7 eV, asymmetry 0,
- Background: $105+1E+0.25E^2$ + noise

Test06: two doublets: (for testing special parameter fixing function)

- Doublet1: Peak1: Intensity 1000, Lorentzian line width 1 eV, peak position 281 eV, Gaussian line width 1 eV, asymmetry 0,
Peak2: Intensity 700, Lorentzian line width 1 eV, peak position 283 eV, Gaussian line width 1 eV, asymmetry 0,
- Doublet2: Peak1: Intensity 800, Lorentzian line width 1 eV, peak position 280 eV, Gaussian Line Width 1 eV, asymmetry 0,
- Peak2: Intensity 560, Lorentzian line width 1 eV, peak position 282 eV, Gaussian line width 1 eV, asymmetry

Test07: Batch Processing-Voigt functions (for testing batch processing)

Sputter Depth Profile with 11 steps, z – Number of sputter steps:

- C1s: One peak 281 eV, intensity varies with z between 200 and 800 Counts,
- O1s: Two peaks,
 1. Peak 530 eV: Linear intensity decreasing with z from 1000 to 0 counts,
 2. Peak 528 eV: Linear intensity increasing with z from 0 to 1000 counts,
- Si2p: Three peaks,
 1. Peak 105 eV: Linear intensity increasing with z,
 2. Peak 103 eV: With maximum of intensity at z=5,
 3. Peak 101 eV: Exponential intensity decreasing.

Test08: Two Peaks with Shirley background [26] (for testing of model function ‘product’ and Shirley background)

Two peaks with 1 eV energy difference, mixing ratio 0.25, *FWHM* 1 eV, asymmetry 0 Shirley background.

Test09: PMMA [26]: (for testing of convergence, model function: Product type)

Four peaks, all peaks have the same mixing ratio of 0.5 and *FWHM* 1 eV:

1. Peak: Position 289 eV, intensity 16.8 %,
2. Peak: Position 286.8 eV, intensity 20.8 %,
3. Peak: Position 285.7 eV, intensity 20.8%,
4. Peak: Position 285 eV, intensity 41.6 %,

and Shirley background

Test10: PVA [26] (for testing of convergence, model function: Product type)

Four peaks, all peaks have the same mixing ratio of 0.5 and *FWHM* 1 eV:

1. Peak: Position 289.2 eV, intensity 24 %,
2. Peak: Position 286.6 eV, intensity 25 %,
3. Peak: Position 285.5 eV, intensity 25%,
4. Peak: Position 285 eV, intensity 26 %,

and Shirley background.

Test11: PVC [26] (for testing of convergence, model function: Product type)

Two peaks, both peaks have the same mixing ratio of 0.5 and *FWHM* 1 eV:

1. Peak: Position 287 eV, intensity 50 %,
2. Peak: Position 285.9 eV, intensity 50 %, and Shirley background.

Test12: PIB [26] (for testing of convergence, model function: Product type)

Three peaks, all peaks have the same mixing ratio of 0.5 and *FWHM* 1 eV:

1. Peak: Position 285.6 eV, intensity 25 %,
2. Peak: Position 285.2 eV, intensity 50 %,
3. Peak: Position 285.0 eV, intensity 25%, and Shirley background.

Test13: Satellites-Al (for testing of correctness of satellite subtraction $AlK\alpha$ -radiation)

- Main peak $\alpha_{1,2}$: 100 %, 0 eV distance to main peak ,
- Satellite peak α_3 : 6.4 %, 9.8 eV distance to main peak,
- Satellite peak α_4 : 3.2 %, 11.8 eV distance to main peak,
- Satellite peak α_5 : 0.4 %, 20.1 eV distance to main peak,
- Satellite peak α_6 : 0.3 %, 23.4 eV distance to main peak,
- Satellite peak β : 0.55 %, 69.7 eV distance to main peak.

Test14: Satellites-Mg (for testing of correctness of satellite subtraction $MgK\alpha$ -radiation)

- Main peak $\alpha_{1,2}$: 100 %, 0 eV distance to main peak,
- Satellite peak α_3 : 8.0 %, 8.4 eV distance to main peak,
- Satellite peak α_4 : 4.1 %, 10.2 eV distance to main peak,
- Satellite peak α_5 : 0.55 %, 17.5 eV distance to main peak,
- Satellite peak α_6 : 0.45 %, 20.0 eV distance to main peak,
- Satellite peak β : 0.5 %, 48.5 eV distance to main peak

Test15: Four peaks as sum of Gaussian and Lorentzian function, synthetic, (for testing the fit setting: sum)

Four peaks with a Lorentzian mixing 0.5 and a *FWHM* of 1 eV:

1. Peak position: 188.1 eV, peak height: 5000 counts
 2. Peak position: 190.1 eV, peak height: 500 counts
 3. Peak position: 192.1 eV, peak height: 2000 counts
 4. Peak position: 194.1 eV, peak height: 1000 counts
- plus a constant background of 100 counts.

Test16: Convolution of a Gaussian function and square root function (for testing the valence-band edge fitting)

1. Gauss function: *FWHM* 2.6 eV
 2. Square root function: zero point 1.5 eV
- plus a background of 30 counts.

Test17: Three spectra in three windows with well defined intensities (for testing the quantification procedure)

1. Window 1: spectrum from test 15
2. Window 2: spectrum from test 15 multiplied by two, energy shift: 500 eV
3. Window 3: spectrum from test 15 multiplied by four, energy shift: 1000 eV.

Fit parameters for the spectra are saved in test17_peak1.par, test17_peak2.par and test17_peak3.par.

Note: For a correct loading and displaying of the project Test17-Quantification_Result.ufp the following setting has to be used: [Preferences - Setting of Programme Parameters - Number of the first Standard Window: <12] and [Preferences - Open Project with Showing of the Quantification and Film Thickness Table] has to be activated.

Test18: Convolution of theta and Gaussian functions (for testing the Fermi-edge calculation)

1. Gaussian function, *FWHM*: 2.6 eV,
2. Theta function, jump discontinuity: 3.25 eV
3. plus constant background,
4. normally distributed noise added.

Test19: Gaussian function plus Tougaard background (for testing the Tougaard background)

1. Gaussian function, *FWHM*: 1 eV, peak height: 1MCounts, position: 102 eV
2. Homogeneous Tougaard background: $B = 2866 \text{ (eV)}^2$, $C = 1643 \text{ (eV)}^2$, $C' = +1$, $D = 0$, $T_0 = 0 \text{ eV}$

Test20: Two lines with 4 peaks, sum of Gaussian and Lorentzian functions, energies: Ga 3d = 104 eV, Ga 2p_{3/2} = 1117 eV (for testing the film thickness estimation method 1)

1. Intensities of Ga 3d and Ga 2p_{3/2} correspond with a thickness d of about 3.5 nm.
2. *IMFP* film was calculated by: $IMFP = 0.103 \cdot E^{0.745}$
3. Take-off angle was 0 degrees.
4. The start parameters for Ga 3p are saved in Test20-start.par.

Note: For a correct loading and displaying of the project Test20-Film-Thickness_Result.ufp the following setting has to be used: [Preferences - Setting of Programme Parameters - Number of the first Standard Window: 1] and [Preferences - Open Project with Showing of the Quantification and Film Thickness Table] has to be activated.

Test21: Six lines with 4 Peaks, sum of Gaussian and Lorentzian functions, angle variation: 0, 30, 60 degree (for testing film thickness estimation, method 2))

1. 3 lines at 0°, 30° and 60° with a thickness $d = 0$.
2. 3 lines at 0°, 30° and 60° with a thickness $d = 2,0 \text{ nm}$.
3. *IMFP* film calculated with: $IMFP = 0.103 \cdot E^{0.745}$.

Test22: Spectrum with 30 peaks, product of Gaussian- und Lorentzian functions, generated synthetically, absolute parameters, normally distributed noise

- All peaks: mixing ratio G/L: 0.5, *FWHM*: 5 eV, asymmetry: 0, peak heights alternate between 25000 and 12500 Counts, peak separation: 20 eV

1. Peak: Position 100 eV; height: 25000 Counts,
 2. Peak: position 120 eV; height: 12500 Counts,
 3. Peak: Position 140 eV; height: 25000 Counts
- and so on.

Test23: Spectrum with 30 peaks, product of Gaussian- und Lorentzian functions, generated synthetically, relative parameters, normally distributed noise

- Peak parameters as in Test22

Test24: Spectrum with 30 peaks, sum of Gaussian- und Lorentzian functions generated synthetically, absolute parameters, normally distributed noise

- Peak parameters as in Test22

Test25: Spectrum with 30 peaks, sum of Gaussian- und Lorentzian functions, generated synthetically, relative parameters, normally distributed noise

- Peak parameters as in Test22

Test26: Spectrum with 30 peaks, convolution of Gaussian- und Lorentzian functions, generated synthetically, absolute parameters, normally distributed noise

- All peaks: *FWHM*-Gaussian line: 0.5 eV, *FWHM*-Lorentzian line: 5 eV, asymmetry: 0, peak heights alternate between 25000 and 12500 Counts, peak separation: 20 eV

Test27: Spectrum with 30 peaks, convolution of Gaussian- und Lorentzian functions, generated synthetically, relative parameters, normally distributed noise

- Peak parameters as in Test26

Test28: Spectrum with 30 doublets, product of Gaussian- und Lorentzian functions generated synthetically, absolute parameters, normally distributed noise

- All peaks of the doublets: mixing ratio G/L: 0.5, *FWHM*: 5 eV, asymmetry: 0, peak heights of the 1. Peaks of doublets: alternate between 25000 and 12500 Counts, peak heights of the 2. Peaks of doublets: half height of the 1. Peaks, separation of doublets: 20 eV, peak separation of the two peaks of the doublet: 5 eV

1. 1. Doublet, 1. peak: position 100 eV; height: 25000 Counts,
2. 1. Doublet, 2. peak: position 105 eV; height: 12500 Counts,
3. 2. Doublet, 1. peak: position 120 eV; height: 12500 Counts,
4. 2. Doublet: 2. peak: position: 125 eV, height: 6250 Counts
and so on.

Test29: Spectrum with 30 doublets, product of Gaussian- und Lorentzian functions, generated synthetically, relative parameters, normally distributed noise

- Peak parameters as in Test28

Test30: Spectrum with 30 doublets, sum of Gaussian- und Lorentzian functions, generated synthetically, absolute parameters, normally distributed noise

- Peak parameters as in Test28

Test31: Spectrum with 30 doublets, sum of Gaussian- und Lorentzian functions, generated synthetically, relative parameters, normally distributed noise

- Peak parameters as in Test28

Test32: Spectrum with 30 doublets, convolution of Gaussian- und Lorentzian functions, generated synthetically, absolute parameters, normally distributed noise

- All peaks of the doublets: *FWHM*-Gaussian line: 0.5 eV, *FWHM*-Lorentzian line: 5 eV, asymmetry: 0, peak heights of the 1. Peaks of doublets: alternate between 25000 and 12500 Counts, peak heights of the 2. Peaks of doublets: half height of the 1. Peaks, separation of doublets: 20 eV, peak separation of the two peaks of the doublet: 5 eV

Test33: Spectrum with 30 doublets, convolution of Gaussian- und Lorentzian functions, generated synthetically, relative parameters, normally distributed noise

- Peak parameters as in Test32

Test34: XAS spectrum with 4 peaks, sum of Gaussian and Lorentzian function, XAS background, generated synthetically, relative parameters, normally distributed noise

- Four peaks, mixing ratio G/L: 0.5, *FWHM*: 1 eV, asymmetry: 0, energy form: Photon energy

1. Peak: position 1292.5 eV, 1000 Counts
2. Peak: position 1294.5 eV, 2000 Counts
3. Peak position 1296.5 eV, 500 Counts
4. Peak position 1298.5 eV, 5000 Counts

- Background: Mixing of error and Arc tangent function: 4 steps at the peak positions, step height: 10% of the corresponding peak height, *FWHM*: 1 eV, Mixing Error - Arc tangent function: 0.5.

Test35: XPS multipoint (area) scan with 1 peak (Si) and two components (Si and SiO₂), generated synthetically, 24x24 recording points (576 spectra), convolution of Gaussian and Lorentzian function, normally distributed noise

- One peak, two components, *GP-FWHM*: 3 eV, *LP-FWHM*: 3 eV, asymmetry: 0

1. Component one: position 99.0 eV, maxima of intensities at the points x=12|y=12, 12|13, 13|12, 13|13, minima of intensities ($I=0$) at the points 11|11, 11|12, 11|13, 11|14, 12|11, 12|14, 13|11, 13|14, 14|11, 14|12, 14|13, 14|14, linear increasing of the intensities from the centre to the edges
2. Component two: position 104.0 eV, minima ($I=0$) of intensities at the points x=12|y=12, 12|13, 13|12, 13|13, maxima of intensities at the points 11|11, 11|12, 11|13, 11|14, 12|11, 12|14, 13|11, 13|14, 14|11, 14|12, 14|13, 14|14, linear decreasing of the intensities from the centre to the edges.

Test36: Test spectrum with two peaks as convolution of Gaussian and Lorentzian function, generated synthetically, peak 1 combined with the Tougaard background generated with

IESCS TestTouA.cor and peak 2 combined with TestTouB.cor (for testing the Advanced Tougaard background for the modelling of the spectral background of inhomogeneous samples)

Two peaks with *FWHM*-Gaussian line: 3 eV, *FWHM*-Lorentzian line: 3 eV:

1. Peak: position 100 eV, peak height: 20000 counts, TestTouA: $B = 300$, $C = 550$, $C' = -1$, $D = 500$, $T_0 = 0$
2. Peak: position 120 eV, peak height: 20000 counts, TestTouB: $B = 200$, $C = 350$, $C' = -3$, $D = 500$, $T_0 = 0$

plus a polynomial background ($a = 1000$, $b = 0.1$, $c = 0.001$, $d = 0$, $e = 0$) and normally distributed noise (setting Tougaard background: see 3.10.28).

Test37: XPS spectrum with 5 peaks, sum of Gaussian and Lorentzian function, relative fit parameters, 2 master peaks

- Five peaks, mixing ratio G/L: 0.5, *FWHM*: 2 eV, asymmetry: 0
 1. Peak: position 188 eV, peak height: 800 Counts, master peak
 2. Peak: position 2 eV, peak height: 0.5, relative to peak 1
 3. Peak position 189 eV, peak height: 600 Counts, master peak
 4. Peak position 3 eV, peak height: 0.666, relative to peak 3
 5. Peak position 6 eV, peak height: 0.333, relative to peak 3.

Test38: XPS spectrum with 5 peaks, product of Gaussian and Lorentzian function, relative fit parameters, 2 master peaks

- Five peaks, mixing ratio G/L: 0.5, *FWHM*: 2 eV, asymmetry: 0
 1. Peak: position 188 eV, peak height: 800 Counts, master peak
 2. Peak: position 2 eV, peak height: 0.5, relative to peak 1
 3. Peak position 180 eV, peak height: 600 Counts, master peak
 4. Peak position 3 eV, peak height: 0.666, relative to peak 3
 5. Peak position 6 eV, peak height: 0.333, relative to peak 3.

Test39: XPS spectrum with 5 peaks, convolution of Gaussian and Lorentzian function, relative fit parameters, 2 master peaks

- Five peaks, *GP-FWHM*: 1.5 eV, *LP-FWHM*: 1 eV, asymmetry: 0
 1. Peak: position 188 eV, peak height: 800 Counts, master peak
 2. Peak: position 2 eV, peak height: 0.5, relative to peak 1
 3. Peak position 180 eV, peak height: 600 Counts, master peak
 4. Peak position 3 eV, peak height: 0.666, relative to peak 3
 5. Peak position 6 eV, peak height: 0.333, relative to peak 3.

Test40: XPS spectrum with 5 doublets, sum of Gaussian and Lorentzian function, relative fit parameters, 2 master doublets

- Five doublets, mixing ratio G/L: 0.5, *FWHM*: 1.5 eV, asymmetry: 0
 1. Doublet: peak1: position: 187 eV, peak height: 800 Counts, peak2: position: 1 eV, peak height: 0.5, master doublet
 2. Doublet: peak1: position: 2 eV, peak height: 0.5, peak2: position: 1 eV, peak height: 0.5, relative to doublet 1
 3. Doublet: peak1: position: 188 eV, peak height: 600 Counts, peak2: position: 1.5 eV, peak height: 0.666, master doublet
 4. Doublet: peak1: position: 3 eV, peak height: 0.666, peak2: position: 1.5 eV, peak height: 0.666, relative to doublet 3
 5. Doublet: peak1: position: 6 eV, peak height: 0.333, peak2: position: 1.5 eV, peak height: 0.666, relative to doublet 3.

Test41: XPS spectrum with 5 doublets, product of Gaussian and Lorentzian function, relative fit parameters, 2 master doublets

- Five doublets, mixing ratio G/L: 0.5, *FWHM*: 1.5 eV, asymmetry: 0

1. Doublet: peak1: position: 187 eV, peak height: 800 Counts, peak2: position: 1 eV, peak height: 0.5 eV, master doublet
2. Doublet: peak1: position: 2 eV, peak height: 0.5, peak2: position: 1 eV, peak height: 0.5, relative to doublet 1
3. Doublet: peak1: position: 188 eV, peak height: 600 Counts, peak2: position: 1.5 eV, peak height: 0.666, master doublet
4. Doublet: peak1: position: 3 eV, peak height: 0.666, peak2: position: 1.5 eV, peak height: 0.666, relative to doublet 3
5. Doublet: peak1: position: 6 eV, peak height: 0.333, peak2: position: 1.5 eV, peak height: 0.666, relative to doublet 3

Test42: XPS spectrum with 5 doublets, convolution of Gaussian and Lorentzian function, relative fit parameters, 2 master doublets

- Five doublets, mixing ratio *GP-FWHM*: 0.5 eV, *LP-FWHM*: 1 eV, asymmetry: 0

1. Doublet: peak1: position: 187 eV, peak height: 800 Counts, peak2: position: 1 eV, peak height: 0.5, master doublet
2. Doublet: peak1: position: 2 eV, peak height: 0.5, peak2: position: 1 eV, peak height: 0.5, relative to doublet 1
3. Doublet: peak1: position: 188 eV, peak height: 600 Counts, peak2: position: 1.5 eV, peak height: 0.666, master doublet
4. Doublet: peak1: position: 3 eV, peak height: 0.666, peak2: position: 1.5 eV, peak height: 0.666, relative to doublet 3
5. Doublet: peak1: position: 6 eV, peak height: 0.333, peak2: position: 1.5 eV, peak height: 0.666, relative to doublet 3

Test43: XAS spectrum with 4 peaks, sum of Gaussian and Lorentzian function, XAS background with 4 steps, 2 master steps and relative fit parameters

- Four peaks, mixing ratio G/L: 0.5, *FWHM*: 1.5 eV, asymmetry: 0

1. Peak: position: 1292.5 eV, peak height: 1000 Counts
2. Peak: position: 2 eV, peak height: 2, relative to peak 1
3. Peak position: 4 eV, peak height: 0.5, relative to peak 1
4. Peak position: 6 eV, peak height: 5, relative to peak 1

- XAS-step background with four steps

1. Step: position: 1292 eV, step height: 100 Counts, E-A mixing: 0.4, *FWHM*: 0.8 eV, master step
2. Step: position: 2 eV, step height: 2, E-A mixing: 1, *FWHM*: 1, relative to step 1
3. Step: position: 1296 eV, step height: 200 Counts, E-A mixing: 0.6, *FWHM*: 1.2 eV, master step
4. Step: position: 4 eV, step height: 1.5, E-A mixing: 1, *FWHM*: 1, relative to step 3

Test44: 10 spectra for testing the *.ppd files

- Ten spectra saved (Survey_01, Survey_02, O 1s_01, O 1s_02, C 1s_01, C 1s_02, S 2p_01, S 2p_02, N 1s_01, N 1s_02 (two identical multi-region measurements))

- Corresponding file: Test44.ppd

3.2.6 Open Wagner Plot...



The data base of Auger parameters integrated in UNIFIT 2023 can be loaded and plotted with the menu point [File - Open Wagner Plot...](see Fig. 7). The plots can be annotated (see 3.7.12) and the data bank can be changed and expanded (see 3.7.11 and book 'Line Positions and Data Formats – Version 2023' 5.1).

3.2.7 Open Image...



[File - Open Image] realizes the input of images and pictures. All common formats are supported (*.bmp, *.wmf, *.tif, *.jpg, ...). The software UNIFIT offers no image processing tools. The loaded image can be saved in a UNIFIT project, printed out, copied via clipboard and exported.

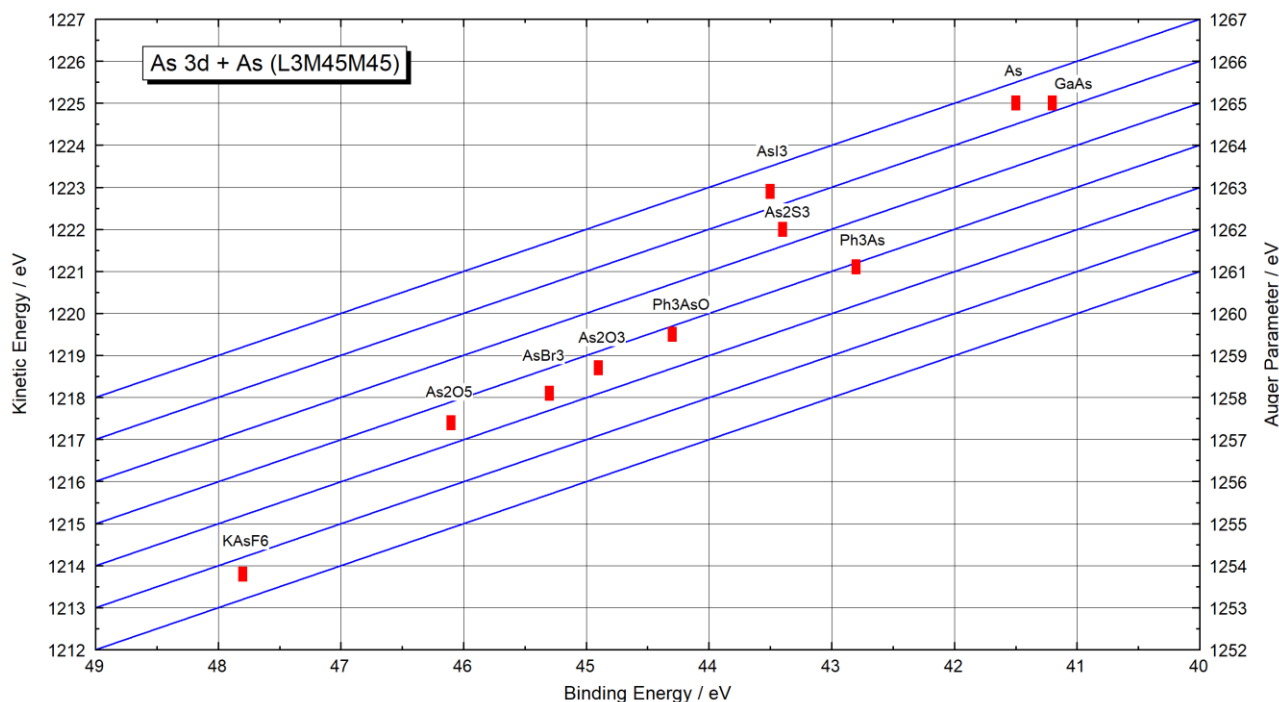


Fig. 7. Chemical state plot (Wagner plot) of the Auger parameters of As 3d + As (L3M45M45), project: Unifit_2023_User_Files\examples\Specials\As_Wagnerplot.ufp, inserted into this document via 'Copy - Paste function' of UNIFIT and Word

3.2.8 Close All Windows



[File - Close All Windows] closes all opened windows. If a window is closed, all fit parameters are deleted and the software controlling flags are restored. The region names in the dialogue [File - Select spectra] are kept. Before the window is closed the projects can be saved.

3.2.9 Close All Standard Windows



[File - Close All Standard Windows] closes all opened standard windows. The 3D windows and parameter windows remain open. If a window is closed, all fit parameters are deleted and the software controlling flags are reset. The region names in the dialogue [File - Select spectra] are kept. Before the window is closed the projects can be saved.

3.2.10 Save Project



All activities (e.g. Peak Fit, Differentiation, Smoothing, etc.) of all opened windows (hidden or visible) can be saved together in one project. If a project is saved, the measurement data are saved additionally in a folder with the same name. The results of a quantitative analysis and film thickness estimation are stored automatically by saving a project. The saving of processing and analysis steps by projects is a simple way to archive the results. (Example: Project name: *\Test project.ufp, name of the directory of measurement data: * \Test project*.*) Before the project will

be saved a backup is stored (e.g. Project_backup_1.ufp). An automatically saving can be activated (see 3.10.10).

3.2.11 Save Project as...

‘Save Project as...’ allows saving a changed project using a different project name. An icon for that menu point is not available.

3.2.12 Save Project Processing Steps/Design Standard Windows...



All activities and design features (e.g. peak fit, differentiation, smoothing, colour, etc.) of all opened standard windows (hidden or visible) can be saved together in one processing-design file (*.ppd). The saving of processing and design steps is a good way to generate templates for the applications using similar analysis problems. The charge correction, formatted titles, formatted annotations and interpolation operations are not saved. Before the file will be saved a windows-selection dialogue is opened. It is not possible to save processing and design steps of windows with the same name. The default folder of the *.ppd files is Unifit_2023_User_Files\My Unifit Project Processing Steps (book ,Line Positions and Data Formats – Version 2023’ 4.7).

3.2.13 Export Image Active Window (400 dpi)...



This menu point allows the easy and quick export of the results to a text processing or a presentation software. The active window is converted to a generally used image format (formats: jpg, bmp, gif, emf etc.). The selected resolution (3.10.14) is displayed additionally (monitor resolution, 400, 600, 800, 1000, 1200 dpi). The form of the window is not changed. The quality of the exported image depends on selected resolution and used data format (see Fig. 8).

3.2.14 Export Images All Displayed Windows (400 dpi)...



This menu point allows the easy and quick export of the results to a text processing or a presentation software of all displayed windows. All displayed window are converted to a generally used image format (formats: jpg, bmp, gif, emf etc.). The selected resolution (3.10.14) is displayed additionally (monitor resolution, 400, 600, 800, 1000, 1200 dpi). The form of the window is not changed. For a following generation into an animated presentation (software: gifanimator.exe) the image should have the extension *.gif. The sub-menu 3.11.12 is an appropriate preparing tool of the Unifit-windows before the export is made. The image names have the structure: Selected name + ”_” + windows number (five digits)(e.g. GaAs_00001.gif, GaAs_00002.gif,...).

3.2.15 Export Images Displayed Windows (400 dpi)...



This menu item corresponds to the menu 3.2.14. However, the selected windows are exported only. Example 3 illustrates the export of all displayed windows and the generation of a animated gif-file. The animated gif-file can be implemented in a PowerPoint presentation (see Example 3).

Example 3: An animated gif file of a longtime-stability measurement has to be created. The animated gif file can be implemented into a PowerPoint presentation. All processing steps for the preparation and the export of the images of the Unifit-standard windows are given. (project: Documents\Unifit_2023_User_Files\examples\XPS\Stability-Measurement-Cu2p3-1100-Spectra-Mono-Source.ufp)

1. Load the Unifit project Documents\Unifit_2023_User_Files\examples\XPS\Stability-Measurement-Cu2p3-1100-Spectra-Mono-Source.ufp with [File - Open Project...].

Following windows are displayed:

- one 'Parameter Plot' window
 - one 'Plot 3D Waterfall 45°' window
 - four 'Cu2p3' standard windows with a peak fit of one peak-fit component.
2. Change the number of the displayed Standard Windows from 4 to 137 with:
 - [Windows – Hide/Show Standard Windows]
 - Select 'Show Every 8th StandardWindow'
 - leave the dialogue with
 3. Rearrange the windows with: Deactivate the option [Windows – Automatic Resize Deactivated] and activate [Windows – Cascade],
 4. Change the stretching factor of the intensity scale for all displayed standard windows to a uniform value with:
 - [Windows – Show Windows Video Sequence]
 - Select all Windows and deactivate windows one and two
 - leave the windows-selection dialogue with
 - The dialogue 'Show Windows Video Sequence' will be opened, the setting is:

| | |
|--|-------------|
| 1. 'Frame Dwell Time in Seconds': | 0.2 |
| 2. 'Same Position of Windows as Active Window': | Activated |
| 3. 'Same Window Size as Active Window': | Activated |
| 4. 'Same Scaling of Intensity Axis of Standard Windows': | Activated |
| 5. 'Same Scaling of Intensity Axis of 3D Windows': | Deactivated |
 - leave the dialogue with
 - After a rescaling of the intensity axes a windows video will be shown. The question appears: Windows sequence is finished. Original intensity scaling of the windows? Press
 5. The batch parameter defines the time index after the start of the measurement. Create spectrum titles using the spectrum title plus the batch parameters for all standard windows with:
 - [Annotation/Design – Spectrum Title 1...]
 - Write in the edit field: Time Index
 - Frame: Without
 - Windows: All Windows of the Same Type: Activated
 - Appendix: Title + Batch Parameter: Activated
 6. Press . The time index is displayed in all standard windows.
 7. Export the images of all standard windows (without the Parameter-Plot Window (window 1) and the 3D-Waterfall 30° Window (window 2)) with [Files – Export Images Displayed Windows (400)...]. The dialogue 'Select Windows' appears. Select all windows without windows 1 and 2. Leave the dialogue with . The 'Save Data' dialogue appears. Select the file type *.gif and the folder **Documents\Unifit_2023_User_Files\AnimatedGIFs**. The main name of the files is Cu2p3. The batch-file numbers are generated automatically. The export process takes some minutes.
 8. After saving the project the UNIFIT programme can be closed. The animated gif-file is generated using the software **Documents\Unifit_2023_User_Files\AnimatedGIFs\gifanimator.exe**.
 9. Open the folder **Documents\Unifit_2023_User_Files\AnimatedGIFs**. Arrange the **Cu2p3_xxxxx.gif** files in that way, that the file with the highest batch-file number is above (**Cu2p3_01136.gif**).
 10. Start the **gifanimator.exe**. Mark all **Cu2p3_xxxxx.gif** files and take the top file **Cu2p3_01136.gif** with the left mouse button and move and load all gif files to the gifanimator via drag-and-drop.

11. Operation steps using the gifanimator.exe:

- Mark all imported images
- Define the duration with 'Image – Duration (1/100 s): 20 (= 0.2 seconds)
- Save the animated gif files with name **Cu2p3-Animated.gif** with 'Save as'
- Close the gifanimator.exe

12. Loading the animated-gif file into the PowerPoint presentation:

- Open the PowerPoint presentation
- Load the **Cu2p3-Animated.gif** in the presentation via the 'Drag-Drop Function' or the 'Copy-Paste Function'
- Use **not** the function 'Insert – Images'

3.2.16 Copy Image Active Window (400 dpi)



This menu point is equivalent to point 3.2.13; however, the created window presentation is copied to the clipboard. The saved image can be loaded using Word or PowerPoint with the call 'Paste' (e.g. Fig. 8 was inserted via 'Paste' in this document). The resolution can be selected at point 3.10.14.

Note: If the graphics are exported incorrectly than change the monitor setting to 'True Colour (32 bit)' using the system setting of Windows. The 'Export Image Window (Copy) – Paste function' with an image resolution of 800, 1000 and 1200 needs a main memory of 1 Gbyte or more.

3.2.17 Export Data Active Window...



The menu item [File - Export Data Active Window...] enables the comfortable transfer of data to conventional scientific graphic and spreadsheet programmes (Origin[®], Excel[®]...). The curves calculated and processed in UNIFIT are exported in ASCII columns. The first column contains the energies/wave numbers. The incorporation of untreated spectrum, processed spectrum, background function, satellite background, and - after a peak fit - components, sum curve and residual in additional columns can be arranged in a dialog box.

A) Activated Standard Window: It is possible to normalize the data before exporting. The value for normalization can be chosen arbitrarily. The following values are given for orientation:

1. Maximum of the processed curve or
2. Maximum of the sum curve or
3. Maximum of components 1 to N.

The normalization is activated only if the check box contains a '✓', triggered by clicking the left mouse button when the pointer is above the box. Furthermore, the exported data can be modified by adding a constant to all columns (see book 'Line Positions and Data Formats – Version 2023', 4.1.1.1).

B) Activated 3D Waterfall 0° Window:

1. column: energy/wave number (step width: smallest step width of the embedded single spectrum),
2. column: intensity,
3. column: intensity, ...

Not available intensity values are interpolated linearly. All intensity values have an offset corresponding to the 3D Waterfall 0° presentation (see book 'Line Positions and Data Formats – Version 2023', 4.1.1.2).

C) Activated 3D Waterfall 0° Plus Window: Example illustrates a plot of two fitted spectra with two components and fittable background:

1. column: energy/wave number (step width: smallest step width of the embedded single spectrum),

2. column: intensities of the 1. component of spectrum 1,
3. column: intensities of the 2. component of spectrum 1
4. column: intensities of the sum curve of spectrum 1
5. column: intensities of the background of spectrum 1
6. column: intensities of the spectrum 1
7. column: intensities of the 1. component of spectrum 2
8. column: intensities of the 2. component of spectrum 2
9. column: intensities of the sum curve of spectrum 2
10. column: intensities of the background of spectrum 2
11. column: intensities of the spectrum 2

Unavailable intensity values are interpolated linearly. All intensity values have an offset corresponding the 3D Waterfall 0° Plus presentation (see book 'Line Positions and Data Formats – Version 2023, 4.1.1.3).

D) Activated 3D Waterfall 45° or 3D Waterfall -45° Window: The 1. Row includes the labelling of the columns (Energy, Batch Parameter Spectrum 1, Batch Parameter Spectrum 2 etc.).

1. column: energy/wave number (step width: smallest step width of the embedded single spectrum),
2. column: intensities of the spectrum 1,
3. column: intensities of the spectrum 2, ...

Not available intensity values are interpolated linearly (see Fig. 9 and book 'Line Positions and Data Formats – Version 2023, 4.1.1.4).

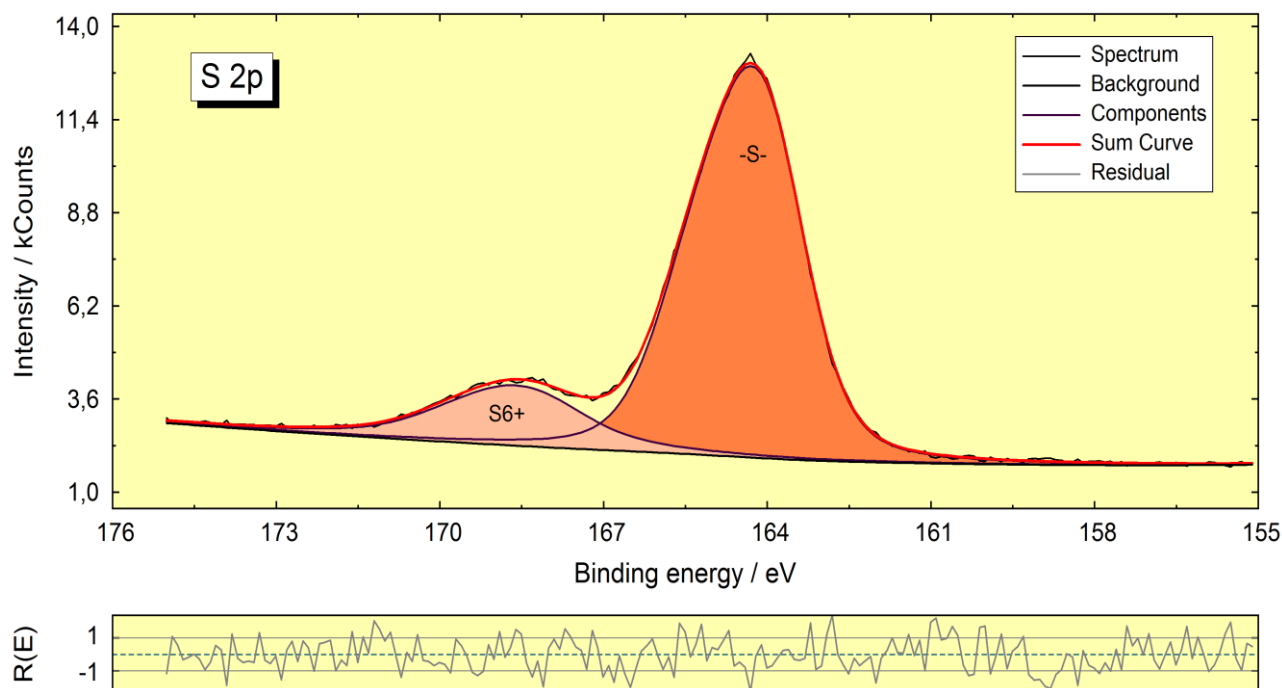


Fig. 8. S 2p spectrum (project: Unifit_2023_User_Files\examples\XPS\S2p_peak_fit.ufp) inserted into this document via 'Copy – Paste function' of UNIFIT and Word

E) Activated Parameter Plot Window: The 1. Row includes the labelling of the columns (Energy, Names of the analyzed lines).

1. column: Batch parameters (angle, sputter time),
2. column: values.

Please see book 'Line Positions and Data Formats – Version 2023, 4.1.1.5).

F) Activated Wagner Plot Window:

1. column: binding energy of the photoelectron line,
2. column: kinetic energy of the Auger line,
3. column: Auger parameter,
4. column: Name of the chemical compound

Please see book 'Line Positions and Data Formats – Version 2023, 4.1.1.6).

G) Activated 'XY 3D Plot 45°', 'XY 3D Plot -45°', 'XY Colour Profile', 'XY 3D Plot 45° Colour Profile' or 'XY 3D Plot -45° Colour Profile' Window: The 1. Row includes the values of the Y-axis (equidistant steps).

1. column: Values of the X-axis (equidistant),
2. column, 2. row: max/min intensity or peak area of the spectrum recorded at point 1|1,
3. column, 2. row: max/min intensity or peak area of the spectrum recorded at point 1|2,
4. column, 2. row: max/min intensity or peak area of the spectrum recorded at point 1|3.
5. column, 2. row: max/min intensity or peak area of the spectrum recorded at point 1|4...
2. column, 3. row: max/min intensity or peak area of the spectrum recorded at point 2|1,
3. column, 3. row: max/min intensity or peak area of the spectrum recorded at point 2|2...

(see book 'Line Positions and Data Formats – Version 2023, 4.1.1.7).

Note: The programme UNIFIT reads data files from measurements with many different formats. Therefore, the export routines can be used as universal converting programme.

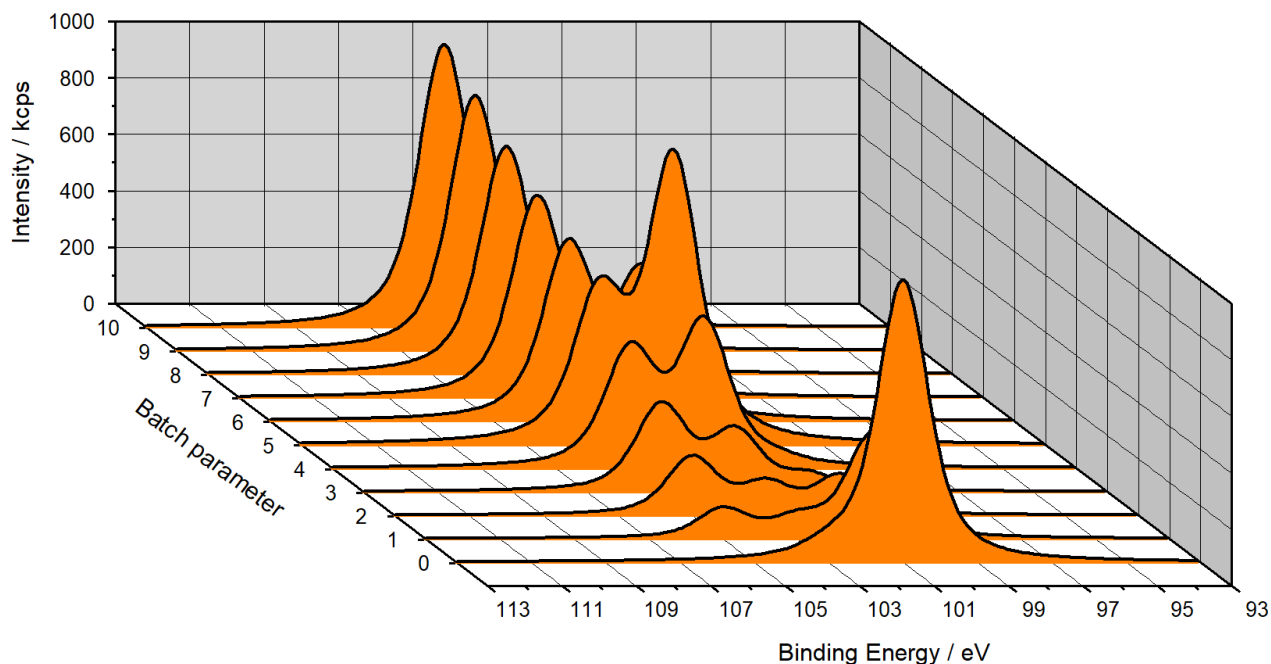


Fig. 9. Example (project: Unifit_2023_User_Files\test spectra\Test07.ufp) of a 3D-waterfall - 45° presentation of the Si 2p spectra, inserted into this document via 'Copy – Paste function' of UNIFIT and Word, three parameter-dependent test functions with 11 steps, z – series parameter:

1. Function: $I_1(z) = 1000 \cdot \exp(-z)$, $E_0 = 101$ eV
2. Function: $I_2(z) = 1000 \cdot \frac{1}{1 + (z - 5)^2}$, $E_0 = 103$ eV,
3. Function: $I_3(z) = 100 \cdot z$, $E_0 = 105$ eV

3.2.18 Export Data All Standard Windows...



The menu item [File - Export Data All Standard Windows...] enables the comfortable transfer of data of all standard windows as described in 3.2.17. The data set of every window is saved in a separate file. The windows number and the region name is integrated into the file name (e.g. four spectra are loaded in the windows 21(C1s), 22 (O1s), 23 (N1s), 24 (Si2p), the file name was selected to 'Data', the generated files are: Data_21_C1s.dat, Data_22_O1s.dat, Data_23_N1s.dat, Data_24_Si2p.dat).

3.2.19 Export Data Standard Windows...



The menu item [File - Export Data Standard Windows...] enables the comfortable transfer of data of the windows selected before as described in 3.2.17. The data set of every selected window is saved in a separate file. The windows number and region name is integrated into the file name (e.g. four spectra are loaded in the windows 21 (C1s), 22 (O1s), 23 (N1s), 24 (Si2p), the file name was selected to 'Data', the generated files are: Data_21_C1s.dat, Data_22_O1s.dat, Data_23_N1s.dat, Data_24_Si2p.dat).

Note: The previously applied mode of data export (active window, all windows, or selected windows) is opened starting the procedure by the icon.

3.2.20 Print Active Window...



The sub-menu [File – Print Active Window...] allows the printing of the active window. As selected in (3.2.22) the spectrum can plotted on the full or half page. As an option, the result of a concentration determination may be placed on the lower half of the printout page. If the preference option 'Display Setting ==> Printer Setting' (3.10.21) is activated then the window will be printed as displayed. In case of a fitted spectrum the fit parameters may be appear optionally on the hardcopy (see Fig. 10), the printing of the acquisition parameters may be arranged, too. If the preference option 'Display Setting ==> Printer Setting' (3.10.21) is deactivated the design of the printout may be defined separately (3.10.20). If a Wagner-Plot window is printed out the auger parameters can be plotted, too.

3.2.21 Print All Displayed Windows...



The sub-menu [File – Print All Windows...] allows the printing of all displayed windows. The design of the printing out can be defined in (3.2.22), (3.10.20) and (3.10.21). The defined printings (3.2.22) are valid for all printed window.

3.2.22 Print Displayed Windows...



The sub-menu [File – Print Windows...] allows the printing of before selected spectra windows. The design of the printing out can be defined in (3.2.22), (3.10.20) and (3.10.21).

3.2.23 Presetting Printer...

This sub-menu offers five options for the definition of the printing out of the spectra:

- Window plus Acquisition Parameters
- Wagner-Plot Window plus Auger Parameters
- Window plus Fit Parameters
- Window plus Quantification Table

- Two Windows on One Page or On the Half Page.

The quantification table (if available) is printed out after the printing of the last window.

3.2.24 Select Spectra...



The sub-routine [File - Select Spectra...] allows the generation of standard windows including the selected regions. The standard windows can be created hidden or visible. The button **Hide Standard Windows** activates the corresponding dialogue (point 3.11.8). Different selecting modes are offered. Several regions can be selected simultaneously. If a second spectrum will be marked and the shift key is pressed, then all spectra between the first and second marked spectrum are selected. For processing spectra of different data files, please, act as follows:

1. Open the first data file.
2. Select the desired regions, the standard windows that contain the selected spectra are generated (hidden or visible).
3. Open the second data file.
4. Select the desired regions standard windows which contain the selected spectra from the second data set are generated and so on.

The programme-internal peak name can be defined manually. The following options are offered:

1. Spectrum name without extension (single and multi-region measurement, e.g. Si 2p, O 1s),
2. spectrum name with batch parameter (SDP, ARXPS, e.g. Si 2p_60),
3. spectrum name with x-axis (x-axis line scan, Si 2p_100),
4. spectrum name with y-axis (y-axis line scan, Si 2p_150),
5. spectrum name with x-axis and y-axis (multipoint measurement, mapping, e.g. Si 2p_100|150),
6. spectrum name with batch parameter, x-axis and y-axis (SDP mapping, e.g. Si 2p_60|100|150).

The region names of the data file loaded the latest appear in the box 'Select Spectra' until you proceed to an operation for a region originating from another data file which requires the original data, like [File - Original/Accept Preferences], [Peak Fit - Iteration] or [File - Export Data...]. The content of the 'Select Spectrum' dialogue will be refreshed.

Example 4: A data file containing C 1s, O 1s and survey is loaded and displayed in window 11 - 13. Afterwards a second data file with Si 2p, N 1s, and Cu 2p3 is loaded and presented in window 14 - 16. The [File - Select Spectra] dialogue box contains the regions of the second data file. During the processing of the C 1s signal, you have to return to the original spectrum. Carrying out the option [File – Original/Accept Preferences Active Window], the regions in [File - Select Spectra] will be substituted by the content of the first data file.

3.2.25 Select Blocks...



This menu option is created for loading parameter-dependent measuring series saved in VAMAS, PHI (*.SDP), PHI (*.ANG) or PHI (*.MAP) formats. The regions (e.g. O 1s, C 1s ...) recorded at different conditions (angle, sputter time) can be selected as batches after loading. After batch choice, the single spectra can be selected in [File - Select Spectra]. The names consist of the batch name (e.g. O 1s) and the corresponding parameter (e.g. 10 min sputter time: O 1s_10).

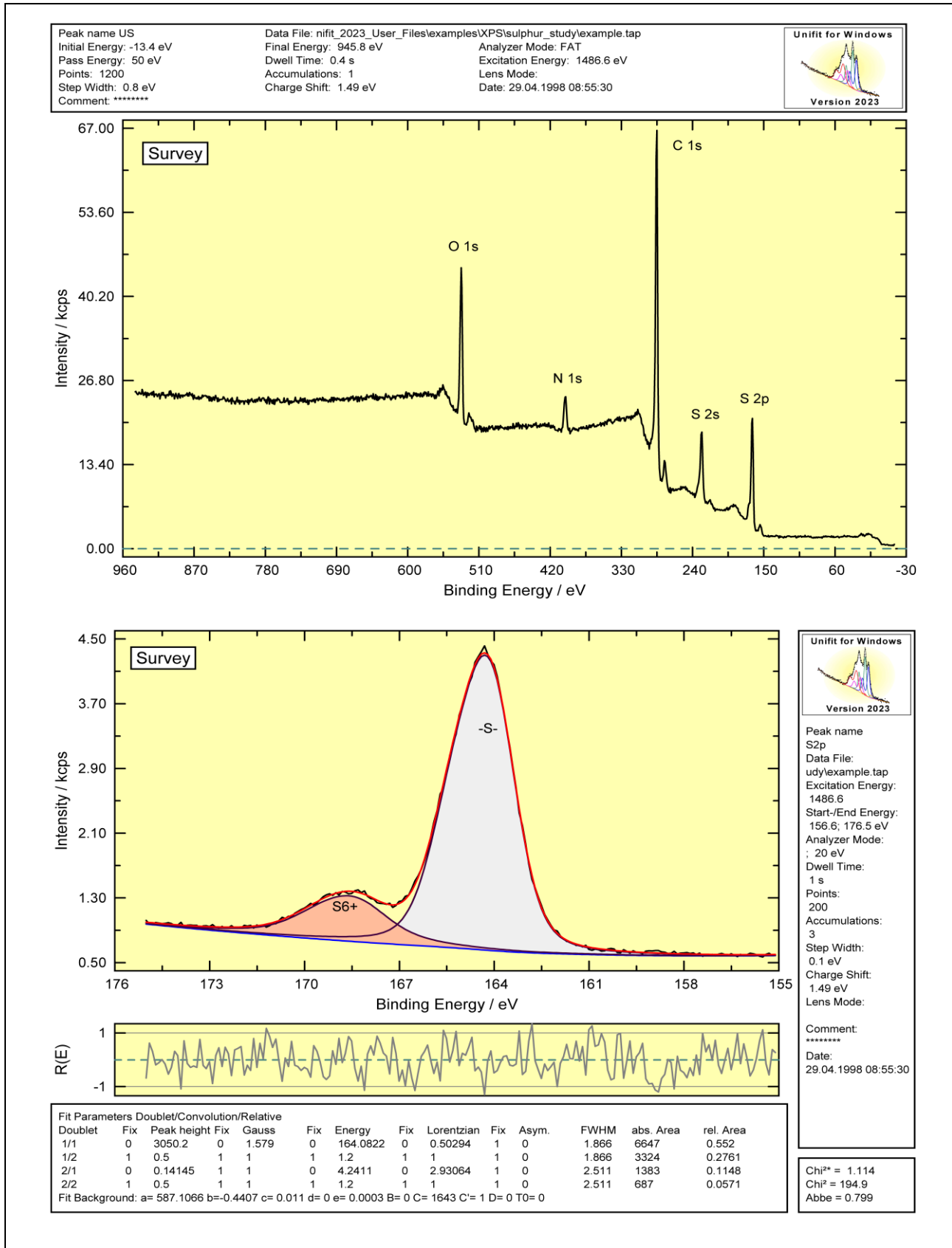


Fig. 10. Plot produced by UNIFIT, project: Unifit_2023_User_Files\examples\XPS\sulphur_study.ufp, spectrometer: VG ESCA3, top: survey spectrum with acquisition parameters, bottom: fitted spectrum with sum curve, components, residual, acquisition parameters and fit parameters

3.2.26 Original/Accept Preferences Active Window



This option allows to undo all processing steps and to re-display one region in its original form. The corresponding file will be re-loaded. Therefore, do not remove the disk with the experimental data! With [File – Original/Accept Preferences Active Window] individual preferences of the window are deleted and the current preference of the programme will be loaded. File – [Original/Accept Preferences Active Window] deletes also the preference of the peak fit of loaded projects. The active window accepts the current preferences of the programme. The charge correction of the activated window (selected with [Modify – Charge Correction Active Window]) is not changed. Also, the charge correction valid for all windows (selected with [Batch Processing – Charge Correction all Windows]) is not changed.

3.2.27 Exit...



The programme can be closed using the menu function [File - Exit...]. The preferences (except for the charge correction) will be saved automatically (Path of the presetting file: Documents\Unifit_2023_User_Files\presetting\presetting.set).

3.3 Modify

This menu contains the options to modify the measured data in many ways.

3.3.1 Undo



[Modify - Undo] allows the user to take back **one hundred** processing steps. This call is active for all window types. Not supported are: i) Wagner-Plot operations, ii) operations at the estimation of transmission functions, iii) windows operations (close, cascade,), batch-processing operations.

3.3.2 Programme-Internal Copying



A spectrum including all data can be copied even after several modifications and/or peak fitting with [Modify – Programme-Internal Copying] and pasted into UNIFIT, only. The export of the image of the activated window via the commonly used ‘Copy – Paste’ Windows function to other programmes can be done with [File – Copy Image Active Window (600 dpi)] (see 3.2.16) or the equivalent pop-up operation.

3.3.3 Programme-Internal Insertion



This option re-loads a spectrum, which has been saved by the programme-internal copying routine into UNIFIT only. A new window is opened automatically.

Note: A simultaneous usage of the software UNIFIT 2023 is possible. One user can execute the software ten times. The functions [Modify – Programme-Internal Copying] and [Modify – Programme-Internal Insertion] can also be used to transfer the spectrum and processing data of a standard window from one activated UNIFIT programme to another activated UNIFIT programme.

3.3.4 Charge Correction Active Window...



This option displays a dialogue box, which allows the X-axis of the active window to be shifted by any value in order to compensate for sample charging effects of non-conducting samples. Displayed is the sum of ‘Charge Correction Active Window’ plus ‘Charge Correction all Windows’.

Note: For shifting energy scales in all or elected windows use the menu [Batch Processing - Charge Correction all Windows...] (see 3.5.1 or 3.5.2).

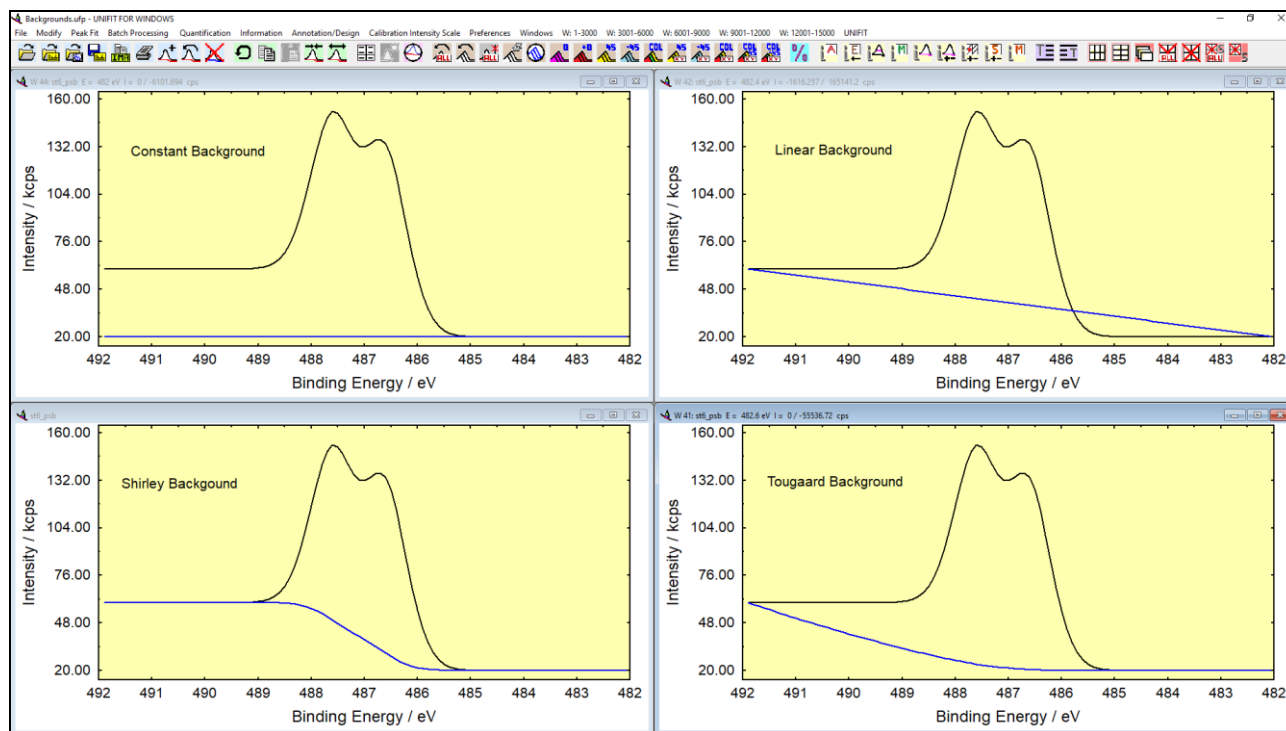




Fig. 11. Screen shot: Test08-test spectrum with constant, linear, Shirley and Tougaard background, project: Unifit_2023_User_Files\examples\Backgrounds.ufp

3.3.5 Correction with IERF: ESCALAB220_MONO_LAXL_50EP.trm

 This menu allows the correction of the spectra with the currently loaded transmission function (IERF). The loaded IERF is displayed simultaneously (example: ESCALB220_MONO_LAXL_50EP.trm, Spectrometer source_Lense mode_Pass energy).

3.3.6 Calculate Background

 This sub-menu performs background subtraction in five different ways before starting the peak fit routine. A sixth possibility of baseline treatment - the inclusion of the background function in the iterative peak-fit procedure - is described in 0. If the background was already subtracted once and [Modify - Calculate Background] is selected again, the previously calculated background is added to the spectra automatically.

The background can be calculated from the startpoint to the endpoint of the region. The number of points to average over to obtain the startpoint and endpoint for the background is defined in [Preferences - Points to Average] and can be changed directly with **Points to Average**.

After re-evaluation of the background using modified parameters for calculation (iteration with Shirley algorithm, new parameters with Tougaard type background), the old and new baseline is displayed to show changes.

The calculated background can either be displayed additionally to the spectrum with the **Plot** button or subtracted from the experimental data with **Subtract** without any difference for further processing steps. The sub-menu can be closed with **Cancel**, keeping the spectrum unchanged. The peak area displayed in the dialogue box after background calculation is given in cps·eV independent

of the option selected in [Preferences – Y-Axis]. The option ‘Backgr. for XPS-Quant. Right Mouse Button’ selects the background for the right-mouse button operations. By activating the option ‘Setting: All Std. Windows’ the background subtraction or plot can be used for all standard windows without using the batch-processing procedure.

3.3.6.1 Constant

The constant background subtracted from the displayed region is equal to the intensity $I(E_2)$ (high-energy side marker (XPS, see Fig. 11) or low photon-energy side $I(E_1)$ (XAS).

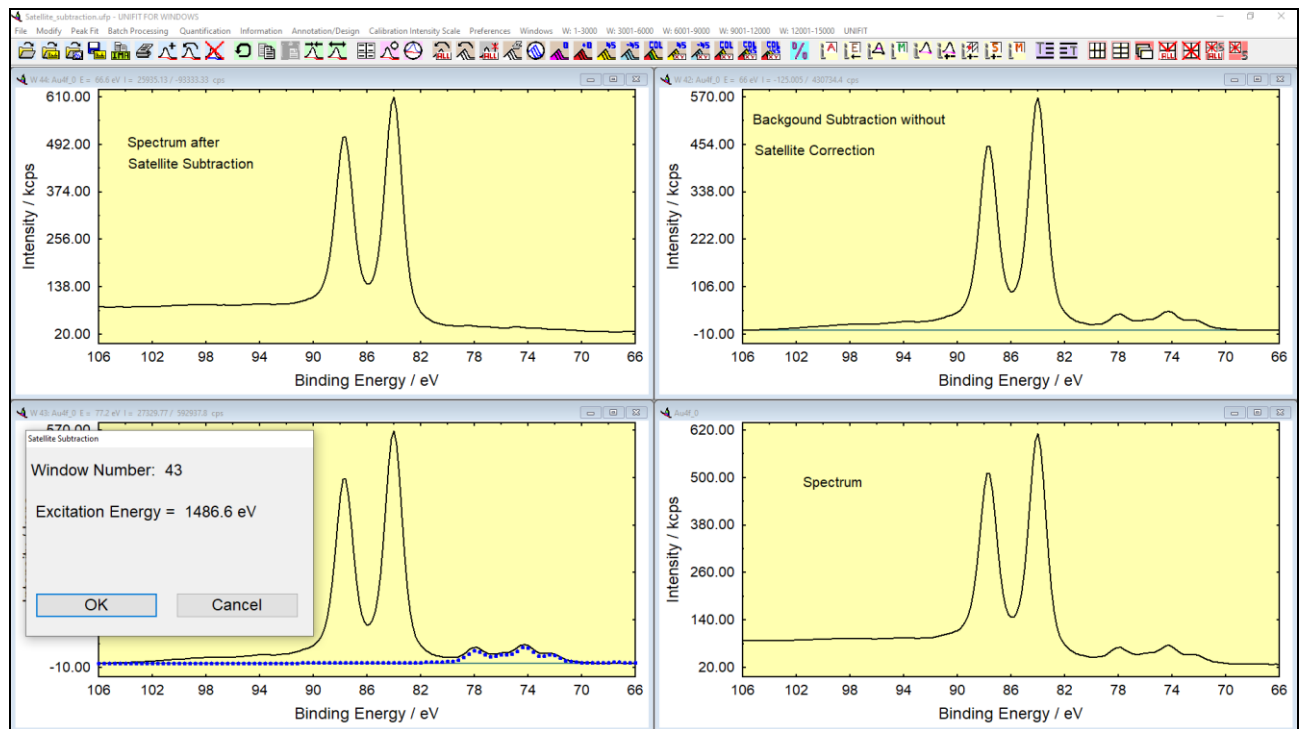


Fig. 12. Screen shot: Au 4f spectrum, Au 4f spectrum minus Shirley background, Au 4f spectrum and excitation satellites, and Au 4f spectrum minus excitation satellites, project: Unifit_2023_User_Files\examples\Satellite_subtraction.ufp

3.3.6.2 Linear

This function calculates a linear baseline between startpoint and endpoint of the spectrum (see Fig. 11). Select or to accept the baseline or click the button to return to the main menu.

3.3.6.3 Shirley

This item calculates a constant baseline between start and end point of the spectrum (see Fig. 11). Select or to accept the background function or click the button to return to the main menu. The baseline can be re-calculated with . Additionally, an iterative procedure can be applied to the Shirley contribution with .

Note: The Shirley background should not be applied to signals with intrinsic asymmetry and cannot be used for survey spectra.

3.3.6.4 Tougaard

A Tougaard background will be calculated in the defined range or between the start and end points of the experimental spectrum. To adjust the background on the spectrum the B parameter can be changed automatically. For the first calculation the parameters are given by: $C = 1643 \text{ (eV)}^2$, $C' = +1$, $D = 0 \text{ (eV)}^2$, $T_0 = 0 \text{ eV}$. After changing B , C , C' , D or T_0 the background function will be calculated and displayed with **Preview** (see Fig. 11), while B is shown in the dialogue box. By changing the parameters with the up and down controls, the new background is displayed automatically. The step width is 10 for the B , C and D parameters and 0.1 for the C' parameter. The gap-energy parameter is defined: $T_0 \geq 0$. The created inelastic electron scattering cross-section $\lambda(E) \cdot K(E, T)$ can be saved and loaded (*.cro). The inelastic electron scattering cross-section can be plotted using menu point 3.7.16.

Note: The Tougaard background is especially suited for signals with intrinsic asymmetry and can be used also for survey spectra.

3.3.6.5 Polynomial+Shirley

This menu item produces the background as a sum of a third order polynomial and the Shirley function. The first calculation considers all parts equally. Then the contribution of linear, square, cubic, and Shirley function can be modified by the user through changing the parameters b' , c' , d' , and e' . The parameter a' is fixed at the minimum of the experimental spectrum. The baseline can be calculated with the changed parameters with **New**. Additionally, an iterative procedure can be applied to the Shirley contribution with **Iteration**.

Note: The previously applied background calculation (constant, linear, Shirley, Tougaard, Polynomial+Shirley) is opened starting the procedure by the icon.

3.3.7 Subtract Background



In case the baseline has only been displayed in the sub-menu [Calculate Background], it can be subtracted from the experimental spectrum at any time.

3.3.8 Subtract Satellite



This menu item allows removing X-ray satellites from spectra produced by non-monochromatic AlK_α or MgK_α sources if the experimental spectrum contains the corresponding primary signal. Energy differences and intensities of the satellites can be edited and changed by the user with [Preferences – Satellite] allowing the definition of five different parameter sets for both excitation sources. The correct subtraction is only possible if the primary peak is included in the measured spectra. A rough background correction must be performed before the satellites can be subtracted as follows:

Method 1 (with Shirley background):

1. Open and display experimental data and activate the window,
2. Select [Modify - Subtract Satellite...] and click **OK**.

Method 2 (with individual background):

1. Open and display experimental data and activate the window,
2. Select [Modify - Subtract Satellite] and click **OK** (see Fig. 12),
3. Select [Modify - Calculate Background - Shirley] (the background subtracted in 2. will be re-added and can be re-defined,

- Click **Subtract** for subtraction of excitation satellites and Shirley background (see Fig. 12, bottom right) or – in preparation of an iterative calculation of the background function during the peak fit - **Cancel** for subtraction of the satellite only.

3.3.9 Reduction



This item allows the reduction of the energy/wave number range of the current display. The reduction limits must have been previously defined by range markers (see 3.1). Steps:

- Load and display the spectrum,
- activate a window for spectrum processing,
- move the mouse pointer to the left energy/wave number limit and press the left mouse bottom for selecting the low energy/wave number side (vertical dashed line appears),
- move the mouse pointer to the right energy/wave number limit and press the left mouse bottom for selecting the high energy/wave number side (second vertical dashed line appears, pressing the right mouse bottom the pop-up menu appears and us the function ‘Remove Reduction Lines’, two new markers can be selected).
- If the two range-marker lines are displayed, then the lines can be shifted by pressing and moving the left mouse button.
- With [Modify – Reduction] or the pop-up menu function ‘Reduction’ the spectrum can be reduced.

With the pop-up operation ‘Remove Reduction Lines’ the reduction-markes lines can be removed.

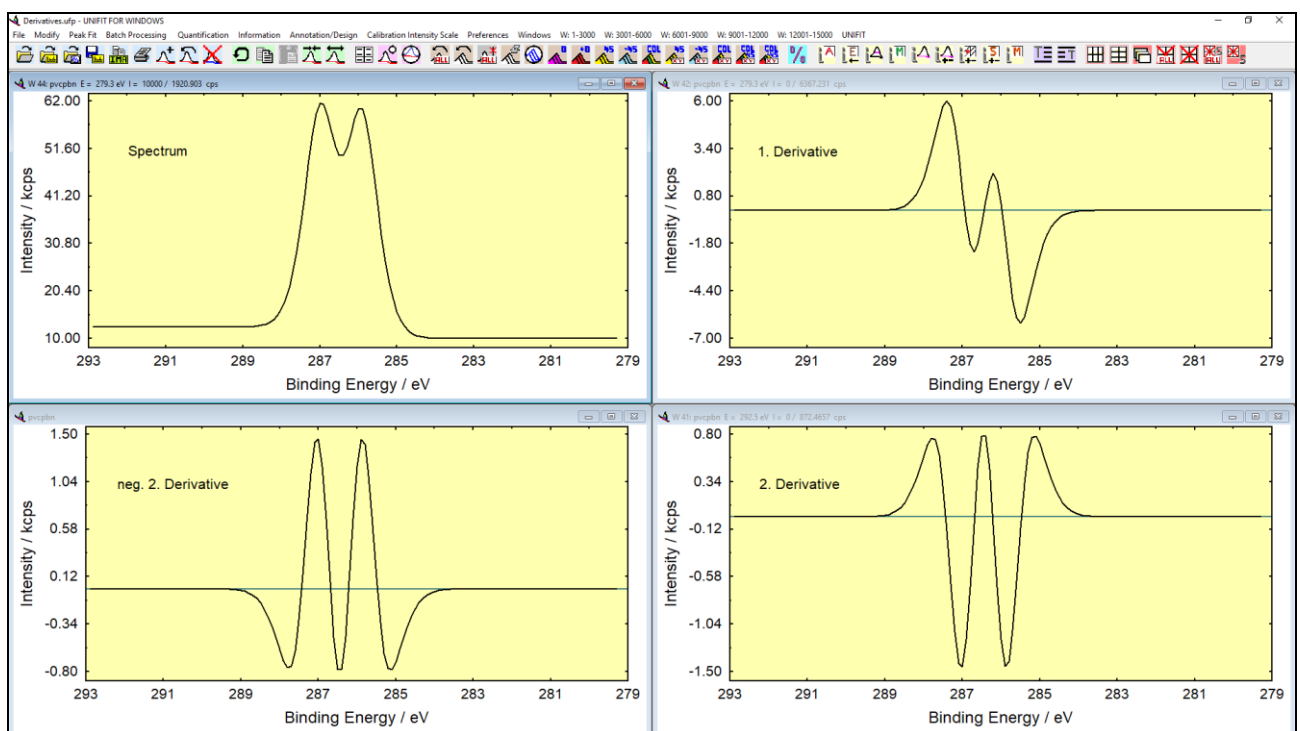



Fig. 13. Screen shot: Test11-test spectrum: 1. derivative, 2. derivative and mirrored 2. derivative (points to average: 3), project: Unifit_2023_User_Files\examples\Derivatives.ufp

3.3.10 Expansion



This option can be used to undo spectrum reduction and to restore the previous spectrum display.

3.3.11 Differentiation

 [Modify - Differentiation] performs a differentiation (see Fig. 13). Define the number of points to differentiate over in [Preferences - Points to Average] or with the direct call **Points to Average**. The point number of the averaging procedure (see 0) is displayed and should be 0.7 times the number of points measured in the range of the *HWHM*. In order to realize a quantification of AES spectra using the peak-to-peak values, the value Max - Min are generated and available in the quantification routine. By activating the option 'Setting: All Std. Windows' the differentiation can be used for all standard windows without using the batch-processing procedure.

Example 5: FWHM Peak: 1.0 eV with step width: 0.1 eV, e.g. number of points FWHM: 10, number of average points (0.7 times HWHM, rounded down): 3 (see Fig. 13)

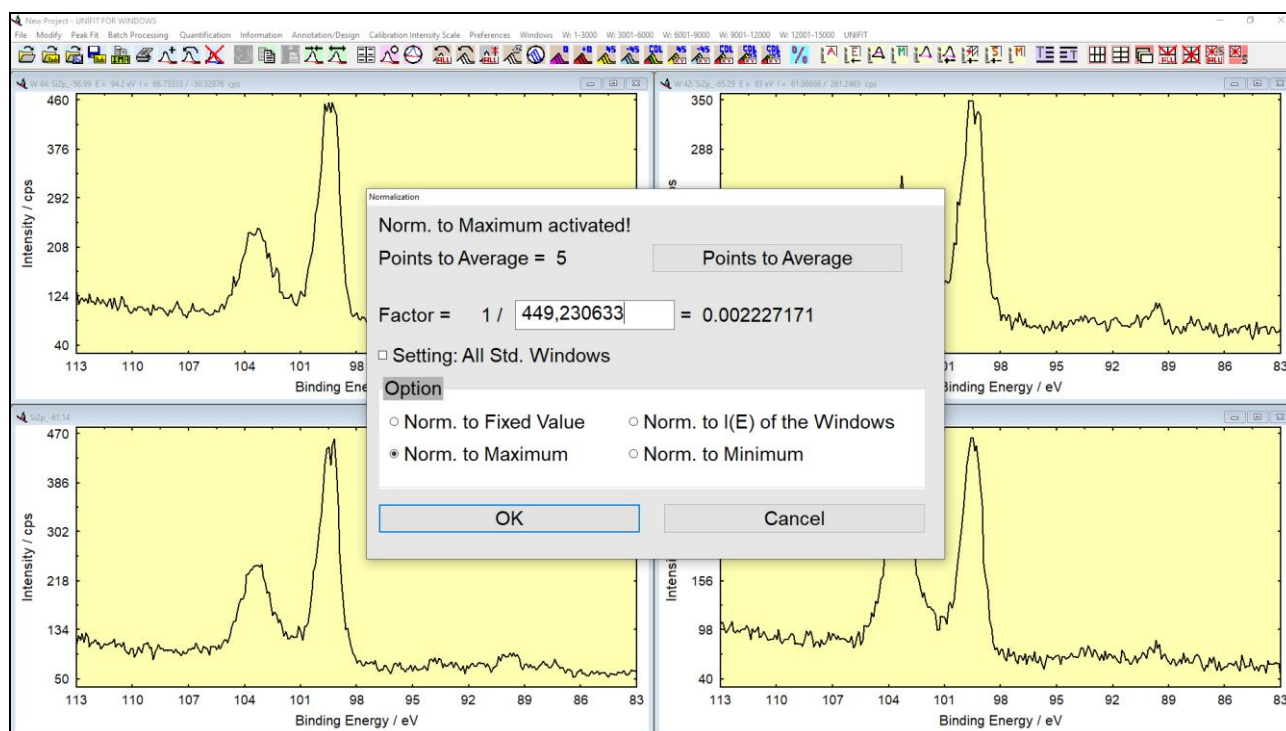




Fig. 14. Screen shot: Dialogue for the normalization of spectra

3.3.12 Integration

 [Modify - Integration] performs an integral spectrum from the right side to the left (XPS, increasing binding energy) and from the left side to the right (XAS, increasing photon energy). This menu point is important for the analysis of XMCD spectra.

3.3.13 Mirror on X-Axis

 To display the negative second derivative of a spectrum, it can be useful to mirror the processed spectrum at the abscissa (see Fig. 13). Sharp maxima result where the experimental spectra has peaks or shoulders allowing a separation/identification of peak energies even in the case of small separation between the components.

3.3.14 Smoothing



The menu option [Modify - Smoothing] allows to improve the signal-to-noise ratio mathematically. Define the points to smooth over in [Preferences - Points of Average] or with the direct call **Points to Average**. The number of points should be 0.7 times the number of points measured in the range of *FWHM* (see 3.7.6).

3.3.15 Spike Correction



In order to remove spikes from a spectrum click [Modify – Spike Correction]. A tick appears in the menu bar and the mouse function is switched to a correction mode. A left mouse key click at a position on the display will set a data point at that position deleting the original one. The procedure can be switched off by clicking [Modify – Spike Correction] again. The tick disappears and the mouse returns to the normal mode. In case of a large number of spectra with spikes, the menu point 3.5.4 should be used. If a spike correction was carried out the re-loading of the original data in the batch processing is deactivated.

3.3.16 Spectrum Manipulation



The functions in this sub-menu manipulate experimental spectra in intensity and energy to prepare them for a subsequent spectrum operation.

3.3.16.1 Energy Shift

Displays a dialogue box which allows to shift the spectrum within the existing energy range keeping - in contrast to [Modify - Charge Correction Active Window...] - the energetic scale is unchanged. The programme adds points at start or end of the experimental spectrum.

3.3.16.2 Correct Intensity

In this menu, the intensity of the experimental spectrum can be changed with a defined normalization factor and an offset.

Note: Only the energy shift or the intensity correction may be used at the batch-processing procedure.

3.3.17 Spectrum Operation



Spectrum operations can be applied firstly only on two spectra of the same number of data points and the same step width. The active window and a second selected one are involved. The result will be displayed in the second window. A later batch processing is possible.

3.3.17.1 Addition

The menu 'Addition' enables the addition of two spectra. The sum of the spectra can be divided optionally by two.

3.3.17.2 Subtraction

[Modify – Spectrum Operation – Subtraction] produces difference spectra elucidating changes in the spectra caused for example by chemical reactions or adsorption processes.

3.3.17.3 Multiplication

This item supplies the product of two spectra.

3.3.17.4 Division

This point produces the quotient of two spectra.

Note: Only the addition, subtraction, multiplication or division of spectra may be used at the batch-processing procedure.

3.3.18 Normalization



This sub-programme gives the user the ability to normalize the spectra from the active window to (see Fig. 14):

1. 'Norm. to Fixed Value',
2. 'Norm. to the Value $I(E)$ of the Windows',
3. 'Norm. to Maximum',
4. 'Norm. to Minimum'.

With the option 'Setting: All Std. Windows' the normalization can be used for all other open standard windows. If the option 'Norm. to $I(E)$ of the Windows' is activated, then the E and I values can be defined by the mouse pointer and pressing the left mouse button. The I -value is transferred to the edit field 'Factor = 1 /'. The I -value can be changed manually, too.

For normalization of parameter-dependent experiment to a maximum, do the following steps:

1. Load the experimental series and switch an appropriate window active.
2. Select [Modify – Normalization...].
3. Select 'Norm. to Maximum'.
4. Activate 'Setting: All Std. Windows'.
5. Press for starting the normalization procedure for all standard windows.

For the calculation of the normalization factor a defined number of average points (excluded the option: 'Norm. to Fixed Value') can be used. The number of average points is displayed and can be changed directly with the call .

3.4 Peak Fit

The extensive peak-fit routine is the most important part of UNIFIT. The peak fit is carried out iteratively by a non-linear parameter optimization according to Marquardt and Levenberg. This procedure converges fast when suitable start parameters are used. However, the fit does not find the absolute minimum in some cases.

The fit parameters of maximal 30 singlet peaks (see 3.10.3) or doublet peaks (i.e. 60 peaks) can be optimized. Five different options can be combined in several ways:

1. Background correction before or during the fit operation (see 3.3.6 and 0),
2. peak model shape as product, sum or convolution of Gaussian and Lorentzian functions (to be selected in [Preferences – Fit Procedure] see 3.10.26),
3. use of absolute or relative fit parameters (to be selected in [Preferences – Fit Parameters] (see 3.10.27),
4. calculation with singlet peaks or doublet signals (see 3.4.1),
5. calculation of a separate background for every peak-fit component (Tougaard background for inhomogeneous samples (see 3.10.28))

The start parameters can be defined through keyboard, mouse or parameter files. Five parameters can be fixed or varied optionally inside ranges given in Min/Max values (see 3.4.4).

In case of a **product** (see also Documents\Unifit_2023_User_Files\test spectra\Test08-Shirley-Productfn-2Peaks-Shirleybg.ufp – Documents\Unifit_2023_User_Files\test spectra\Test12-Pib-Productfn-3Peaks-Shirleybg_Result.ufp) or a **sum** function (see also Documents\Unifit_2023_User_Files\test spectra\Test15-Sumfn-4Peaks-Linearbg.ufp and Documents\Unifit_2023_User_Files\test spectra\Test15-Sumfn-4Peaks-Linearbg_Result.ufp) the fit parameters are:

1. Intensity; Units counts and cps,
2. Gauss-Lorentzian mixing ratio: 0...1, 0 = pure Gaussian, 1 = pure Lorentzian,

3. *FWHM*: XPS: Kinetic or binding energy (eV), AES: kinetic energy (eV), XAS: photon energy (eV), RAMAN: wave number (cm⁻¹),
4. Peak position: XPS: binding or kinetic energy (eV), AES: kinetic energy (eV), XAS: photon energy (eV), RAMAN: wave number (cm⁻¹),
5. Asymmetry: -1...1, at the low kinetic energy (RAMAN: wave number) side the value of the asymmetry parameter will be negative.

The default parameter set is saved in 'Documents\Unifit_2023_User_Files\settings\paraset1.par'.

In case of a **convolution** the Lorentzian function is substituted by the Doniach-Sunjic function. The five fit parameters are:

1. Intensity: counts or cps,
2. Gaussian width: XPS: kinetic or binding energy (eV), AES: kinetic energy (eV), XAS: photon energy (eV), RAMAN: wave number (cm⁻¹),
3. Peak position: XPS: kinetic or binding energy (eV), AES: kinetic energy (eV), XAS: photon energy (eV), RAMAN: wave number (cm⁻¹),
4. Lorentzian width: XPS: kinetic or binding energy (eV), AES: kinetic energy (eV), XAS: photon energy (eV), RAMAN: wave number (cm⁻¹),
5. Asymmetry: 0...1, at the low kinetic energy (RAMAN: wave number) side gives a positive asymmetry parameter while negative asymmetry is not defined for convolution.

Additionally, the *FWHM* of the components (not available analytically) is calculated and displayed.

The default parameter set is saved in 'Documents\Unifit_2023_User_Files \settings\paraset2.par'.

The fit parameters can be saved, printed, copied as image and edited. The background data will be saved together with the other parameters if the baseline is determined iteratively during the fit procedure. All the peak parameters may be varied completely free, varied within a chosen interval or fixed at certain values. The fit parameter limits are not valid for the smaller doublet components. The parameters may be determined independently on absolute scales or they may be treated as relative parameters, which are related to the leading peak of a doublet model peak or to the corresponding master peak. The first peak is always a master peak. In case of absolute fit parameters, a definition of slave peaks is not possible (all main peaks are master peaks). The colour code of the fit-parameter input dialogue is:

RED: Master peak, activated for input,

GREEN: Master peak, not activated for input,

BLUE: Slave peak, activated for input,

WHITE: Slave peak, not activated for input.

The following definitions are given:

IFP = Input/Show fit parameter

MPC_m = master peak component m, absolute parameter values, component m is the master peak with the highest component number, but lower as the activated component (e.g. the component 5 is activated for input, component 1 and 3 are master peaks, m = 3)

MPC_n = master peak component n, absolute parameter value

SPC_n = slave peak component n, absolute parameter value

MMPC_n = Master and main peak (peak 1) of the doublet n, absolute values

SMPC_n = Slave and main peak (peak 1) of doublet n, absolute values

DPC_n = doublet peak (peak 2) of the doublet n, absolute value

(doublet n includes both peaks, main peak (peak 1) and doublet peak (peak 2))

v = variable (empty)

f = fixed (tick)

r = relatively fixed (grey with tick, only applicable for the 2. peak of the doublet beginning with the 2. doublet, preferences: relative parameter)

1. Singlet peaks, absolute parameters

Parameter (without peak position/eV):

Fixing f

Master peak component 1: IFP = MPC1 absolute
 Master peak component n: IFP = MPCn absolute

Parameter Peak position/eV:

Master peak component 1: IFP = MPC1 absolute
 Master peak component n: IFP = MPCn absolute

2. Doublets, absolute parameters

Parameter (without peak position/eV): Fixing f

Master/main peak component 1: IFP = MMPC1 absolute
 Doublet component 1: IFP = DPC1 relative to MMPC1
 Master/main peak component n: IFP = MMPCn absolute
 Doublet component n: IFP = DPCn relative to MMPCn

Parameter Peak position/eV:

Master/main peak component 1: IFP = MMPC1 absolute
 Doublet component 1: IFP = DPC1 relative to MMPC1
 Master/main component n: IFP = MMPCn absolute
 Doublet component n: IFP = DPCn relative to MMPCn

3. Singlet peaks, relative parameters

Parameter (without peak position/eV): Fixing f

Master peak component 1: IFP = MPK1 absolute
 Master peak component n: IFP = MPCn absolute
 Slave peak component n: IFP = SPCn/MPCm relative to MPCm

Parameter peak position/eV:

Master peak component 1: IFP = MPC1 absolute
 Master peak component n: IFP = MPCn absolute
 Slave peak component n: IFP = SPCn – MPCm relative to MPCm

4. Doublets, relative parameters

Parameter (without peak position/eV): Fixing f

Master/main peak component 1: IFP = MMPC1 absolute
 Doublet component 1: IFP = DPC1/MMPC1 relative to MMPC1
 Master/main peak component n: IFP = MMPCn absolute
 Doublet component n: IFP = DPCn/MMPCn relative to MMPCn
 Slave/main component n: IFP = SMPCn/MMPCm relative to MMPCm
 Doublet component n: IFP = DPCn/SMPCn/MMPCm rel. to SMPCn/MMPCm

Fixing r
 Doublet component n (n > 1): IFP = DPCn/MMPCn abs. to DPCm/MMPCm

Parameter peak position/eV:

Master/main peak component 1: IFP = MMPC1 absolute
 Doublet component 1: IFP = DPC1 – MMPC1 relative to MMPC1
 Master/main peak component n: IFP = MMPCn absolute
 Doublet component n: IFP = DPCn – MMPCn relative to MMPCn
 Slave/main peak component n: IFP = SMPCn – MMPCm relative to MMPCm
 Doublet component n: IFP = DPCn - SMPCn - MMPCm rel. to SMPCn - MMPCm

Fixing r
 Doublet component n: IFP = DPCn - MMPCn abs. to DPCm - MMPCm

The relative Min/Max values are given by:

1. Min/Max (without peak position):


Min/Max (relative) = Min/Max (absolute) / parameter value (absolute)

2. Min/Max peak position:

Min/Max (relative) = Min/Max (absolute) – peak position (absolute)

The advantages and disadvantages of the different fit procedures are listed in table 5. Figure 15 and 16 show the same fit-parameter values using relative (Fig. 15) and absolute (Fig. 16) fit parameters of a fit of S 2p. Possible sources of errors of a non-optimal fit are shown in table 6.

3.4.1 Manual Input of Start Parameters

 This procedure allows the input of start parameters by keyboard or mouse. After selecting the number of peaks, fit parameter limits and start parameters will be defined in separate tables (see Figs. 15 and 16). Depending on the preferences, the parameters can be fixed in different ways. The previously applied procedure for peak shape modelling (product, sum or convolution) is displayed in the title labelling of the dialogue box. The previously applied mode for parameter input (singlet peaks or doublets) is opened starting the procedure by the icon. The intensities and peak positions of the second component of the doublet are inserted automatically by using the correct peak name (region name saved in the measurement file, also displayed in the title bar of the windows). The values for the doublets are saved in Unifit_2023_User_files\settings\Doublet.dda (see 3.7.11). With the buttons **-AP** and **AP+** the number of the activated peak-fit component can be decreased or increased stepwise. The buttons **-DS** and **DS+** change the dialogue size. The number of peak-fit components can be decreased and increased with the buttons **-PN** and **PN+**. If relative fit parameters are used the activated peak-fit component can be defined as master (main) or slave peak with the buttons **Masterpeak** or **Slavepeak**. However, the first peak is always a master peak.

Tab. 5. Advantages and disadvantages of different fit procedures

| Option | Advantages | Disadvantages | Application |
|---|--|--|---|
| Background: Subtraction before starting the peak fit | Low number of fit parameters, simple fit handling, fast convergence | Lorentzian function cannot be described accurately during the peak fit | Simple analytical problems, signals with low Lorentzian contribution |
| Background: Iterative calculation during the fit routine | Better description of the Lorentzian function, background can be influenced during the fit procedure, background parameters can be saved | Six additional parameters, handling of the fit routine is more complex | Spectra with high energetic resolution and high Lorentzian contribution, peaks in the region of inelastic scattered secondary electrons |
| Peak modelling: Product or sum of Gaussian and Lorentzian functions (see Fig. 17) | Fast convergence, a value for <i>FWHM</i> is obtained | Inaccurate description of core level peaks results in non-satisfying fit for spectra with high resolution and sufficiently strong Gaussian or Lorentzian contributions | Simple analytical problems, fast fit of spectra with pure Gaussian- or Lorentzian line shape, interest in <i>FWHM</i> |
| Peak modelling: Convolution of Gaussian and | Adequate description of core level peak shape, determination | No value for <i>FWHM</i> , slow iteration | Synchrotron radiation excited spectra, spectra of high |

| | | | |
|-------------------------------------|--|--|---|
| Lorentzian functions, (see Fig. 17) | of basic parameters (Gaussian and Lorentzian width) | | energetic resolution, peaks of transition metals, interest in basic parameters |
| Fit parameters: Absolute | Parameter values immediately available, Simple start parameter input | Only coupling of parameters of the 2. peak for a doublet is possible | Simple analytical problems |
| Fit parameters: Relative | Allows coupling of parameters in different ways | Input of start parameters more complex | Known behaviour of peak parameters (e.g. constant energetic distance in serial experiments) |
| Peak mode: Singlet peaks | Simple parameter input | Unsuited for coupled pairs of lines | s-lines, one component of significantly separated doublets |
| Peak mode: Doublet peaks | Coupling of peaks possible | Handling more complex | Doublet structures of p-, d-, f-lines |

Tab. 6. Possible sources of errors for non-optimal peak fit results

| Findings | Reason | Line of action | Example |
|---|---|--|--|
| Correspondence between experimental spectra and calculated sum curve unsatisfying even after several iterations | System sticks in a local minimum | Disturb the system by varying start parameters sufficiently strong | Doubling of intensity of each component |
| Convergence incomplete | Min/Max values too close to the fit parameters | Select larger Min/Max range | Increase Max value for Lorentzian width from 2 to 2.5 |
| Mismatch between flanks of experimental spectra and calculated sum curve | Selected peak shape doesn't describe the experimental function accurately | Select [Fit Procedure – Convolution] | 3d- and 4f-signals of transition metals with high resolution (comparable contribution of Gaussian and Lorentzian function) |
| Mismatch between experimental spectra and calculated sum curve in the region of peak tails | Inadequate Background subtraction before starting peak fit | Fit baseline together with the peak | Signals with strong Lorentzian contribution |
| No change in one parameter, although it is not fixed | Min/Max values prevent change, the parameter has reached the limit | Change the fit parameter limits | |

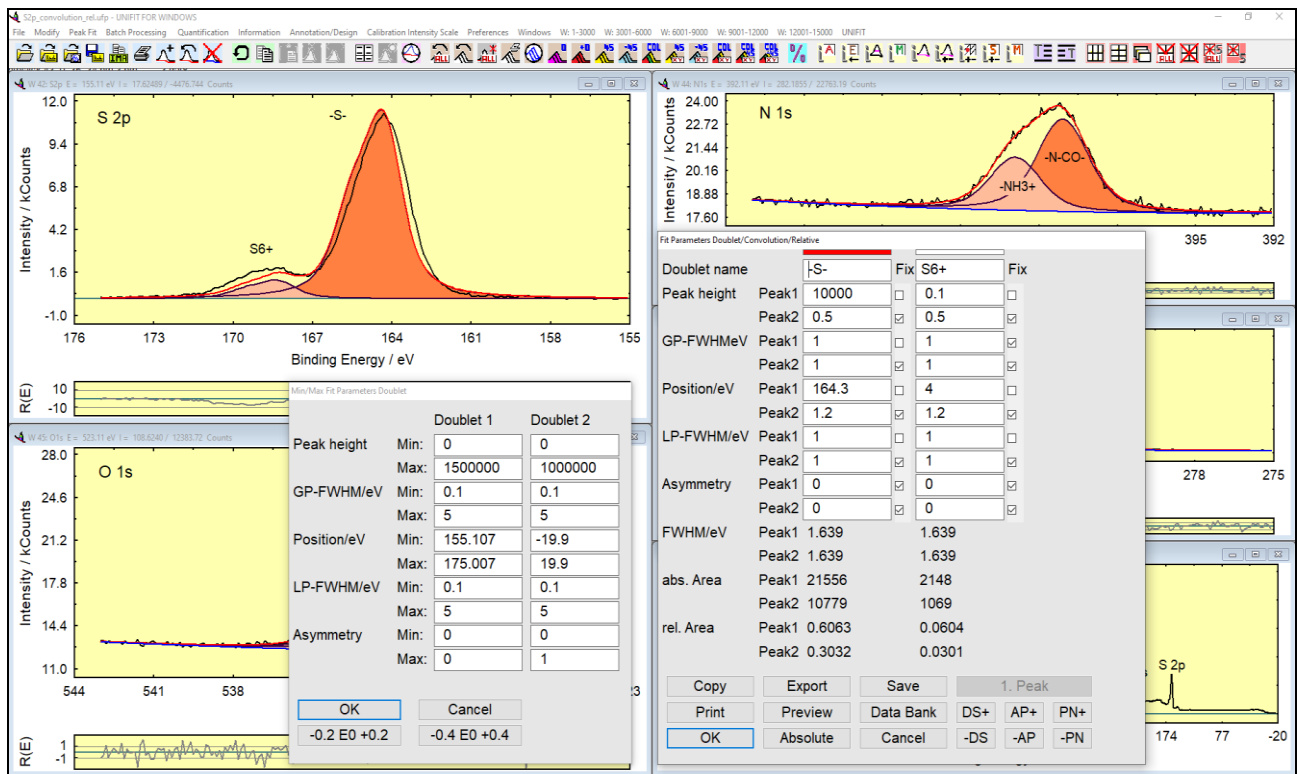


Fig. 15. Example of relative start parameters of two S 2p doublets and their Min/Max values, parameters correspond to the absolute values in Fig. 16, Fit procedure: convolution, project: Documents\Unifit_2023_User_Files\examples\XPS\S2p_convolution_rel.ufp

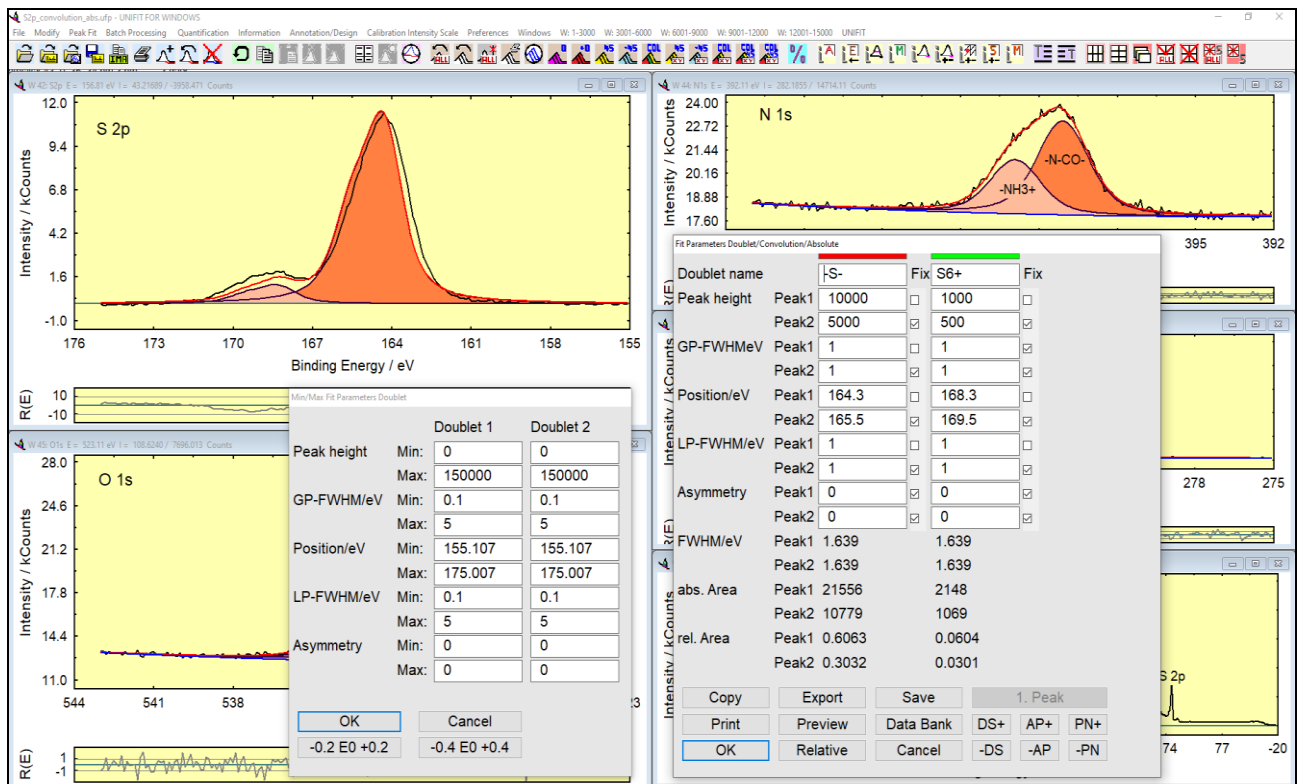


Fig. 16. Example of absolute start parameters of two S 2p doublets and their Min/Max values, parameters correspond to the relative values in Fig. 15, Fit procedure: convolution, project: Documents\Unifit_2023_User_Files\examples\XPS\S2p_convolution_abs.ufp

3.4.1.1 Singlet Peaks

Use sub-menu 'Singlet Peaks' to fit independent, uncoupled signals (e.g. C 1s, O 1s, N 1s, S 2s ...), (see also Test01.ufp – Test03.ufp, directory: Documents\Unifit_2023_User_Files\test spectra). Act as follows:

1. Select [Peak Fit – Manual Input of Start Parameters – Singlet Peaks] or the pop-up command [Peak Fit Input Parameters Singlet Peaks],
 2. define the number of components in the next dialogue box and click ,
 3. accept or change Min/Max-values in the table 'Min/Max Fit Parameters Peak' (see 3.4.4), choose or leave the procedure with ,
 4. define the start parameters in the table 'Fit Parameters Peak...' (see 3.4.4) by
 - a) entering the values with the keyboard,
- Note:** Move between the fields with the left mouse button or the Tab-key.
- b) pressing Alt-Y, ALT-Z or left mouse button to copy the position of the mouse pointer from the display into energy and intensity start parameters. Hold the Shift key and press the left mouse button for switching to the next component without changing the parameters or use the buttons and .
5. Set a '✓' in the 'Fix' boxes if required. Switching on the 'Fix' option has the following effects:
 - a) **absolute parameters:** fixing the parameter completely,
 - b) **relative parameters:** keeps – starting with peak two - the values relative to the corresponding parameter of the first peak or the relevant master peak unchanged, e.g. energy shift or ratio between the other parameters will stay constant.

Note: The fit procedure (product, sum or convolution) as well as the chosen fit parameters (absolute or relative) are displayed in the title bar of the fit-parameter table. Set '✓' by clicking the left mouse button when the pointer is above the box or by pressing the space bar.

6. or the parameters if desired, accept the parameters with ,
7. start peak fit with [Peak Fit – Iteration],
8. define the number of iterations and iteration cycles and confirm with .

The peak components may be labelled optionally with the names of the chemical species in the fit-parameter table. An image of the fit-parameter table is copied in the clipboard with the call (see Fig. 18). The call realizes an image export using a standard format (jpg, gif, wmf, bmp, etc.).

3.4.1.2 Doublet Peaks

Use sub-menu 'Doublet Peaks' to fit coupled lines (e.g. S 2p, Au 4f, Ga 3d, etc.).

Act as follows:

1. Select [Peak Fit – Manual Input of Start Parameters – Doublet Peaks] or the pop-up command [Peak Fit Input Parameters Doublet Peaks],
2. Define the number of doublets in the upcoming dialogue box and click , accept or change the Min/Max-values in table 'Min/Max Fit Parameters Doublet' (see 3.4.4), click or leave the procedure with .

Note: Min/Max-values affect only the first component of each doublet.

3. Define the start parameters in table 'Fit Parameters Doublet...' (see 3.4.4) by
 - a) entering the values with the keyboard

Note: Move between the fields with the left mouse button or the Tab-key. Make sure the peak names are correct.

b) or pressing Alt-Y, ALT-Z or left mouse button to copy the position of the mouse pointer from the display into energy and intensity start parameters. If available, energetic shifts and intensity ratios of doublet components are saved in a database and will be used for calculation of energy and intensity start parameters of the second component of a doublet automatically. Hold the Shift key and press the left mouse button for switching to the next component or use the buttons and .without changing the parameters.

Note: Set '✓' by clicking the left mouse button when the pointer is above the box or by pressing the space bar. The fit procedure (product, sum or convolution) as well as the chosen fit parameters (absolute or relative) is displayed in the title bar of the fit-parameter table.

4. Set an '✓' in the 'Fix' boxes for the parameters of **first doublet peaks** if desired. Switching on the 'Fix' option has the following effects (see Fig. 19):
 - a) **absolute parameters:** fixing the parameter completely,
 - b) **relative parameters:** keeps – starting with doublet two - the values relative to the corresponding parameter of the first doublet or the relevant master peak unchanged, e.g. energy shift or ratio between the other parameters will stay constant.
5. Set an '✓' in the 'Fix' boxes for parameters of **second doublet peaks** to keep a constant shift or ratio to the corresponding parameter of the first peak of the same doublet (**absolute and relative parameters**).
6. Set a grey square in the 'Fix' boxes for parameters of **second doublet peaks** – starting with doublet two - to adopt the relations calculated for the first doublet during the iteration e.g. energy shift and ratio of the other parameters (**absolute and relative parameters**).

Note: Set '☐' by double-clicking the left mouse button when the pointer is above the box or by pressing the space bar twice.

7. or the parameters if desired, accept the parameters with .
8. Start peak fit with [Peak Fit – Iteration],
9. define the number of iterations and iteration cycles and confirm with .

An image of the fit-parameter table is copied in the clipboard with the call . The call realizes an image export using a standard format (jpg, gif, wmf, bmp, etc.) (see Fig. 18).

3.4.2 Input Start Parameters Using Data Bank



This menu point permits the input of the start parameters via the data bank of chemical shifts integrated in UNIFIT. In case of using this method for setting the start parameters the charging at all peaks have to be corrected. For a certain finding of the reference element lines the names of the regions have to be correct (e.g. S 2p, C 1s, Ag 3d5, etc.).

The number of components does not need to be defined before. With the selection of a component the name of the chemical component will be displayed in the fit-parameter table and the activated window, too. The component names inserted into the window presentation can be deleted or changed with [Annotation/Design – Spectrum Labelling 1].

3.4.2.1 Singlet Peaks

After selecting this menu point, the list of available lines is opened. A line can be selected clicking on using the left mouse key. All components are deleted with . If all peaks were selected click and the Min/Max and parameter tables will be opened. If a file of adequate chemical shifts is not available or the region name is incorrect an error message is shown.

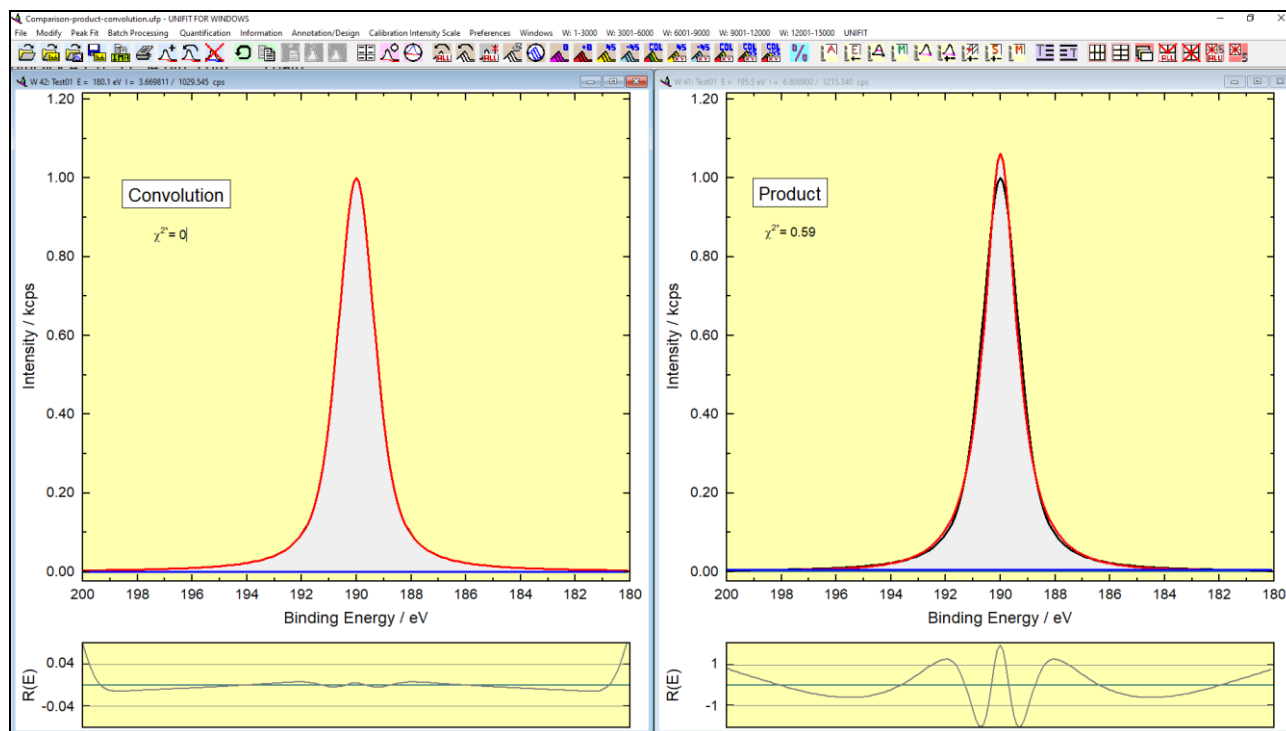


Fig. 17. Screen shot: Comparison of a fitted model function of Gaussian and Lorentzian width of 1 eV each and a peak height of 1000 counts, left: convolution, right: product function (Test spectrum Test01), background was iteratively calculated parallel with the peak fit, project: Unifit_2023_User_Files\examples\XPS\Comparison_product_convolution.ufp

3.4.2.2 Doublet Peaks

This menu point works in the same way as the menu point 3.4.2.1 but according to the values of the file Doublet.dda (see book 'Line Positions and Data Formats – Version 2023', 5.5) two lines will be generated.

| Doublet name | Peak height/ Counts | GP-FWHM/ eV | Position/ eV | LP-FWHM/ eV | abs. Area/ Counts·eV | rel. Area/ % |
|--------------|------------------------|----------------|-----------------|----------------|-------------------------|-----------------|
| S2p | 10000 | 1 | 164.3 | 1 | 21556 | 60.63 |
| | 5000 | 1 | 165.5 | 1 | 10779 | 30.32 |
| S6+ | 1000 | 1 | 168.3 | 1 | 2148 | 6.04 |
| | 500 | 1 | 169.5 | 1 | 1069 | 3.01 |

Fig. 18. Fit parameter table of the S 2p doublet (see Fig. 16) via 'Copy – Paste function' integrated into this document

Example 6: The measurement *Unifit_2023_User_Files\examples\XPS\sulphur_study\example.tap* was recorded using the spectrometer ESCA3 with the Al-twin anode. The following operations should be made on the S 2p peak:

- Energy calibration with respect to C 1s = 285.0 eV,
- satellite subtraction,
- subtraction of a Tougaard background,
- peak fit with a product model function, absolute parameters and the background for homogeneous samples,
- the intensity ratio of the 2 doublet lines is fixed to 1:2,
- the peak separation is fixed to 1.2 eV.

1. Start UNIFIT,
2. select [Preferences – Fit Procedure – Product], ticked,
3. select [Preferences – Fit Parameters/XAS Background Parameters - Absolute], ticked,
4. select [Preferences – Tougaard Background Calculation – Homogeneous Sample], ticked, select [Preferences – Y-Axis – Counts] and [Preferences – X-Axis – XPS: Binding Energy...], select [Windows - Hide Standard Windows - Show all Standard Windows], be sure that the number of maximal peak-fit components is larger than two with the call: [Preferences – Setting of Programme Parameters...],
5. load the measurement data with [File - Open Spectra - XPS - ESCA3(*.TAP)], select directory **Unifit_2023_User_Files\examples\XPS\sulphur_study** and open **example.tap** and read the file with ,
6. in ‚Select Spectra‘ select C 1s and S 2p (with the left mouse button), select ‚Internal Spectra Names‘ to ‚Peak name without Extension‘ and press ,
7. activate the C 1s window, estimate the maximum of the C 1s peak with [Information - Minimum/Maximum],
8. calculate the charge correction (difference to 285.0 eV, e.g. maximum at 286.7 eV, charging: 1.7 eV),
9. subtract the charging from all opened windows with [Batch Processing – Charge Correction all Windows], input 1.7 eV, press , all spectra will be shifted by 1.7 eV,
10. activate and maximize the S 2p window,
11. subtract the satellite with [Modify – Subtract Satellite], press , the satellite will be subtracted from the S 2p spectrum,
12. subtract a Tougaard background from the spectrum with [Modify – Calculate Background - Tougaard], activate ‚Adjust B-Parameter‘ and (spectrum is now corrected for satellite and background),
13. select [Peak Fit – Manual Input of Start Parameters – Doublet Peaks] or select the pop-up command [Peak Fit Input Parameters Doublet Peaks], input ‚Doublet Number‘ 2, press ,
14. the Min/Max menu is opened automatically and the Min/Max values are shown for all the fit parameters of the main peaks,
15. accept the given values by pressing ,
16. the parameter table ‚Fit Parameter Doublet/Product/Absolute‘ will be opened automatically, move the mouse pointer to the maximum of the first doublet ($E = 164$ eV, $I = 10580$ counts) and press the left mouse button, move the mouse pointer to the second maximum ($E = 168$ eV, $I = 1555$ counts) and press the same mouse button, (I and E values of both doublet peaks are written automatically in the table), fix the same values as shown in Fig. 19, press , your fit should have the same appearance as Fig. 19, bottom left, compare with the right table,
17. accept values by pressing ,
18. the dialogue ‚Input Number of Iterations‘ will be opened, choose the number of iteration steps = 22 and the number of cycles = 2 and start the iteration process with ,
19. the optimization is running, when the system has stopped your result should be like Fig. 19, top left.

3.4.3 Load Start Parameters



Fit parameters saved before with extension *.par can be loaded by [Peak Fit – Load Start Parameters]. The parameters are saved in the same format independent of the selected preferences. However, loading them again, current preferences for fit parameters and fit procedure will be taken into account and the parameters are re-calculated accordingly. An example is given in

the book 'Line Positions and Data Formats', 4.3. The parameters of the spectral background fitted parallel with the peak fit will be saved together with the fit parameters in the files *.par.

Act as follows:

1. Select [Peak Fit – Load Start Parameters],
2. Select parameter file in the dialogue box and confirm with **OK**,
3. Change/accept Min/Max values and confirm with **OK** or leave the dialogue box without changes with **Cancel**,
4. Change/accept start parameters and fixing – confirm with **OK**,
5. Select [Peak Fit – Iteration],

Define the number of iterations and confirm with **OK** – then the fit will be started.

Note: [Batch Processing – Batch Processing] can be used for copy of fit parameters between windows as well. The number of peaks can be changed after loading a parameter set by selecting [Peak Fit – Manual Input of Parameters – Singlet Peaks/Doublets] and defining the number in the dialogue box.

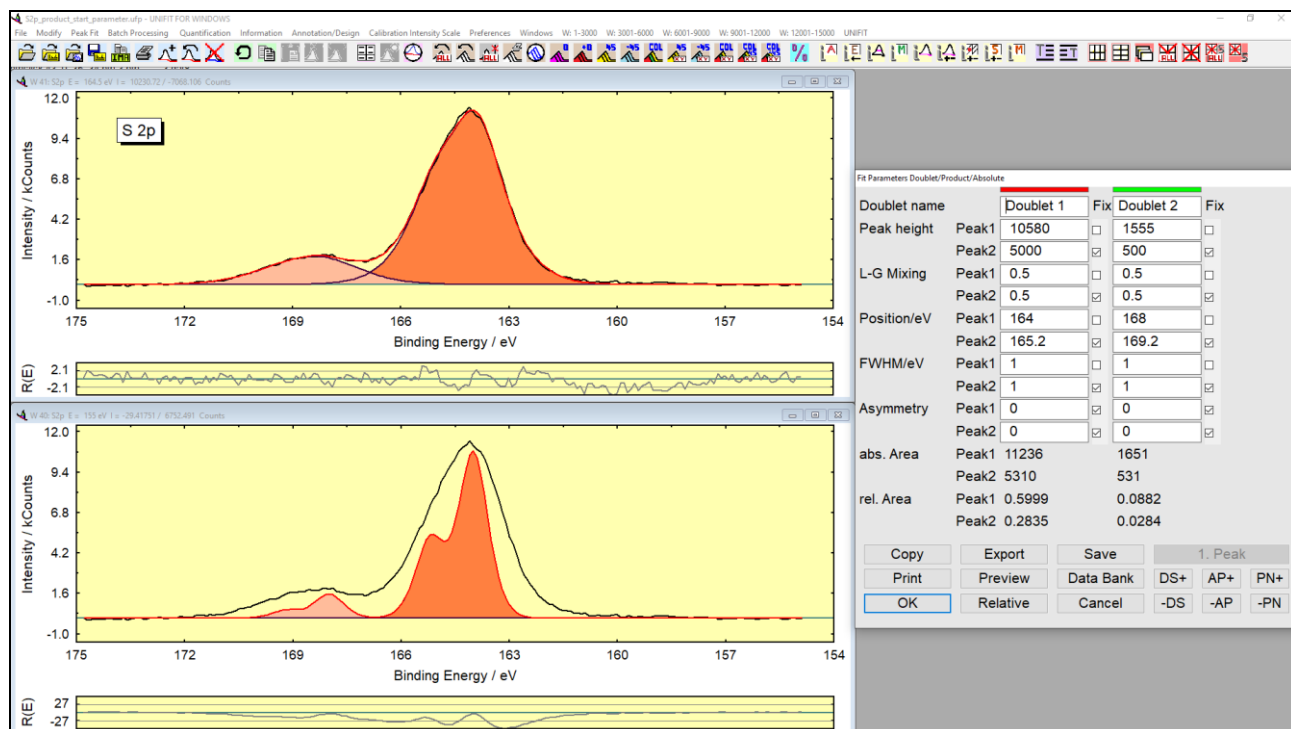



Fig. 19. Screen shot: Dialogue for the fit parameters of an S 2p peak with two doublets, product fitting procedure and absolute parameters, bottom left: start iteration with start parameters, top left: fitted spectrum, right: fit-parameter table with start parameters, project: Unifit_2023_User_Files\examples\XPS\S2p_product_start_parameter.ufp

3.4.4 Show/Correct Fit Parameter Limits

 The limits of all singlet or the first doublet peaks may be changed selecting [Peak Fit - Show/Correct Fit Parameter Limits] or the pop-up command [Peak Fit Show Parameter Limits]. A dialogue box appears which allows defining the minimum and maximum values for a parameter for the peak in question. They will be saved additionally to the fit parameters. A

predefined energy range of the peak positions of all peak-fit components can be activated using two buttons: **-0.2 E0 +0.2** and **-0.4 E0 +0.4**.

Act as follows:

1. Select [Peak Fit – Show/Correct Fit Parameter Limits],
2. Change/accept Min/Max values and confirm with **OK** or leave the dialogue box without changes with **Cancel**.

3.4.5 Show/Correct Fit Parameters

By selecting [Peak Fit - Show/Correct Fit Parameters] or the pop-up command [Peak Fit Show Parameters] a dialogue box appears which allows to edit and to change the start parameters for the fit procedure and the relation between them. The parameters can be saved as absolute values with **Save**, printed with **Print** or accepted for peak fitting with **OK**. **Preview** will show the result of the manually corrected peaks. This option is a special feature to test the changed parameters. With the buttons **-AP** and **AP+** the active peak-fit component can be changed. The number of peak-fit components can be decreased or increased with the buttons **-PN** and **PN+**. The buttons **-DS** and **DS+** change the dialogue size.

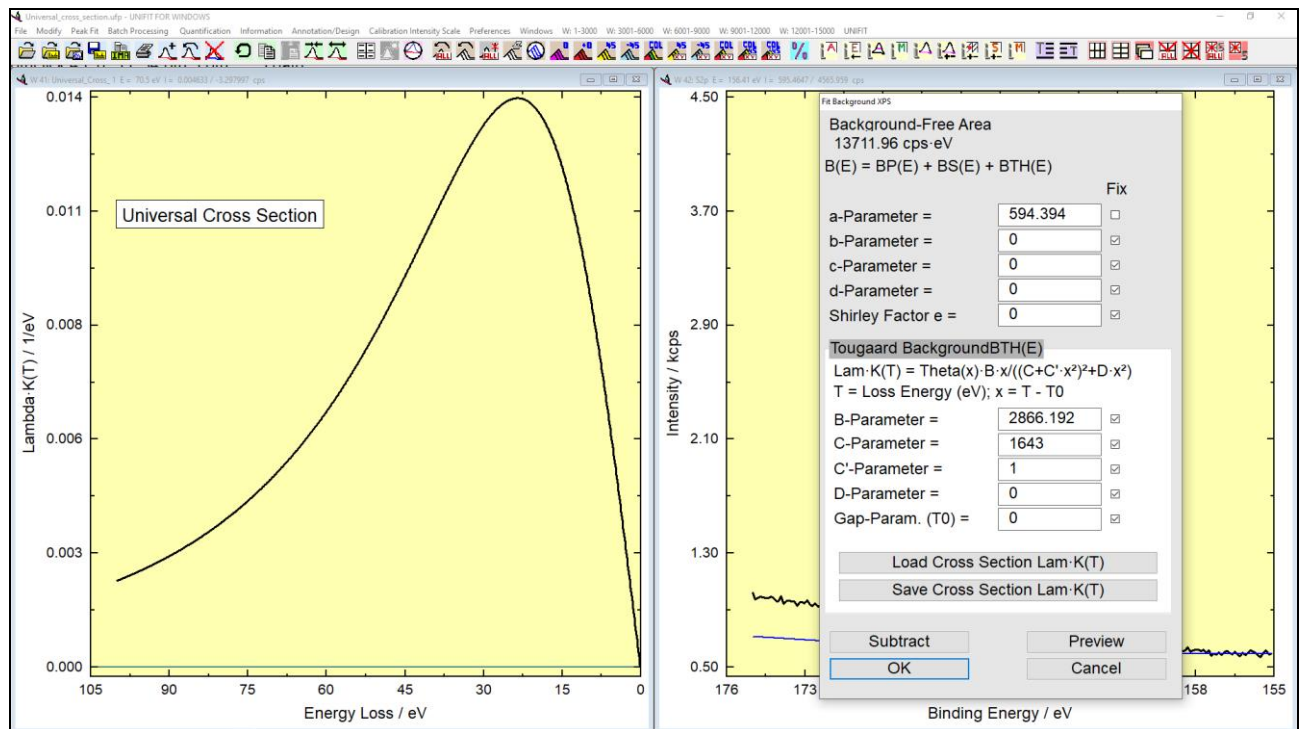


Fig. 20. Screen shot: Left: plot of inelastic electron scattering cross-section using UNIFIT (example: Universal cross section), right: dialogue menu of the fittable background for the input parameters, project: Documents\Unifit_2023_User_Files\examples\Specials\Universal_cross_section.ufp

In case of relative fit parameters the commands **Masterpeak** and **Slavepeak** define the active peak-fit component. The fit parameters of a master peak are absolute. The fit parameters of the slave peaks are defined always relative to the corresponding master peak (the corresponding master peak is the master peak with the highest number, but lower than the number of the slave peak, e.g. peak fit with five components: 1. component: master peak, component 1: slave peak, relative to the component 1, component 2: slave peak, relative to the component 1, component 4: master peak, component 5: slave peak, relative to the component 4). Test projects are saved: Unifit_2023_User_Files\test spectra\Test37.ufp - Test43.ufp.

Copy and **Export** generate an image of the fit-parameter table. **Cancel** closes the dialogue box without accepting changes. The preferences for the fit parameters can be changed and saved as special files (Unifit_2023_User_Files\settings\paraset1.par for the product and sum function or Unifit_2023_User_Files\settings\paraset2.par for convolution) using the **Save** button, too. Additionally, the absolute and relative peak areas are given when a previous peak fit was performed. Act as follows:

1. Select [Peak Fit – Show/Correct Fit Parameters] or the pop-up command [Peak Fit Show Parameters].
2. Change/accept start parameters and fixing – confirm with **OK** or leave the dialogue box without accepting the changes with **Cancel**.
3. Select [Peak Fit – Iteration] or the pop-up command [Peak Fit Iteration].
4. Define the number of iterations and confirm with **OK** which starts the fit,
5. Edit/change the parameters after the fit procedure directly with **Show Fit Parameters** or by using [Peak Fit – Show/Correct Fit Parameters] again.

3.4.6 Fit Background



The sub-routine ‘Fit Background’ can be used only under the pre-condition that no background subtraction has been carried out during the data modification.

3.4.6.1 Fit Background XPS (HOM)

The start approximation for an iterative calculation of the XPS background simultaneously with the peak fit has to be defined before input of other peak-fit parameters (see 3.4.1). The background function is described by a combination of ten different contributions (see also Test04-Voigtfn-0.3eVLorentz-1.7eVGauss+Polynom2.G-Bg_Result.ufp and Test05-Voigtfn-2Peaks+Polynom2.G-Bg_Result.ufp). One background for the complete spectrum is calculated.

The parameters a - d define the polynomial part: constant, linear, square and cubic part. The e parameter defines the part of the Shirley background. The Shirley part will be calculated using experimental data before starting the peak fit procedure and using the calculated sum curve afterwards.

The parameters B , C , C' , D and the energy-gap parameter T_0 define the inelastic electron scattering cross-section of the Tougaard background (see also Test19-Tougaard-Background_Result.ufp). With $B = 0$ the part of the Tougaard background can be set to zero independent of the value of the C , C' , D and T_0 parameters (see Fig. 20, right). The parameters of the Cross Section can be saved with **Save Cross Section Lam·K(T)** and loaded with **Load Cross Section Lam·K(T)**. A manual approach of the parameters B , C , C' , D and T_0 may be carry out in the menu 3.3.6.2. Each background parameter can be fixed (tick ‘Fix’ in the background parameter dialogue box) or varied. The fitted background will be saved together with the other fit parameters. A start set of parameters will be suggested by the programme: the background parameter for the constant (minimum of the experimental spectrum) and the Shirley contribution; the B parameter set to 0 and fixed. The parameters $C = 1643$, $C' = 1$, $D = 0$ and $T_0 = 0$ describe the Universal Cross-Section. Now the user can edit, re-fix the background parameters and calculate and draw the modified background with **Preview**. **Subtract** removes the background from the spectra and with **OK** the background settings for the peak fit will be accepted. The sub-routine is closed without changes by clicking **Cancel**.

The advantage of this procedure is shown by comparing the residual function $R(E)$ and the χ^2 for the spectrum obtained with unfitted background in Fig. 21. Further examples are presented in 3.10.26 and in the files Au_survey_fit.ufp and SiO2_Cross_Section_fit.ufp (folder: Documents\Unifit_2023_User_Files\examples\XPS).

Note: If the B -parameter is zero and fixed, then the parameters C , C' , D and T_0 are automatically fixed.

3.4.6.2 Fit Background XPS (INHOM)

The difference of this menu point to 3.4.6.1 is the calculation of the Tougaard-background function. For every peak-fit component a separate Tougaard background with different inelastic electron scattering cross-sections may be calculated (see 2.1.1.7.2). This permits the better estimation of the spectral backgrounds of XPS measurements of laterally inhomogeneous samples. The number and the sequence of the Tougaard-background functions and peak-fit components have to be the same. The fit parameters of the Tougaard-background functions can be defined as absolute values or relative to the first one (see 3.10.27).

The start approximation for an iterative calculation of the XPS background parallel with the peak fit has to be defined before input of other peak fit parameters (see 3.4.1). If the peak fit is carried out with n peak-fit components then the background function is described by a combination of $5+5 \cdot n$ different contributions (e.g. $n = 4$, number of fit parameters of the background = 25, see also Test36-InhomogeneousSample-2Peaks-with-2IESCS_Result.ufp with $n = 2$). The parameters B_i , C_i , C'_i , D_i and T_{0i} define the inelastic electron scattering cross-sections of the Tougaard backgrounds ($i = 1$ to n). With $B_i = 0$ the part of the Tougaard background can be set to zero independent of the value of the C_i , C'_i , D_i and T_{0i} parameters (see Fig. 22, right).

The parameters of the inelastic electron scattering cross-sections of the selected background number can be saved with **Save Cross Section Lam·K(T)** and loaded with **Load Cross Section Lam·K(T)**. Each background parameter can be fixed (tick 'Fix' in the background parameter dialogue box) or varied. The parameters of the fitted background will be saved together with the other fit parameters. The user can edit and re-fix the background parameters and calculate and draw the modified background with **Preview**. **Subtract** removes the background from the spectra and with **OK** the preferences for the peak fit will be accepted. The sub-routine is closed without changes by clicking **Cancel**.

Note: The processing time of a peak fit with inhomogeneous Tougaard-background functions [Peak Fit - Fittable Background XPS (INHOM)] is about twenty times longer with respect to the usage of the homogeneous Tougaard background [Peak Fit - Fittable Background XPS (HOM)].

3.4.6.3 Fit Background XAS

Before the input of the fit parameters (see 2.1.2.6) is carried out the fit background XAS has to be defined (see also Test34-XAS-4Peaks-Sum-EAbg-Relative_Result.ufp). The fit parameters, absolutely or relatively, correspond to the choice of the fit parameters of the peak fit. After calling the menu [Peak fit - Fit Background XAS] an input box appears for the selection of the number of steps and the choice 'Single Steps or Doublet Steps' for the background calculation. The iteration treatment of the variable or fixed background-fit parameters corresponds to the selected peak-fit routine.

3.4.6.3.1 Step Number = 0

With a choice of the step number like zero the background is generated without step function (eqn. (41)) and only with a polynomial and the Shirley background. Five fit parameters describe the background.

The background function is described by a combination of five different contributions. The parameters $a - d$ define the polynomial part: constant, linear, square and cubic part. The e parameter

defines the part of the Shirley background. The Shirley part will be calculated using experimental data before starting the peak fit procedure and using the calculated sum curve afterwards.

Each background parameter can be fixed (tick 'Fix' in the background parameter dialogue box) or varied. The fitted background will be saved together with the other fit parameters. The programme will suggest a start set of parameters: the background parameter for the constant (minimum of the experimental spectrum) and the Shirley contribution. Afterwards, the user can edit and re-fix the parameters, recalculate and re-draw the background with . removes the background from the spectra and with the preferences for the peak fit are accepted. The sub-routine is closed without changes by clicking .

Example 7: *The magnetic moment of a thin Co film (21 mono layers) on BaTiO₃ using a XMCD experiment of a Co L-absorption edge has to be calculated. The sample was excited with left and right circularly polarized light. The sample was magnetized in-plan. The files 21MLCoMinus.SX7 and 21MLCoPlus.SX7 are saved in the folder: **Unifit_2023_User_Files\Examples\XAS\XMCD**. The result of the example with all used windows is saved in the UNIFIT project: **Unifit_2023_User_Files\Examples\XAS\XMCD.ufp**.*

1. *The preferences of the XAS-fit background with [Preferences - Fit Parameters/XAS-background parameters - Relative], the number to average points of 5 with [Preferences - Points to Average], labelling of the X-axis with [Preferences - X-axis - XPS: Binding Energy/XAS: Photon Energy], labelling of the Y-axis with [Preferences - Y-axis - Counts], number of displayed windows to 'Show all Standard Windows' with [Windows - Hide Standard Windows].*
2. *Load spectrum 21MLCoMinus into windows 1 and spectrum 21MLCoPlus into window 2 with [File - Open Spectra - XAS - MAXlab Scan Zeiss (*.SX7)] and the input options:*

| | |
|-----------------------|---|
| CT: 3: | Data |
| CT:2: | Reference |
| Step Width: | 0.2 eV (Note: in case of a different value change it) |
| Initial Energy: | 770 eV |
| Final Energy: | 810 eV |
| Normalization Enable: | activated |
3. *Activate and copy window 1 with [Modify - Copy].*
4. *Insert the copied window with [Modify - Insert], window 1 and window 3 include the spectrum 2MLCoMinus.*
5. *Generate the sum spectrum in window 3: Activate window 2 with [Modify - Spectrum Operation - Addition], the menu 'Spectrum Addition' is opened, input window number 3 for the addition operation, and activate 'Division by 2' and click . Windows 3 shows the averaged spectrum of window 1 and window 2.*
6. *Calculate the step height of the sum spectrum: Activate window 3, go to [Peak Fit - Fit Background XAS], Number of steps = 2, Activate 'Single Steps' and click . The menu Fit background XAS appears with relative background parameters. The parameter setting is:*

| | |
|---|-----------------------|
| - Height: Step 1: is not changed, free; | Step 2: 0.5, fixed, |
| - E/A-Mix: Step 1: 0.5, free; | Step 2: 1, fixed, |
| - Position: Step 1: 778 eV, free; | Step 2: 15 eV, fixed, |
| - FWHM: Step 1: 2 eV, free; | Step 2: 1, fixed. |

Parameters a to e fixed. The parameters are not changed. Activate 'Adjust a and Height Parameters' and press . Read the step height (value: 3.7105) and click . The menu will be closed.
7. *Normalization of spectra: Divide all opened windows by the step height with [Modify - Spectrum Manipulation - Correct Intensity] and the factor 1/3.7105.*

8. Subtract a constant background from each spectrum with [Modify - Calculate Background - Constant] and .
9. Correction with the magnetic field correction: Activate window 2 and open the information panel with [Information - Correction of the Magnetic Field], read the values 0,997 and 1 of the Minus and Plus spectrum, quotient Plus/Minus = 1/0,997. Activate windows 1 and change the intensity with [Modify - Spectrum Manipulation - Correct Intensity] with the factor 1/1.003 (1.003 = 1/0,997). Now, the step height is the same (=1) of both spectra, Plus and Minus.
10. Generation of the 3D Waterfall 0° Plot: Copy window 1 and insert the copied as window 4. Activate window 2. Calculate the difference spectrum (window 4 minus window 2) with [Modify - Spectrum Operation - Subtraction]. Window 4 includes the difference spectrum.
11. Exchange the window 2 with window 3: Activate window 3 and [Windows - Change Windows Numbers] and put in window number 2.
12. Define the batch parameters of all windows with [Annotation/Design - Edit Parameters Standard Windows], the dialogue 'Selection Acquisition Parameters' appears, select 'Batch parameter', the new batch parameters are: window 1: Minus, windows 2: Sum, windows 3: Plus, windows 4: Difference. Close menu with .
13. Generate a 'Plot 3D Waterfall 0°' of all windows in window 5 with [Batch Processing - Plot 3D Waterfall 0°], select all windows and click and select 'Modified Spectrum'.
14. Change the design of windows 5: Activate windows 5 and use the menu point [Annotation/Design - Plot Intensity Axis] with the following setting:
 - Offset: 0.05
 - Stretching: 0.95
 - Curve distance: 0
 - Show Zero Line: Difference spectrum,
15. Select [Annotation/Design - Plot Parameter Axis] and annotate the Axis with 'Intensity', deactivate 'Labelling of Scale Lines'.
16. Create a legend (position: top, right) in window 5 with [Annotation/Design - Legend/Select Curves], activate 'Show Legend', activate for all curves 'Plot', select a suitable position of the annotation. Modify the colour of the curves with [Preferences - Display - 3D Plot Waterfall/XY 3D Plot/Colour Profile Display...].
17. Calculation of the magnetic moments: Take back the constant background of window 2 with [Modify - Calculate Background - Constant], close the background menu with .
18. Copy the sum spectrum window 2 and insert the spectrum into window 6.
19. Calculation of the XAS background in window 6: Activate window 6 and open the menu XAS background with [Peak Fit - Fit Background XAS] in the same way and with the same parameters as in point 6 and leave the menu by clicking the button . The background is subtracted from the spectrum creating a so-called 'White-line'.
20. Copy window 6 and insert the spectrum (window 7 will be generated, sum). Copy window 4 (Difference) and insert the spectrum into window 8.
21. Generate the integral curves of the spectra in window 7 (sum) and 8 (difference): Activate window 7 and calculate the integral curve with [Modify - Integration], Activate window 8 and generate the integral curve, too. Window 7 includes the integral of the sum curve and window 8 the integral of the difference curve.
22. Calculation of the magnetic moments: Extract the necessary data in the following way from windows 7 and 8:

| | |
|--------------------|--|
| $I = 76.609$ | Intensity of the last channel in windows 7 ($E = 810$ eV) |
| $C = I/N = 30.767$ | with $N =$ number of d-holes (2.49) for Co, calculated in literature |
| $A = -17.736$ | Intensity in window 8 at $E = 791$ eV (0.6 eV larger than the minimum) |
| $B' = -8.208$ | Intensity of the last channel in window 8 |

$$B = B' - A = 9.528$$

23. Calculate the magnetic moments using the sum rule formalism (m_s : spin moment of the valence band, m_o : orbital moment of the valence band):

$$m_s = -\frac{A - 2B}{C} = 1.196 \qquad m_o = -\frac{2(A + B)}{3C} = 0.178$$

The values are in μ_B .

Correction of the calculated values with the angle (50°) and the helicity (95% polarized light) gives the correction factor $X = 1/(0.95 \cdot \sin(50^\circ)) = 1.374$.

$$m_{s,korr} = m_s \cdot 1.374 = 1.643, \quad m_{o,korr} = m_o \cdot 1.374 = 0.244$$

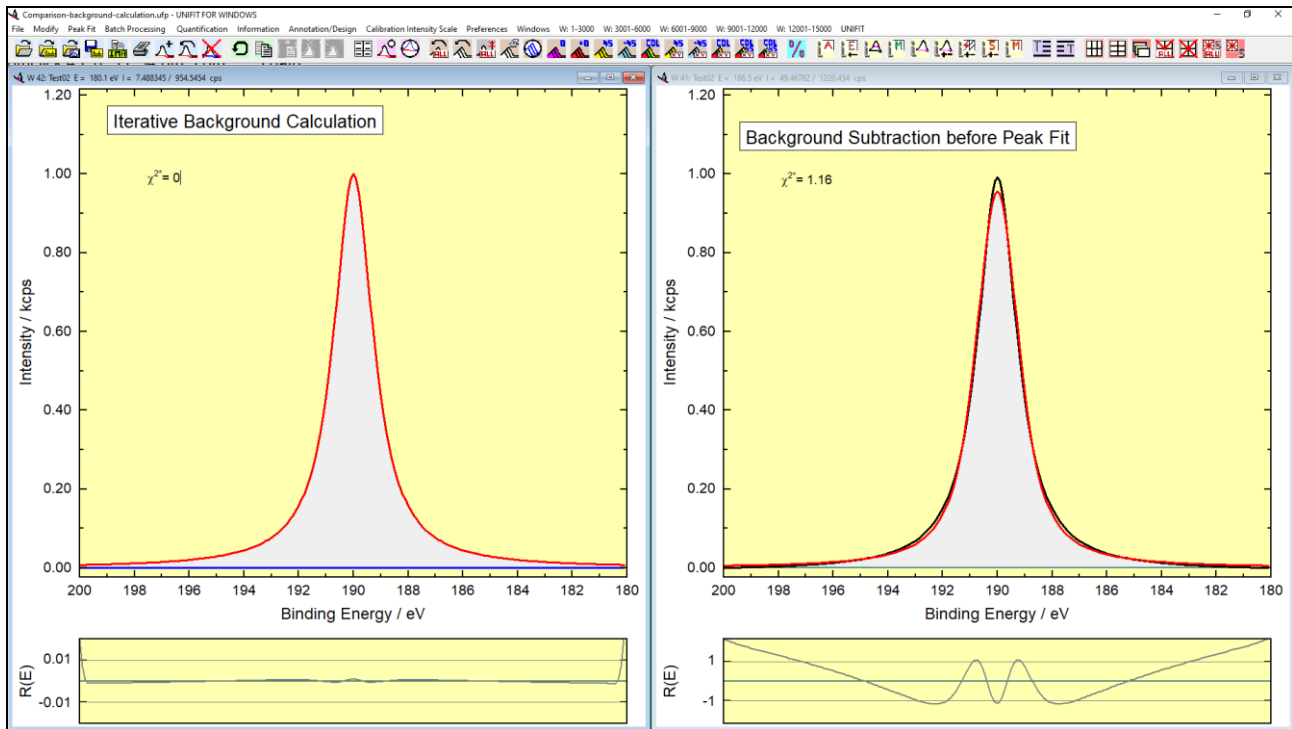


Fig. 21. Voigt function (Test02-Voigtfn-1.7eVLorentz-0.3eVGauss_Result.ufp, without statistical noise) with 1.7 eV Lorentzian width and 0.3 eV Gaussian width, left: iterative background calculation, right: background subtracted before starting peak fit, Fit procedure: convolution, project: Unifit_2023_User_Files\examples\XPS\Comparison_background_calculation.ufp


3.4.6.3.2 Step Number > 0

By choosing the step number NS greater than zero the background is generated without Shirley function and is calculated only with a polynomial and a step background (sum of error and Arc tangent function) consisting of NS separate steps (Eqn. (44)). Four plus $4 \cdot NS$ fit parameters in case of single steps and four plus $8 \cdot NS$ fit parameters in case of doublet steps describe the background. The parameters $a - d$ describe the polynomial with constant, linear, square and cubic part. The parameter $e = 0$ and is fixed and not selectable. For each step the step height h_s , the mixing parameter M_{VS} (from 0 to 1), the step position E_{OS} and the $FWHM = 2\beta_s$ can be defined. By click with the mouse on the topical window and open XAS dialogue the step position can be defined easily. The active input line is marked with a red bar and changes after each mouse click. If the option 'Adjust the a -Param. and Height Param.' is activated, the parameter and the height parameters are adjusted that the background is at the left and right side of the spectrum like the measuring

intensity of the spectrum (see Fig. 23). Example 7 demonstrates a calculation of the magnetic moment using a XMCD measurement.

Each background parameter can be fixed (tick 'Fix' in the background-parameter dialogue box) or varied. The fitted background will be saved together with the other fit parameters. The programme will suggest a start set of parameters: the background parameter for the constant (minimum of the experimental spectrum) and the Shirley contribution. The user can edit and re-fix the parameters, recalculate and re-draw with **Preview** the background. **Subtract** removes the background from the spectra and **OK** accept the preferences for the peak fit. The sub-routine is closed without changes by clicking **Cancel**. The background parameters of the step function can be exported as image using **Copy** or **Export**.

3.4.7 Iteration

 [Peak Fit – Iteration...] or the pop-up command [Peak Fit Iteration] can be selected after appropriate background treatment, input of fit parameter limits (Min/Max values), and definition of start parameters for curve fitting. The components and the sum curve will be calculated and presented using the given parameters. The number of iterations per cycle (maximum 200) and the number of cycles can be defined in the 'Input Number of Iterations' dialogue box. The total number of iterations is the "Number of Iterations per Cycle" multiplied by "Number of Cycles". The start parameter quality can be estimated from the experimental spectrum and the sum curve. If the deviation is too large, leave the procedure with **Cancel** and correct the parameters with [Peak Fit – Show/Correct Fit Parameters].

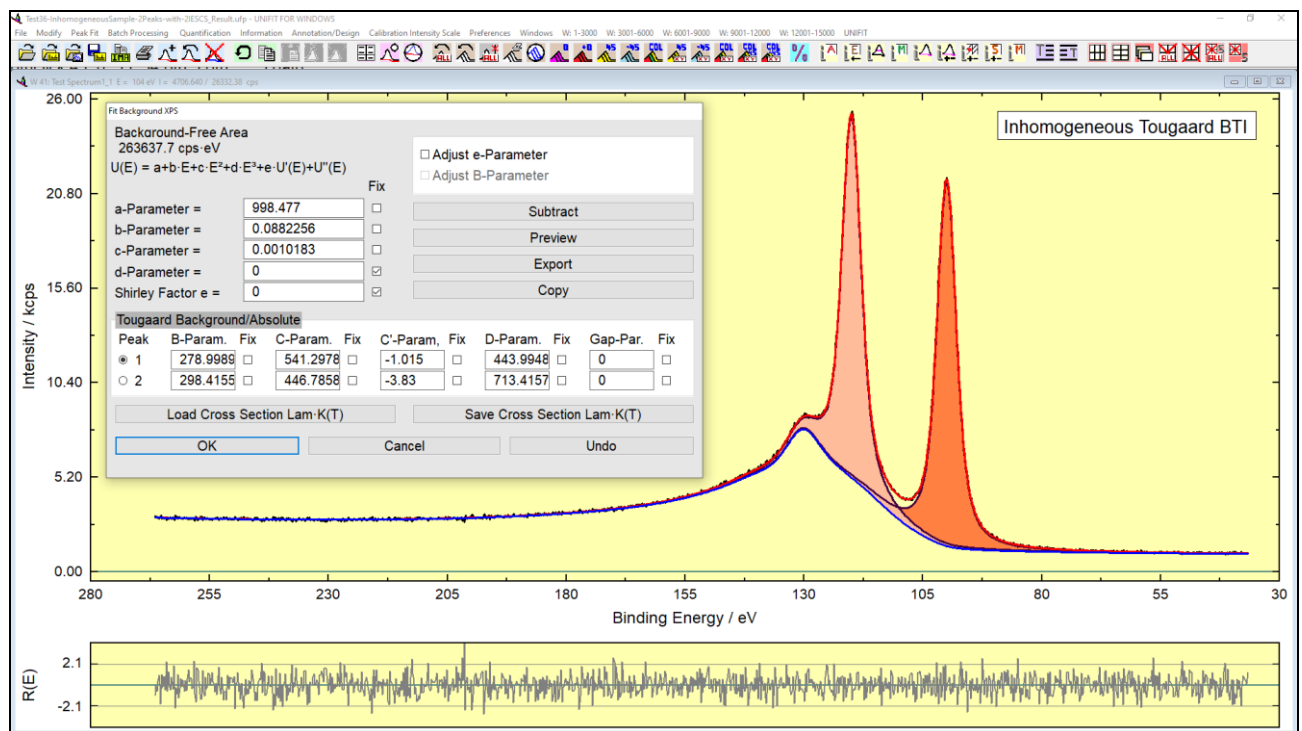



Fig. 22. Left: peak fit of a test spectrum using the fittable background for inhomogeneous samples, fit with two components and two separate Tougaard-background functions, project: Unifit_2023_User_Files\test spectra\Test36-InhomogeneousSample-2Peaks-with-2IESCS_Result.ufp, right: dialogue menu of the fittable background (INHOM) for the input of the background parameters

The peak fit starts with **OK**. The presentation of components, sum curve, residual, and – optimized during the peak fit – background function will be updated after a “good iteration” (e.g.

decreasing χ^2). Iteration number, χ^{2*} , χ^2 , and *Abbe* criterion will be displayed in the title bar of the window. The dialogue box 'Stop Iterations' pops up after the given iterations are finished or the ESC key is pressed. It contains the final values of χ^{2*} , χ^2 and *Abbe* criterion. Press 'Iterations **continue!**' to start additional iteration cycles, 'Iterations **end!**' to leave the procedure, **Show Fit Parameters** to watch the calculated parameters, **Show Fit-Parameter Limits** in order to display the Min/Max values. If the background has been fitted together with the peaks additionally **Show Background Parameters** appears and allows editing the background parameters.

3.4.8 Show Fit-Parameter Errors

 This menu item was developed for calculation of fit-parameter errors after peak fitting (see Fig. 24). According to the chosen option the user can calculate the errors with the method 'Matrix Inversion' or 'Iterative Calculation'. The errors can be shown absolute or relative to the fit parameters. The errors can be exported as image table by **Export** or **Copy**. **Print** transfers the error data to a printer. With **Save** the calculated errors can be stored (*.dat). The button **Absolute** or **Relative** shows the absolute or relative fit-parameter errors. The dialogue can be closed with **OK**. If the user wants to print or export fit-parameter errors from more than one window, he can use [Batch Processing – Print Fit-Parameter Errors] and [Batch Processing – Export Fit-Parameter Errors].

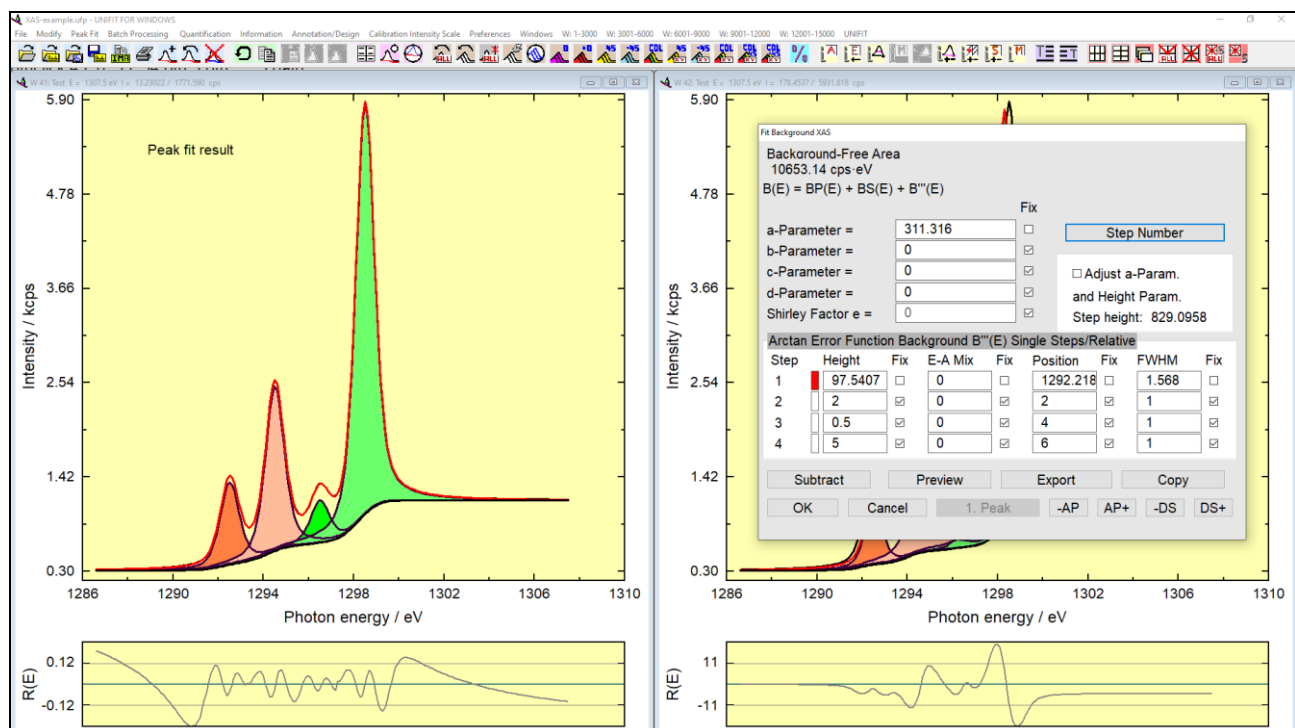


Fig. 23 Left: XAS test spectrum and model curve with four components and step background, right: Menu of the fittable XAS background consisting of polynomial, Shirley background and step background (one step is described by four parameters: Height, E-A Mixing, Position, FWHM), Project: Unifit_2023_User_Files\examples\XAS\XAS-example.ufp

The fit-parameter errors calculation should be made directly after the peak fit. If the programme shows the message 'Negative parameter errors! Iteration not complete!', then the user can choose between two options:

1. Start a new iteration process to find a better approach for the peak fit, or
2. Fix critical parameters to set the errors of these parameters equal zero.

If one activates this menu point after a successful error calculation, the errors are shown without a new calculation. A new estimation of the fit-parameter errors can be activated, when the user subtracts the background or carries out a new iteration and chooses the menu point [Peak Fit - Show fit-parameter errors].

Note: If the peak fit was carried out with the inhomogeneous Tougaard-background functions (Fittable Background XPS (INHOM)) or a XAS spectrum was fitted then the calculation of the fit-parameter errors is not possible.

3.4.9 Export Curvature Matrix



For the estimation of the parameter errors a curvature matrix H (77) is calculated. The diagonal terms are a measure of the errors of independent parameters. The non-diagonal terms give error values of the correlation between the parameters. The curvature matrix H can be exported with the menu point [Peak Fit - Export Curvature Matrix]. The export of the curvature matrix is possible only from that window in which at last a fit-parameter error calculation was carried out.

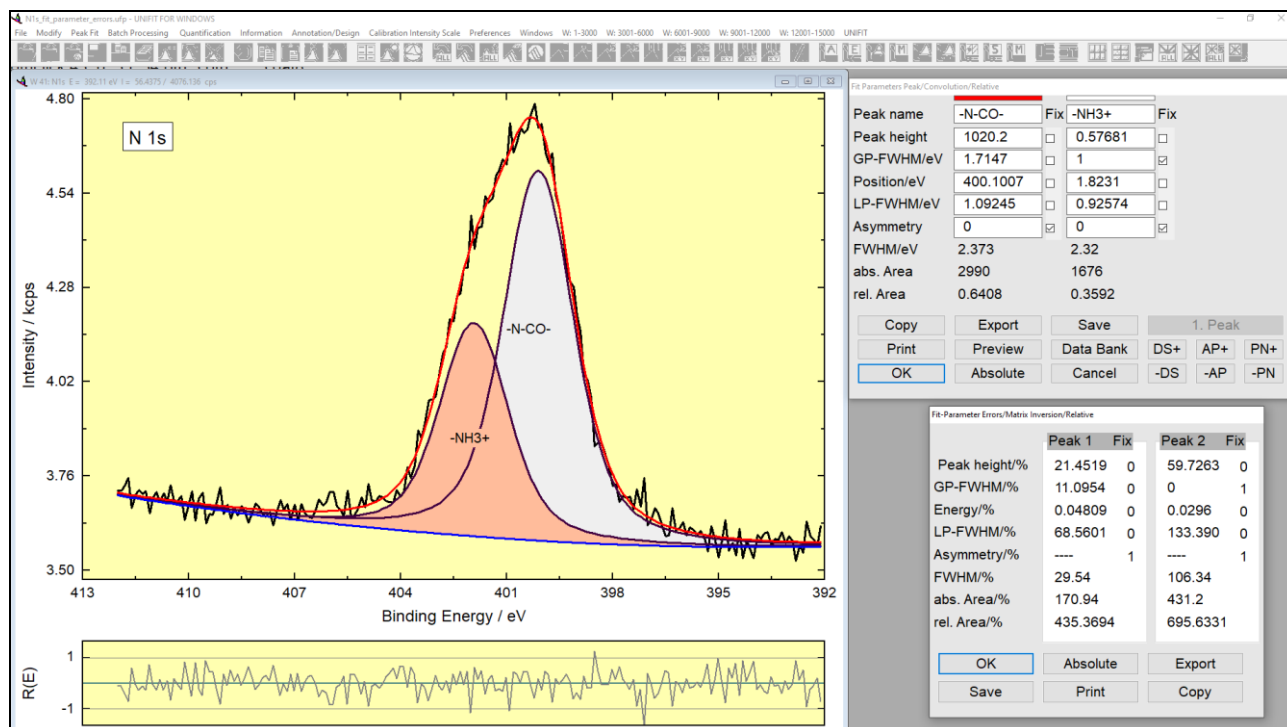


Fig. 24. Fit parameters and fit-parameter errors (relative) of the N 1s peak (2 components); parameter: relative, fit procedure: convolution, calculation of fit-parameter errors: Matrix inversion, project: Unifit_2023_User_files\examples\XPSN1s_parameter_errors.ufp


3.4.10 Valence-Band Edge $SQR(E)*G(E)$




This sub-routine permits the estimation of the upper valence-band edge. Independent of the preferences the model function is a convolution of square root and Gaussian functions. The valence band edge is determined by the zero point of the square root function. The *FWHM* of the Gaussian function is fixed at a certain value or variable. The background can be estimated parallel to the fit. If the background was not estimated before, a constant background will be subtracted

automatically. The number of iteration cycles is set to 100 and not variable. But the iteration process can be repeated (see also Test16-Valence-Band-Edge_Result.ufp).

3.4.11 Valence-Band Edge $mE * G(E)$

 This sub-routine permits the estimation of the upper valence-band edge. Independent of the preferences the model function is a convolution of a linear function and a Gaussian function. The valence band edge is determined by the zero point of the linear function. The *FWHM* of the Gaussian function is fixed at a certain value or variable. The background can be estimated simultaneously to the fit. If the background was not estimated before, a constant background will be subtracted automatically. The number of iteration cycles is set to 100 and not variable. But the iteration process can be repeated.

3.4.12 Fermi Edge $\Theta(E) * G(E)$

 This sub-routine permits the estimation of the Fermi edge. Independent of the preferences the model function is a convolution of Theta and Gaussian functions. The Fermi edge is determined by the jumping discontinuity of the Theta function. The *FWHM* of the Gaussian function is fixed at a certain value or variable. The background can be estimated simultaneously to the fit. If the background was not estimated before, a constant background will be subtracted automatically. The number of iteration cycles is set to 100 and not variable. But the iteration process can be repeated (see Test18-Fermi-level_Result.ufp).

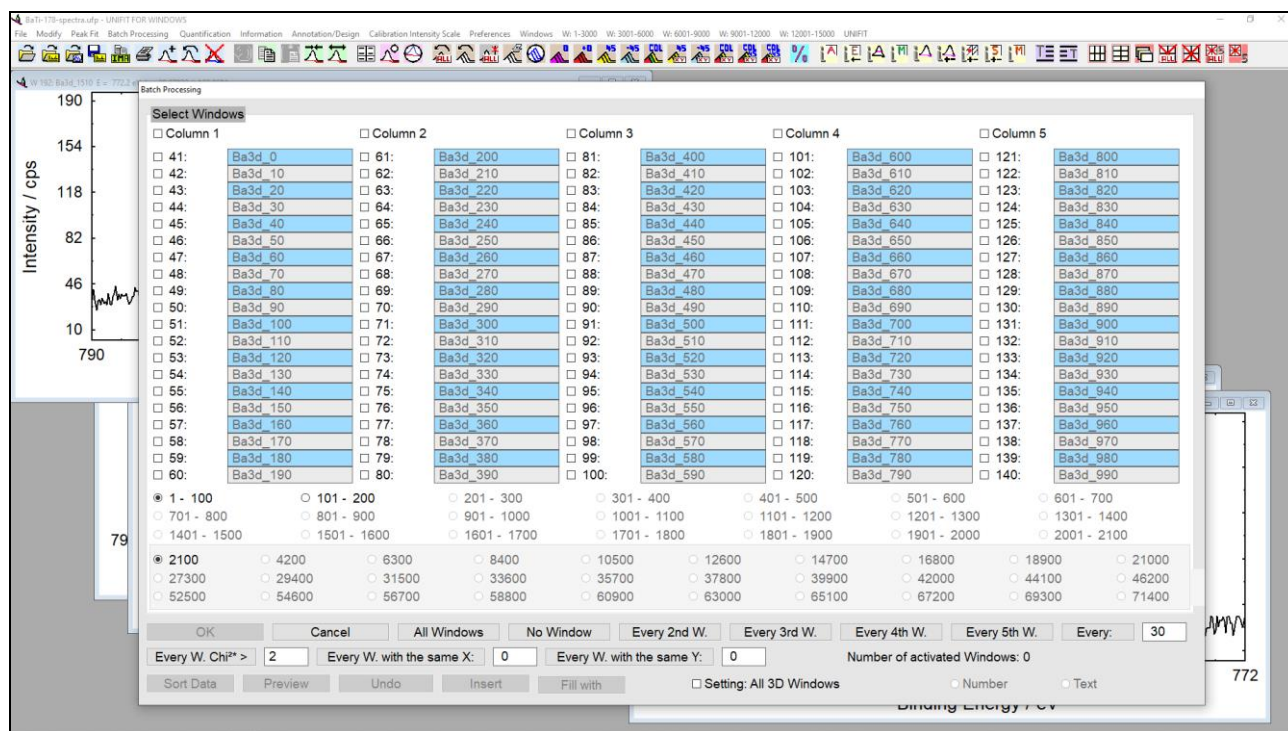


Fig. 25. Dialogue of the standard windows selection for using the batch processing, Project: Documents\Unifit_2023_User_Files\examples\XPS\BaTi-178-Spectra.ufp

3.5 Batch Processing


The batch-processing sub-menus serve as fast and comfortable serial treatment and offer different 3D plots and a plot of parameter dependent measurements. The sub-menus 3.5, 3.5.3 and 3.5.4 change all windows. If the menu 3.5.2, 3.5.4, 0, 3.5.7, 3.5.7, 3.5.10, 3.5.10, 0, 0, 3.5.13, 0, 3.5.13, 3.5.133.5.16, 3.5.16, 3.5.16 or 3.5.20 will be called a selection dialogue of standard spectra is

opened (see Fig. 25). The displayed check boxes of the standard windows can be selected by the two types of radio buttons:


- '1 - 100'...'75501 - 75600'.
- '2100'...'75600'.

The selection of the second type of radio buttons defines the appearance of the first type. According to the number of generated standard windows (visible or hidden) the radio buttons are disabled or enabled. The standard windows can be selected individually, in columns or in a defined sequence. The following options are offered: **All Windows**, **No Window**, **Every 2nd W.**, **Every 3rd W.**, **Every 4th W.** and **Every 5th W.**. The option **Every:** allows the definition of the sequence by the user. The last five options select the windows from the first well-chosen window. Three special selection options are: **Every W. Chi^{2*} >** , **Every W. with the same X:** and **Every W. with the same Y:** . The number of the selected windows is displayed.

3.5.1 Charge Correction All Windows

 This option displays a dialogue box, which allows shifting the X-axis for all windows in order to compensate e.g. charging effects in several regions of one sample additionally to the value defined in [Modify – Charge Correction Active Window]. The charge correction is set to “0” and will not be saved with the preferences or when quitting the programme.

3.5.2 Charge Correction Windows

 This processing routine is the same as described in 3.5 but works not for all windows. The defined charge correction affects only the selected windows using dialogue Fig. 25.

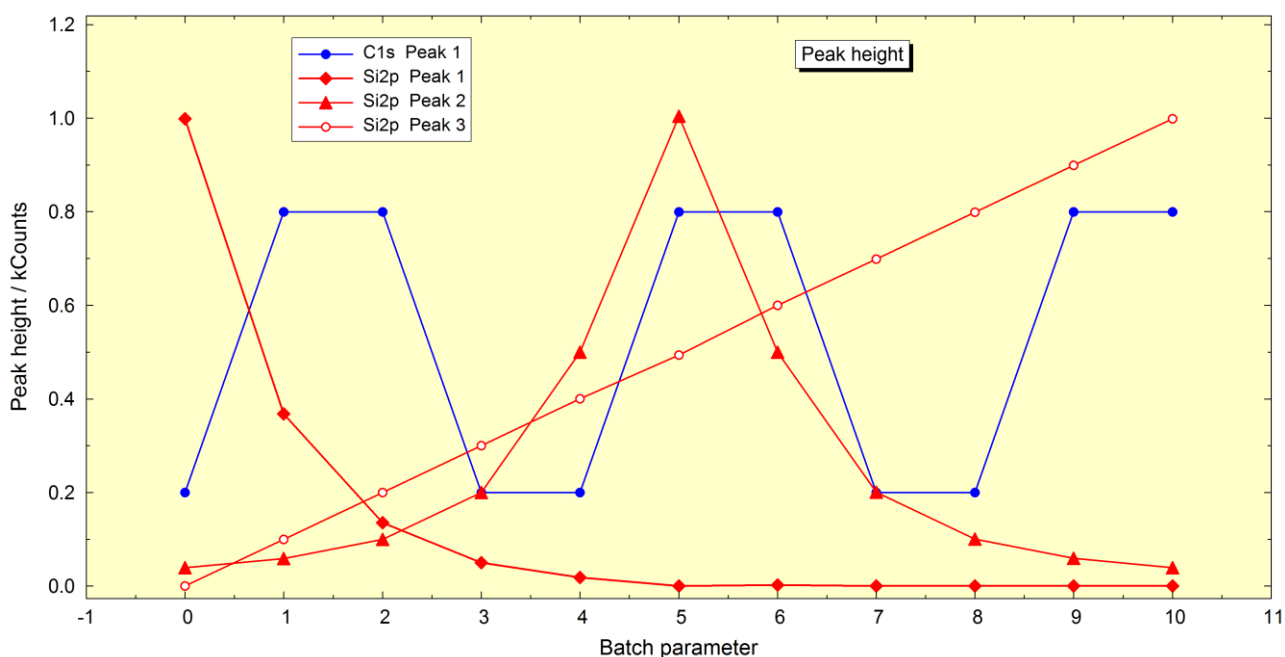


Fig. 26. Created Fit-parameter plot of peak heights of Si 2p and C 1s from the test files 'Test07' using UNIFIT, project: Unifit_2023_User_Files\test spectra\Test07-Batch-Fit-Voigtn-Si3Peaks-O2Peaks-C1Peak_Result.ufp

3.5.3 Original/Accept Preferences All Windows



[Batch Processing – Original/Accept Preferences all Windows] recalls the original spectra in all open windows. All operations done before will be reversed. Only the charge correction persists.

3.5.4 Original/Accept Preferences Windows



This processing routine is the same as described in 3.5.3 but works not for all windows. The recall of the original data is carried out only with the selected windows. The windows can be selected using the dialogue Fig. 25.

3.5.5 Spike Correction All Windows



[Batch Processing – Spike Correction All Windows] permits the correction of spikes of a large series of spectra. The control parameters of the spike procedure can be defined manually by the user (see 3.10.16). The theoretical basic is described in chapter 2.9. Optionally, the spectra modified using the Laplace operator can be displayed. The Unifit projects RAMAN-Before-Spike-Correction.ufp and RAMAN-After-Spike-Correction.ufp in the folder Unifit_2023_User_Files\examples\RAMAN demonstrate the efficient working of the procedure using realistic Raman spectra.

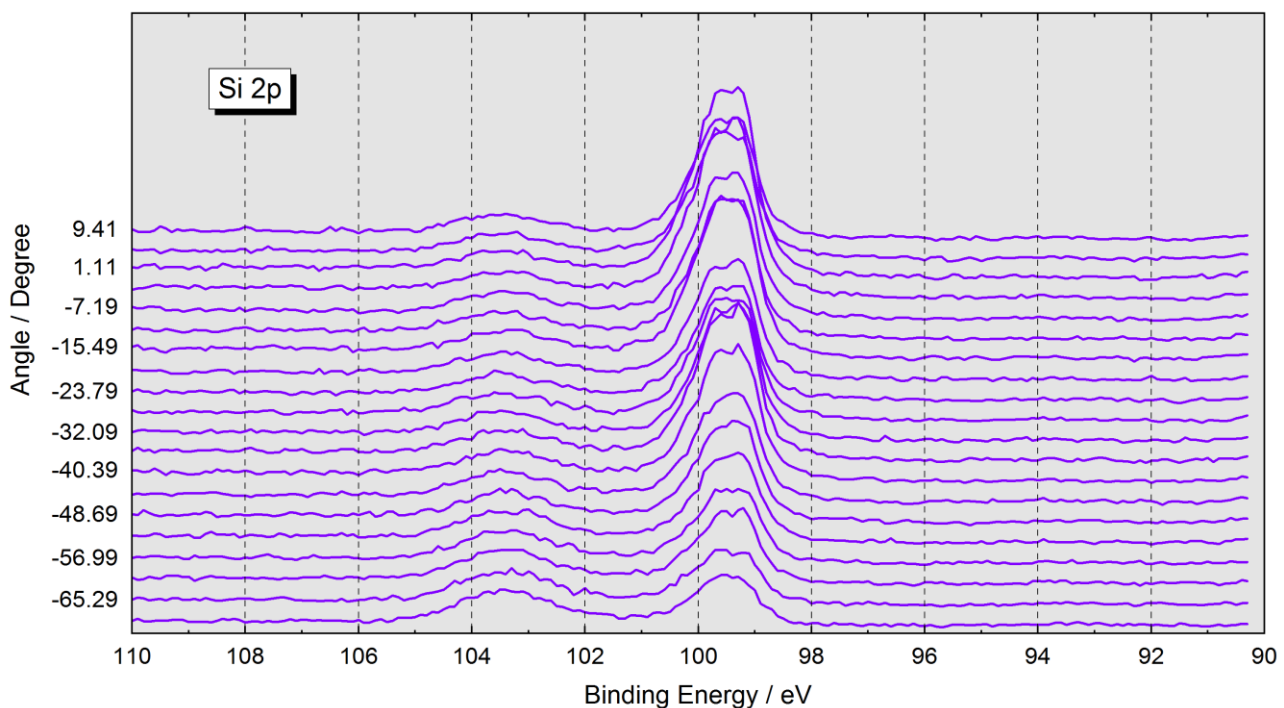



Fig. 27. Example of a presentation 'Plot 3D Waterfall 0°' of the Si 2p spectra of an ARXPS measurement of SiO₂ with UNIFIT, the plot was exported as BMP-file using UNIFIT and then inserted as graphic into Word document, a dispersion of the binding energy with the angle variation cannot be observed, project: Unifit_2023_User_Files\examples\XPS\Angle_Resolved_Measurement_Si.ufp

3.5.6 Print Fit Parameters




This option permits a simultaneous print of the final fit parameters of several windows presenting the fitted peaks without printing the spectra. Only windows can be selected for which a peak fit has already been carried out.

3.5.7 Export Fit Parameters

 The final peak fit parameters of all windows for which a peak fit already has been carried out can be exported simultaneously using [Batch processing – Export Fit Parameters]. An additional window allows the selection of parameters to be exported (see book ‘Line Positions and Data Formats – Version 2023’ 4.1.3). The first column includes the batch parameters. If the batch parameters are not available, then the window numbers are shown.

3.5.8 Plot Fit Parameters/Min/Max/Areas

 The call ‘Plot Fit Parameter/Min/Max/Areas’ plots the minima, maxima or estimated background free peak areas or one kind of fit parameters (peak height, peak position, etc.), the peak area or the relative peak area with respect to a batch parameter, window number, x position, y position or other values (see Fig. 26). The windows including fitted peaks can be selected freely. The legend names are created using a combination of the region name and the component name of the peak fit (e.g. see Fig. 26, region name: C 1s, component name: Peak 1). The handling is similar to the **Parameter Plot** of the menu point ‘Quantification - Concentration’ (see 3.6.1, 4.2 and 4.5).

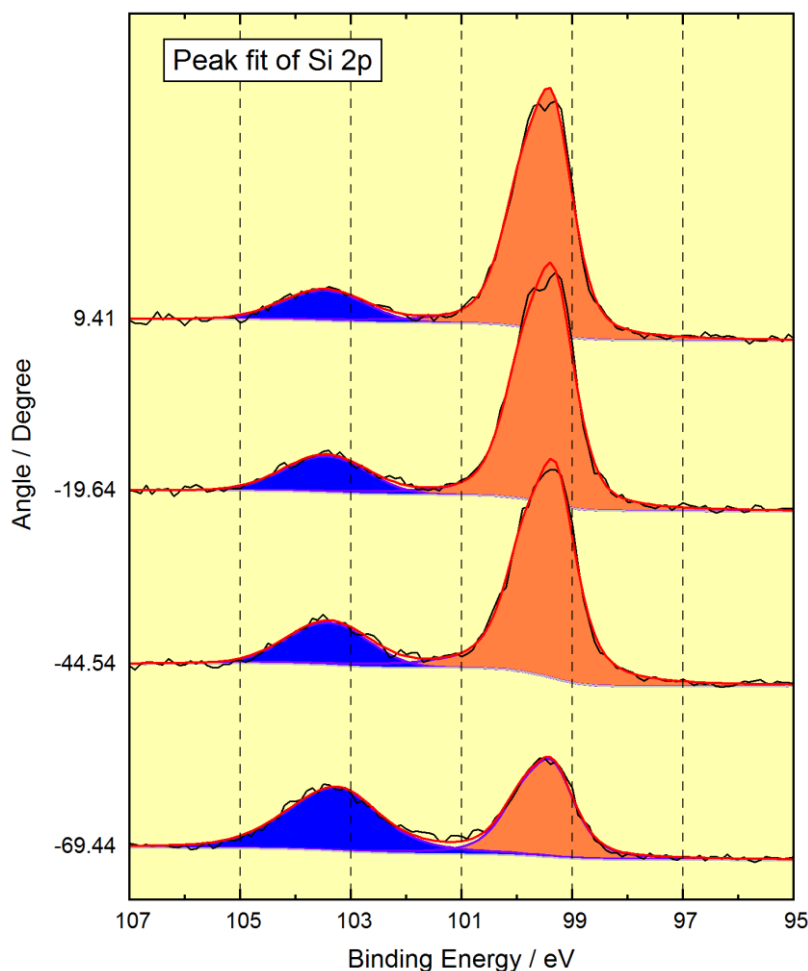


Fig. 28. Example of a presentation ‘Plot 3D Waterfall 0° Plus’ of fitted spectra of an ARXPS measurement of SiO₂ with UNIFIT, the plot was copied using UNIFIT and then inserted via paste as graph into a text processing document, the different height of the SiO₂ signal with the angle variation can be observed, project: Unifit_2023_User_Files\examples\XPS\Angle_Resolved_Measurement_Si.ufp

3.5.9 Print Fit-Parameter Errors



This option permits a simultaneous print of final fit-parameter errors of several windows. Only windows can be selected for which the error calculation of the fit parameter already has been carried out. The results are rounded to a reasonable value.

3.5.10 Export Fit-Parameter Errors



The peak fit-parameter error of several windows can be exported simultaneously using [Batch processing –Export Fit Parameters Errors]. Only windows for which the error calculation has been performed can be selected. An additional window allows the selection of parameters to be exported. If no series parameter is available, the first column shows the number of each window.

Note: If spike corrected spectra in the batch processing are used then the loading of the original spectra has to be deactivated.

Note: Select the active window in the parameter-dependent experimental series so that the corresponding spectrum presents all identified components as clearly as possible.

Note: An alternative way to create a batch-processing procedure using standard windows of different spectra (Survey, C 1s, O 1s, Si 2p...) may be the sub-menus 3.2.4 and 3.2.12.

3.5.11 Batch Processing



The batch processing menu serves a fast and comfortable serial treatment of parameter dependent measurements. 75599 windows (75600 minus the active one) can be processed in one step. All options of the 'Modify' sub-menu and the peak fit can be included into the batch processing. All steps performed in the active window will be transferred to the windows selected for batch processing. The steps will be displayed once more in an information window before starting the batch processing. The peak fit will be started with the settings of the active window. The number can be defined in preferences setting 3.10.29.2. For a better result, however, the iterative cycles will be repeated once-again (e.g. if the defined number of iterations is 22, then the number of iterations during the batch processing at every window is 44). The batch processing can be cancelled with ESC. If the option [Preferences - Batch Processing - Load Original Spectra] is ticked (activated), then before the batch processing steps are carried out the original spectra are loaded.

Example 8: Make a peak fit (two singlet peaks, convolution, absolute. background for homogeneous samples) of all 576 spectra of the synthetically generated multipoint (area) scan test profile *Si-SiO₂-24x24.vms* saved in the folder *Unifit_2023_User_Files\test spectra\Test35-AreaScan-Si2p-24x24*. Generate the presentations 'XY 3D Plot 45°', 'XY 3D Plot -45°', 'XY 3D Colour Profile' and 'XY 3D 45° Colour Profile' of the Si and SiO₂ components after the peak fit. Additionally, create a parameter plot of the peak intensities of the two different components (Si and SiO₂) of the fitted spectra using the spectra at the positions X=Y (all 24 spectra from the diagonal positions). The project *Unifit_2023_User_Files\test spectra\Test35-AreaScan-Si2p-24x24.ufp* includes the result of the example.


1. Start UNIFIT,
2. select [Preferences – Fit Procedure – Convolution] and [– Fit Parameter/XAS-Background Parameter/XPS-Tougaard Background (INHOM) – Absolute] and [- Tougaard-Background Calculation – Homogeneous Sample],
3. be sure that the maximal number of peak-fit components is larger than two and the number of the first standard window = 11 with [Preferences – Setting of Programme Parameters],

4. load 'Si-SiO₂-24x24.vms' with [File – Open Spectra - XPS - VAMAS(*.VMS;*.NPL)] (folder: **Unifit_2023_User_Files\test spectra\Test35-AreaScan-Si2p-24x24**),
5. after loading the dialogue 'Select Spectra' is displayed,
6. select the number of displayed spectra with **Hide Standard Windows**, the dialogue 'Hide/Show Standard Windows' is opened,
7. select 'Show Every 64th Standard Window' and press **OK**,
8. in the dialogue 'Select Spectra' the information 'Every 64th spectrum is displayed!' is shown,
9. select 'Internal Spectra Names' to 'Peak name plus _X-Position/Y-Position',
10. select all spectra with **Select all** and load all spectra by pressing **OK** (the spectra names include the batch parameter and also the x and y recording position, e.g. spectrum at the position x = 12 and y = 4: Si2p_4-12/12/4),
11. activate window 448,
12. load parameter **Test35-AreaScan-Si2p-24x24.par** with [Peak Fit – Load Start Parameter...] (includes an adjustable background) from the directory: **Unifit_2023_User_Files\test spectra\Test35-AreaScan-Si2p-24x24**,
13. the dialogue 'Fit Background XPS' will be opened, confirm the background parameter with **OK**,
14. the dialogue 'Min/Max Fit Parameters Peak#' will be opened, confirm the parameters with **OK**,
15. the dialogue 'Fit Parameters Peak/Convolution/Absolute' will be activated, confirm the fit parameters with **OK**,
16. the dialogue 'Input Number of Iterations' will be opened,
17. define number of iterations (20) with the following definitions: 'Number of Iterations per Cycle = 10' and 'Number of Cycles = 2', start the iteration with **OK**,
18. if the peak fit of spectrum 448 is finished the dialogue 'Stop Iterations' will be activated, select **end!** for closing the peak fit in the activated window,
19. Define the number of the iterations during the batch processing with [Preferences – Batch Processing – Input Number of Iterations...] to: Number of Iterations per Cycles: 10, Number of Cycles: 2,
20. select [Batch Processing – Batch Processing], the standard window selection dialogue appears,
21. select **All Windows** and confirm with **OK**,
22. start the batch-processing with **OK**, a progress bar appears,
23. if the peak fit of all 576 spectra is finished the peak fit components (include the information of the chemical composition) can be presented with respect to the recording position,
24. activate [Batch Processing – XY 3D Plot 45°], the standard window selection dialogue appears, select **All Windows** and confirm with **OK**,
25. the curve selection dialogue will be opened, select 'Component 1' and 'abs. Area' for the presentation of the Si component and confirm with **OK**,
26. the generated plot presents the Si component with respect to the recording position x and y (see Fig.32),
27. repeat points 23 and 24 with the area of component 2 for the presentation of SiO₂
28. repeat point 23 and 24 with 'XY 3D Plot -45°' (see Fig. 33), 'XY 3D Colour Profile' (see Fig. 34) and 'XY 3D 45° Colour Profile' for the additional XY plots, the design of the generated XY plots can be changed with [Preferences - Display - 3D Plot Waterfall 0°/45°/-45°/Colour Profile Display...] or the functionality of the right mouse button,
29. activate window 448,

30. select 'Batch Processing - Plot Fit Parameters/Min/Max/Area', the standard windows selection dialogue appears, select the first window ($x=1, y=1$), select with the number , every 25th spectrum is now selected (W11, W36, W61,...), confirm with .
31. the dialogue 'Parameter Plot' is opened, select 'Create new Plot', use for the X-axis 'X-Position' and for the Y-axis 'Peak height', confirm with , the parameter plot appears, the design of the parameter plot can be changed with [Preferences - Display - Parameter Plot Display...], this sub-menu can also be activated by pressing the right mouse button.

Note: The corresponding pop-up commands offer quick operations for all special 3D windows. The commands of the pop-up menu of the different 3D windows are adjusted to the different 3D windows.

3.5.12 Plot 3D Waterfall 0°

 With [Batch Processing – Plot 3D Waterfall 0°] original spectra, background functions, processed spectra, sum or component curves (after peak fit) shown in different standard windows may be plotted above each other in one plot (see Fig. 27). There is no shift of individual spectra in this plot. By pressing the shift key and clicking the right mouse button the order of the spectra within this plot may be reversed. Clicking the middle mouse button will activate or deactivate a line connecting the maxima of the shown spectra. Up to 300 windows can be chosen (see 3.10.3). The offset, stretching factor and the distance of curve separation can be changed [Annotation/Design – Plot Intensity Axis].

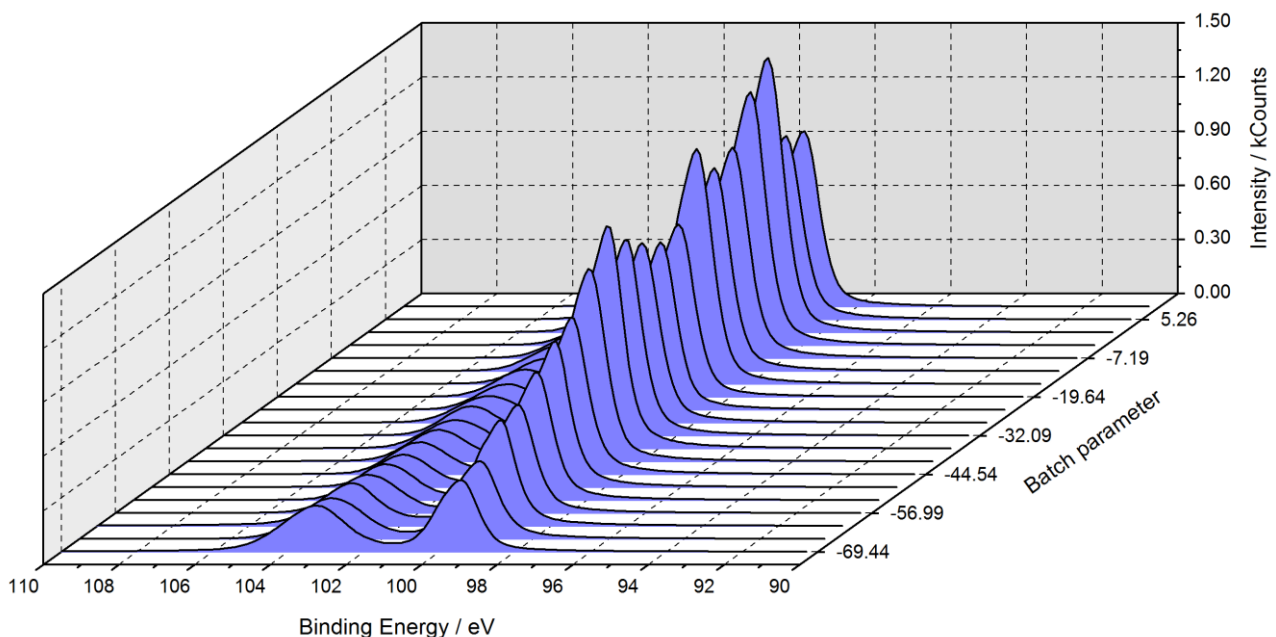


Fig. 29. Example of a presentation 'Plot 3D Waterfall 45°' of an ARXPS measurement of SiO_2 on Si with UNIFIT, plot of the sum curve (after peak fit), exported using UNIFIT and then inserted as graph into this Word document, the intensity variation of the Si peak shows a clear forward scattering effect, project: Unifit_2023_User_Files\examples\XPS\Angle_Resolved_Measurement_Si.ufp

3.5.13 Plot 3D Waterfall 0° Plus (fitted spectra)



This menu point permits additionally the plot of the components of fitted spectra (see Fig. 28). The spectra, sum curves, components and backgrounds of different spectra can be plotted together in one frame. A normalization of the curves from the selected windows is recommended. The number of displayed curves should not exceed 21 (see 3.10.3). The offset, stretching factor and the distance of curve separation can be changed [Annotation/Design – Plot Intensity Axis]. By pressing the shift key and clicking the right mouse button the order of the spectra within this plot may be reversed.

3.5.14 Plot 3D Waterfall 45°



With [Batch Processing – Plot 3D Waterfall 45°] original spectra, background functions, processed spectra, sum or component curves (after peak fit) shown in different windows may be plotted above each other in one plot (see Fig. 29). The shift of individual spectra in this plot results in a viewing angle of about 45°. By pressing the shift key and clicking the right mouse button the order of the spectra within this plot may be reversed. Up to 300 windows may be chosen (see 3.10.3). The fill colour, the colour, form and thickness of the curves on the monitor may be chosen with [Preferences – Display - 3D Plot Waterfall 0°/45°-45°/Colour Profile Display] and for printing out [Preferences – Printer - 3D Plot Waterfall 0°/45°-45°/Colour Profile Printer].

3.5.15 Plot 3D Waterfall -45°



With [Batch Processing – Plot 3D Waterfall -45°] the same plots are possible as in the point 3.5.13. But the viewing angle is -45° (see Fig. 30).

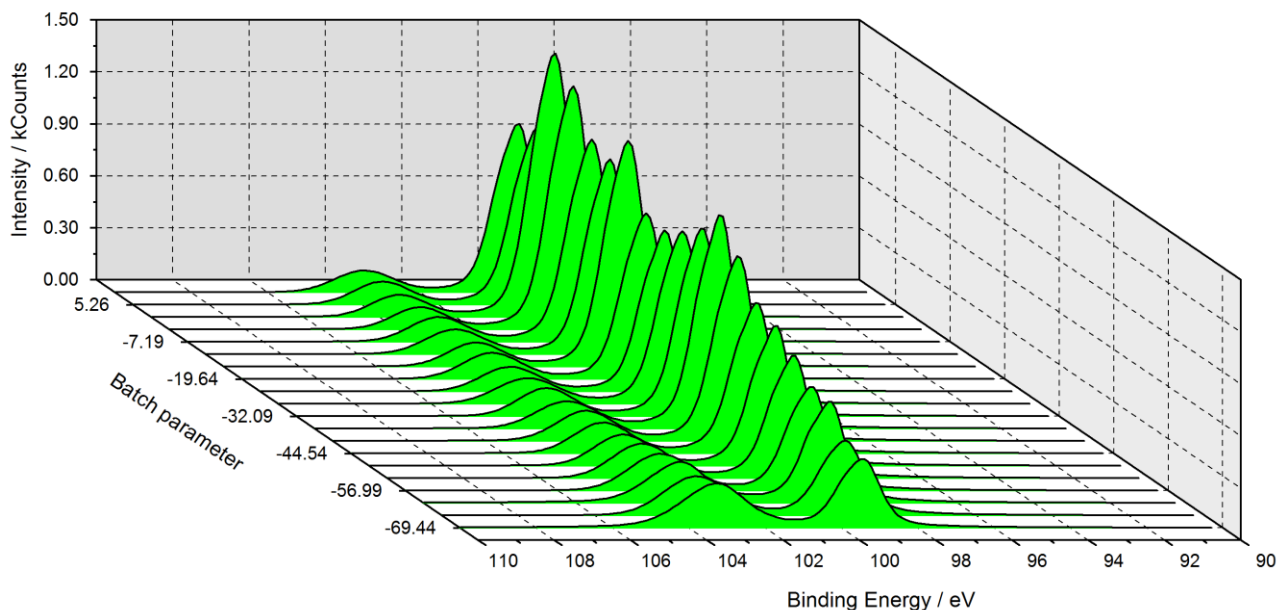


Fig. 30. Example of a 3D presentation -45° of an ARXPS measurement of SiO₂ on Si using UNIFIT, plot of the sum curve, exported using UNIFIT and inserted as graph into text processing document, the SiO₂ peak shows no forward scattering effect, project: Unifit_2023_User_Files\examples\XPS\Angle_Resolved_Measurement_Si.ufp


3.5.16 Plot 3D Colour Profile



With [Batch Processing – Plot 3D Colour Profile] spectra, background functions, processed spectra, sum and component curves (after peak fit) shown in different windows may be presented together in one plot (see Fig. 31). The intensities of the spectra are illustrated using a

colour profile (see Fig. 31, minimum colour: white, maximum colour: black). The minimum and maximum colour and the superposition of the colours can be defined optionally R+G+B, R+B+G, etc.). Additionally, two rainbow profiles are offered (see 3.10.19). If a batch parameter is not available, then the window numbers are used. By pressing the shift key and clicking the right mouse button the order of the spectra within this plot may be reversed.

3.5.17 XY 3D Plot 45°

 With [Batch Processing – XY 3D Plot 45°] the maxima, minima, positions of minima and maxima, background-free areas, peak areas of the sum or component curves (after peak fit) and all fit results of the peak-fit components (after peak fit) with respect to the x and y recording positions may be plotted in one window (see Fig. 32). The area described by the x and y positions has to be a rectangle. By pressing the shift key and clicking the right mouse button the order of the values within this plot may be reversed. The fill colour, the colour, form and thickness of the curves on the monitor may be chosen with [Preferences – Display - 3D Plot Waterfall 0°/45°-45°/Colour Profile Display] and for printing out [Preferences – Printer - 3D Plot Waterfall 0°/45°-45°/Colour Profile Printer].

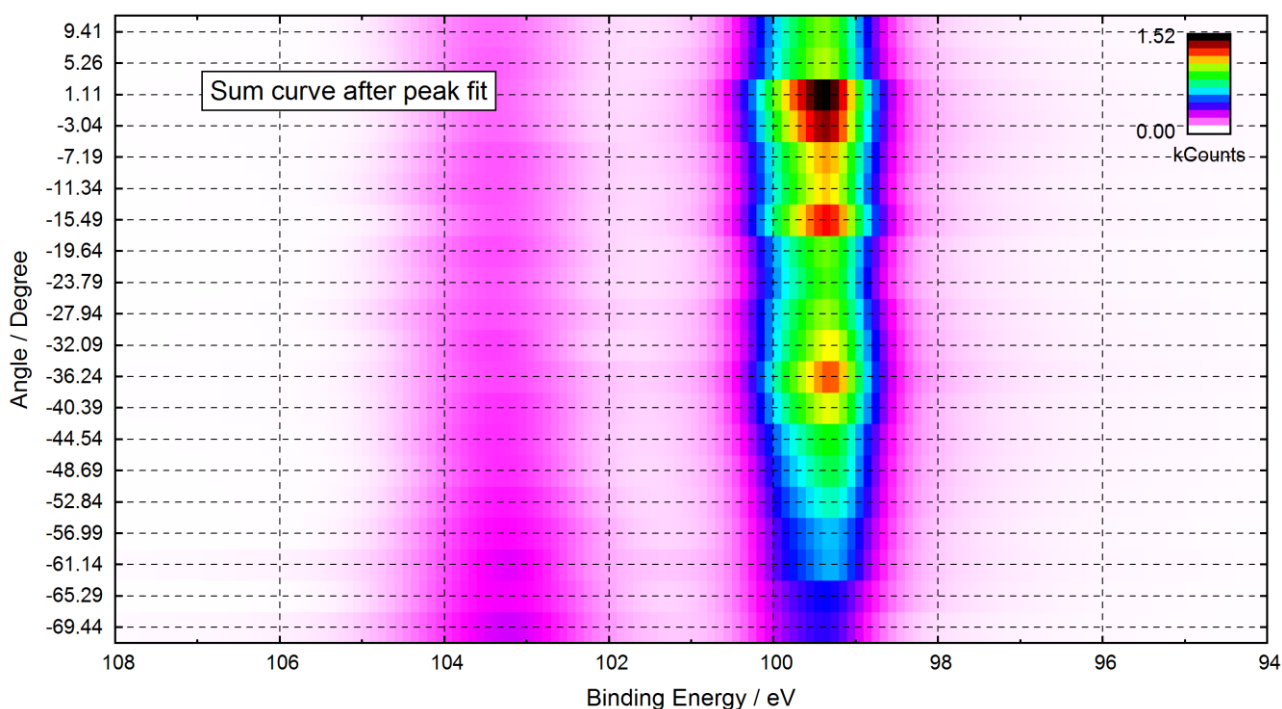



Fig. 31. Example of a presentation ‘Plot 3D Colour Profile’ (colour profile: Rainbow 2) of an ARXPS measurement of Si 2p using UNIFIT, the plot of the sum curve after peak fit was exported (600 dpi) using UNIFIT and then inserted as graphic in the text processing document, the plot shows clearly the forward scattering of the Si crystal peak (different colour) with respect to larger emission angles, project: Unifit_2023_User_Files\examples\XPS\Angle_Resolved_Measurement_Si.ufp

3.5.18 XY 3D Plot -45°

 With [Batch Processing – XY 3D Plot -45°] the maxima, minima, positions of minima and maxima, background-free areas, peak areas of the sum or component curves (after peak fit) and all fit results of the peak-fit components (after peak fit) with respect to the x and y recording positions may be plotted in one window (see Fig. 33, Example 8 and 4.4). The area described by the x and y positions has to be a rectangle. The shift of individual spectra in this plot results in a

viewing angle of about 45°. Pressing the shift key and clicking the right mouse button the order of the values within this plot may be reversed. The fill colour, the colour, form and thickness of the curves on the monitor may be chosen with [Preferences – Display - 3D Plot Waterfall 0°/45°-45°/Colour Profile Display] and for printing out [Preferences – Printer - 3D Plot Waterfall 0°/45°-45°/Colour Profile Printer].

3.5.19 XY 3D Colour Profile



With [Batch Processing – XY 3D Colour Profile] the maxima, minima, positions of minima and maxima, background-free areas, peak areas of the sum or component curves (after peak fit) and all fit results of the peak-fit components (after peak fit) with respect to the x and y recording positions may be plotted in one window (see Fig. 34 and 4.4).

The area described by the x and y positions has to be a rectangle. The intensities of the values are illustrated using a colour profile. The minimum and maximum colour and the superposition of the colours can be defined optionally R+G+B, R+B+G, etc.). Additionally, two rainbow profiles are offered (see 3.10.19). If a batch parameter is not available, then the window numbers are used. With the button **Number of Points x2** the number of plotted points can be increased stepwise at two. The intensities of the additional point are calculated using a linear interpolation (see Fig. 35). By pressing the shift key and clicking the right mouse button the order of the spectra within this plot may be reversed.

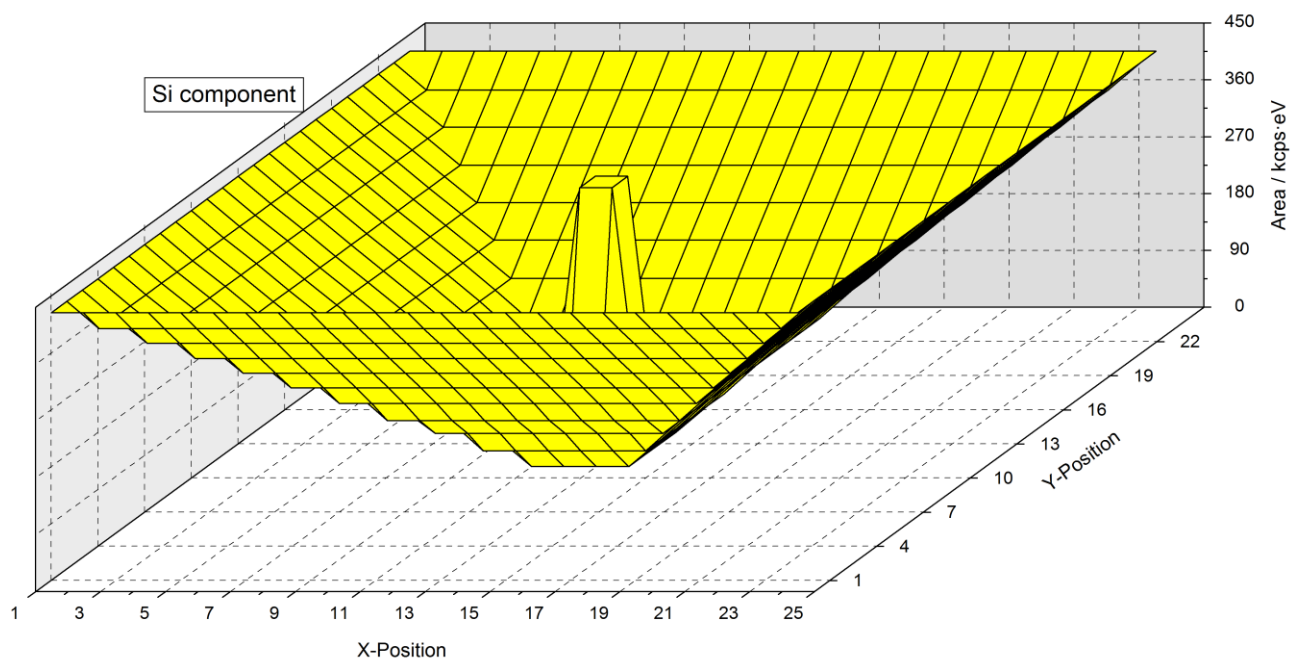


Fig. 32. Example of a presentation 'XY 3D Plot 45°' of a test profile of SiO₂ and Si with UNIFIT, the plot was created using UNIFIT and then inserted as graph into Word document via copy and paste, the maxima of the Si-peak areas are shown in the centre and edges, of the project: Unifit_2023_User_Files\test spectra\Test35-AreaScan-Si2p-24x24.ufp

3.5.20 XY 3D 45° Colour Profile



With [Batch Processing – XY 3D 45° Colour Profile] the maxima, minima, positions of minima and maxima, background-free areas, peak areas of the sum or component curves (after peak fit) and all fit results of the peak-fit components (after peak fit) with respect to the x and y recording positions may be plotted in one window (see Fig. 36). This presentation is a

combination of 'XY 3D Colour Profile' and 'XY 3D Plot 45°'. With the button the number of plotted points can be increased stepwise at two. The intensities of the additional point are calculated using a linear interpolation (see Fig. 35).

3.5.21 XY 3D -45° Colour Profile



With [Batch Processing – XY 3D -45° Colour Profile] the maxima, minima, positions of minima and maxima, background-free areas, peak areas of the sum or component curves (after peak fit) and all fit results of the peak-fit components (after peak fit) with respect to the x and y recording positions may be plotted in one window (see Fig. 37).

This presentation is a combination of 'XY 3D Colour Profile' and 'XY 3D Plot -45°'. With the button the number of plotted points can be increased stepwise at two. The intensities of the additional point are calculated using a linear interpolation (see Fig. 35).

Example 9: Extract the peak areas of the two peaks from an angle-resolved series (ARXPS) of Si 2p recorded with an ESCALAB220iXL and saved as *Si_angle_resolved_measurement.vms* in the folder *Unifit_2023_User_Files\examples\XPS\Angle_Resolved_Measurement_Si-Doublets*. Elemental Si and SiO₂ have to be separated by peak fit using two doublets. The excitation satellites must be subtracted before starting the fit procedure.

1. Start UNIFIT,
2. select [Preferences – Fit Procedure – Sum], [Preferences – Fit Parameter/XAS -Background Parameters/XPS-Background Parameters (INHOM) – Relative], [Preferences – Tougaard-Background Calculation – Homogeneous Samples], be sure that the maximal number of peak-fit components is larger than two and the first standard window is settled to 20 with [Preferences – Setting of Programme Parameters...],
3. select the number of displayed spectra with [Windows – Hide/Show Standard Windows], the dialogue 'Hide Standard Windows' is opened, select 'Show all Standard Window' and press ,
4. load 'Si_angle_resolved_measurement.vms' with [File – Open Spectra – XPS - VAMAS(*.VMS;*.NPL)],
folder: *Unifit_2023_User_Files\examples\XPS\Angle_Resolved_Measurement_Si-Doublets*,
5. select block Si 2p, leave the dialogue with , select all Si 2p spectra with , select 'Internal Spectra names' to 'Peak name plus Batch parameter', to 'Show All Standard Windows' and leave the dialogue with ,
6. switch window 20 active and subtract the satellite with [Modify – Subtract Satellite],
7. load parameter set *Si2p-Doublet.par* with [Peak Fit – Load Start Parameters...]
(includes an adjustable background) from the same directory,
8. accept the parameters of the fittable background, accept the Min/Max values and the start parameters, define ten iterations per cycles and two cycles and start the iteration with ,
9. if the peak fit is finished the dialogue 'Stop Iterations' appears, close the iteration procedure by pressing the button ,
10. define the number of iterations during the batch processing with [Preferences – Batch Processing – Input Number of Iterations...] to ten iterations per cycle and 2 cycles,
11. select [Batch Processing – Batch Processing] for starting the batch processing,
12. select and confirm with ,
13. start the batch processing with ,

14. after finishing the peak fit for all windows select [Batch Processing – Plot Fit Parameters/Min/Max/Areas], select **All Windows** with **OK**, the parameter-plot dialogue is opened,
15. create the parameter plot with, X-axis: Batch parameter, Y-axis: abs. Area, leave the dialogue with **OK**,
16. the parameter plot is generated with four curves (two doublets),
17. the doublet curves can be added by call {Annotation/Design – Legend/Select Curves},
18. select in the column 'Sum' for the two curves 'Si2p Doublet 1/1' and 'Si2p Doublet 1/2' and press the button **Create Sum Curve**, a fifth curve is generated and can be plotted by selection the curve five in the column 'Plot' (sum of curve 1 and 2),
19. uncheck in the column 'Sum' the curves and select in the column 'Sum' 'Si2p Doublet 2/1' and 'Si2p Doublet 2/2' and press the button **Create Sum Curve**, a sixth curve is generated and can be plotted (sum of curve 3 and 4),
20. uncheck in the column 'Plot' the curves 1 – 4, select in the column 'Plot' only the curves 5 and 6, press the button **Preview**,
21. rename the curves 5 and 6 in the edit field 'Annotation' to 'Si' and 'SiO₂',
22. design the parameter plot using the design tools 3.8.9, 3.8.12 and 3.10.19.4 (available also using the right mouse button), compare the result with the project **Unifit_2023_User_Files\examples\XPS\Angle_Resolved_Measurement_Si-Doublets.ufp**,
23. if the parameter-plot window is completely designed then the image can be copied with [File – Copy Image Active Window] (right mouse button) and inserted into a document or a presentation.


Note: The automatically generation of more than one 3D window can be made if the used standard windows have a suitable order. For instance, the windows 41 - 139 include the spectra of the first multipoint measurement, window 140 - 238 include the spectra of the second multipoint measurement and so on. The spectra of the 10th multipoint measurement are in the windows 932 - 1030. Then ten 'XY 3d Plots' can be generated automatically by selecting the windows 41 - 139 and choosing of ten for the 'Number of 3D Plots' (example: **Unifit_2023_User_Files\Examples\XPS\As2p3-SDP-MultiPointMeasurement-WindowsVideoSequence.ufp**).

3.6 Quantification

The sub-routine 'Quantification - Concentration' allows a quantitative analysis from the experimental intensity data or peak-to-peak values (AES). The background-free areas or peak-to-peak values of the peaks weighted with sensitivity will be used for determination of element percentages. The components of a fitted peak will be included separately. The quantification from survey spectra requires a loading in different windows and the reduction and background correction at the energy range of the selected peak. The number of chosen elements defines the number of windows. An integrated parameter plot permits the presentation of the results.

Note: For the XPS quantification using the survey the pop-up menu offers the helpful commands without satellite subtraction [Use Peak for Quantification (Mono), Shirley Background] – Shirley Background or with satellite subtraction [Use Peak for Quantification (Twin), Shirley Background]. Before using these commands the peak should be labelled and separated using reduction-marker lines.

3.6.1 Concentration

 With [Quantification – Concentration] a dialogue appears containing the names of all open windows (see also Test17). Select windows (peaks) for quantitative determination of sample composition with the left mouse button or the TAB and space key. Confirm the selection with **OK** or leave the procedure with **Cancel**. By clicking **OK** a concentration table will appear. The name of the current sensitivity-factor file (Sens. Fact. or SF) (empirical values or theoretical Sigma values (*.sen)) and the transmission function *IERF* (*.trm) are displayed. The names of the empirical sensitivity factors start with ‘Wagner’ (e.g. Wagner-AES-PHI700-3kV-Differential.sen).

The quantification table contains 15 columns (see Fig. 38):

1. Select box for choosing the peaks for quantification,
2. window number,
3. number of components per window (e.g. Window 2 with peak fit using two components: Window 21, Window 22; Window 3 with peak fit using three components: Window 31, Window 32, Window 33; Window 4 with peak fit using two components: Window 41, Window 42; Window 5 with peak fit using two components: Window 51, Window 52),
4. peak name, which may also be edited here
 - an extension has to be started with the underline character or two spaces, e.g. S 2p to S 2p_sulphate or S 2p to S 2p sulphate),
 - by changing the name (e.g. from US to O 1s) and pressing the bottom **Calculate** the new values for σ , λ and $T(E)$ (*IERF*) can be loaded from the data bank,
5. batch parameter (if a batch parameter is not available then the window number is used)
6. a) Integral XPS or AES peaks: background-free peak or component area (cps·eV) (for peaks without background subtraction this value will be 0),
b) Differentiated AES peaks: Peak-to-Peak value, difference of the maximum and minimum value after a differentiation.
7. kinetic energy or binding energy for this signal (according to presetting),
8. ionization cross section σ (not for empirical sensitivity factors, Wagner-....sen),
9. inelastic mean free path of the electrons λ (not for empirical sensitivity factors, Wagner-....sen),
10. correction factor of the transmission function (*IERF*) loaded (not for Wagner sensitivity factors, all file names with empirical data starts with 'Wagner'),
11. sensitivity factors found automatically for each peak name in the SF file. If no sensitivity factor is found for a signal, this cell will be a dashed line (---),
12. areas with sensitivity factors applied (components),
13. areas with sensitivity factors applied (sum of the components of an element),
14. calculated fractions of chemical states [at%],
15. calculated element concentration [at%].

Note: The last two columns have no meaning for parameter-dependent series consisting of the same line recorded under different conditions (angle, sputter time).

The peak names can be edited and changed. By clicking **Calculate** the table will be re-calculated searching for a new sensitivity factor. If the SF-file does not contain a suitable value a “-” appears and the value “1” is used for calculation. The sensitivity factor or σ , λ and $T(E)$ (*IERF*) can also be edited, changed and included with **Calculate**.

Save the data with **Save 1 (*.con)** (*.con, see book ‘Line Positions and Data Formats – Version 2023’ 4.1.4) for normal experimental data or **Save 2 (*.dat)** (*.dat) for parameter-dependent series (see book ‘Line Positions and Data Formats – Version 2023’ 4.1.5).

Print transfers the table to a printer, **Next Windows** displays the next part of the table in case of a large number of peaks. In case of a very large number of spectra windows the user can define the first displayed window with **First Window (1 - 20)** **11**. The possible window numbers are displayed into the button (e.g. 1 - 20). The quantification table can be exported via the ‘Copy – Paste function’ using **Copy** or with **Export** (see Fig. 39). The dialogue can be closed with **Cancel**. With the call **Load Sens.-Fact./Sigma Values** a list box will show all files with extension *.SEN from the folder ‘My documents\Unfit_2023_User_Files\sensitivity factors’. These files are different sets of empirical sensitivity factors (e.g. Wagner-XPS-SF.sen contains Wagner factors for XPS) or theoretical ionization cross sections σ (e.g. AlScofld.SEN contains Scofield values [27] for AlK_{α} excitation). Files from empirical factors can be distinguished from the theoretical calculated ones by starting the file names with the letters WAG.

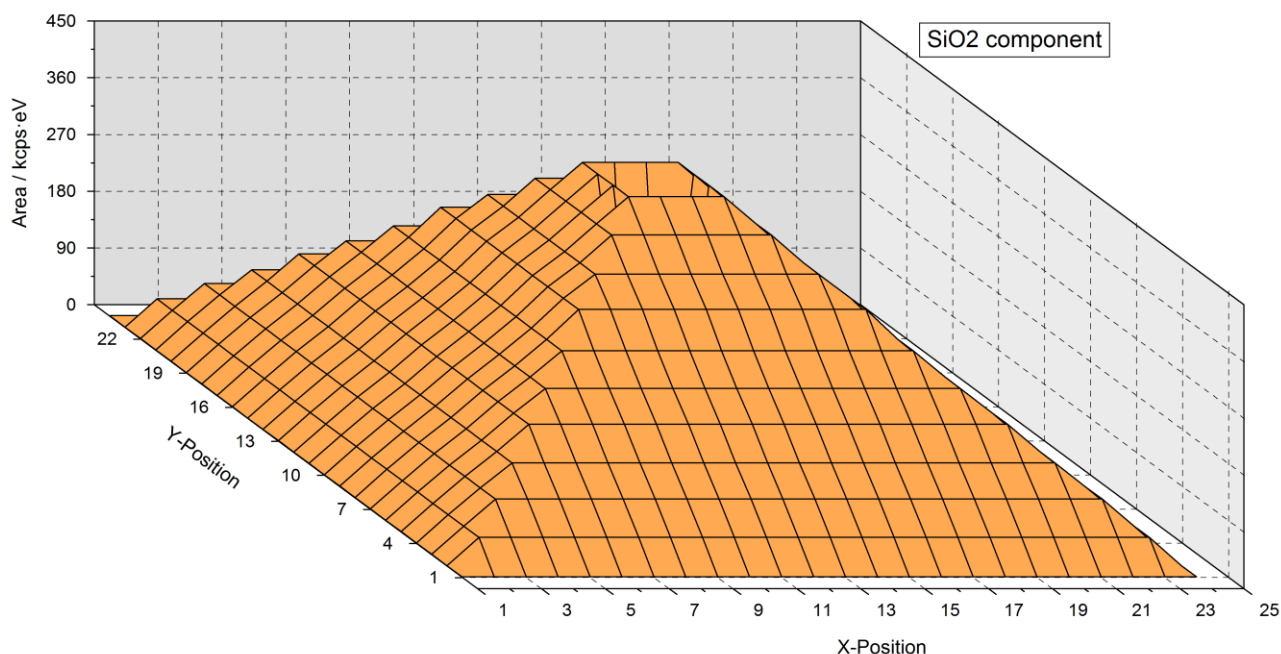


Fig. 33. Example of a presentation ‘XY 3D Plot -45°’ of a test profile of SiO_2 and Si with UNIFIT 2023, the plot was created using UNIFIT and then inserted as graph into Word document via copy and paste, the minima of the SiO_2 -peak areas are shown in the centre and edges, project: Unifit_2023_User_Files\test spectra\Test35-AreaScan-Si2p-24x24.ufp

Files for individual sensitivity factors for special equipments can be generated by users with any editor programme or directly in UNIFIT with the call [Information – Add/Edit/Show Sens.Fact./Sigma Values] (see 3.7.14). The required file structure for the ASCII data is presented in book ‘Line Positions and Data Formats- Version 2023’ 5.3.

With the call **Load Transmission Function** the predetermined factors of the transmission function can be loaded to calculate the sensitivity factors and integrate these improved values into the concentration analysis (If E_0 is zero or negative, then the default value 1000 eV is used). This procedure can only be used if the Scofield factors and the inelastic mean free path of the electrons ($IMFP$ or λ) are loaded in advance. Into the Wagner sensitivity factors, a roughly approximated transmission function E^{-1} is already included. UNIFIT uses the following equation for the calculation of $IMFP$:

$$IMFP = 0.103E^{0.745} \quad (124)$$

The values 0.103 and 0.745 are the mean k and m values calculated according to table 1 of Tanuma et. al. [28], valid over an energy range from 500 to 2000 eV. The sensitivity factor is given by the product of Sigma, Lambda and the transmission factor $\sigma \cdot \lambda \cdot T$. **Reset Sens. Fact.** reads the values σ , λ and T or an empirical sensitivity factor from the current data banks and activates a new calculation of the quantification table. With the alternated button **All Lines 100%** and **Par. Lines 100%** the at-% calculation is related to all peaks or to the lines with the same batch parameters.

Note: The option **Par. Lines 100%** is a very important function if more than one multi-region measurements are loaded using the input function 'batch-file loading'. The at-% quantification can be calculated exactly related to every separate measurement.

Parameter Plot permits a quick plot of the quantification results. Series parameters, X- positions, Y-positions, the window numbers or other values may be used for the X-axis. The peak areas, normalized peak areas, the fractions of chemical states from the fitted lines or the atomic concentration of the sum curve (information about the element concentration) may be applied for the Y-axis (see Fig. 40). New data can be added to an already existing parameter plot.

Refresh Plot refreshes the parameters plot with the same design. However, added lines are deleted and have to be implemented again.

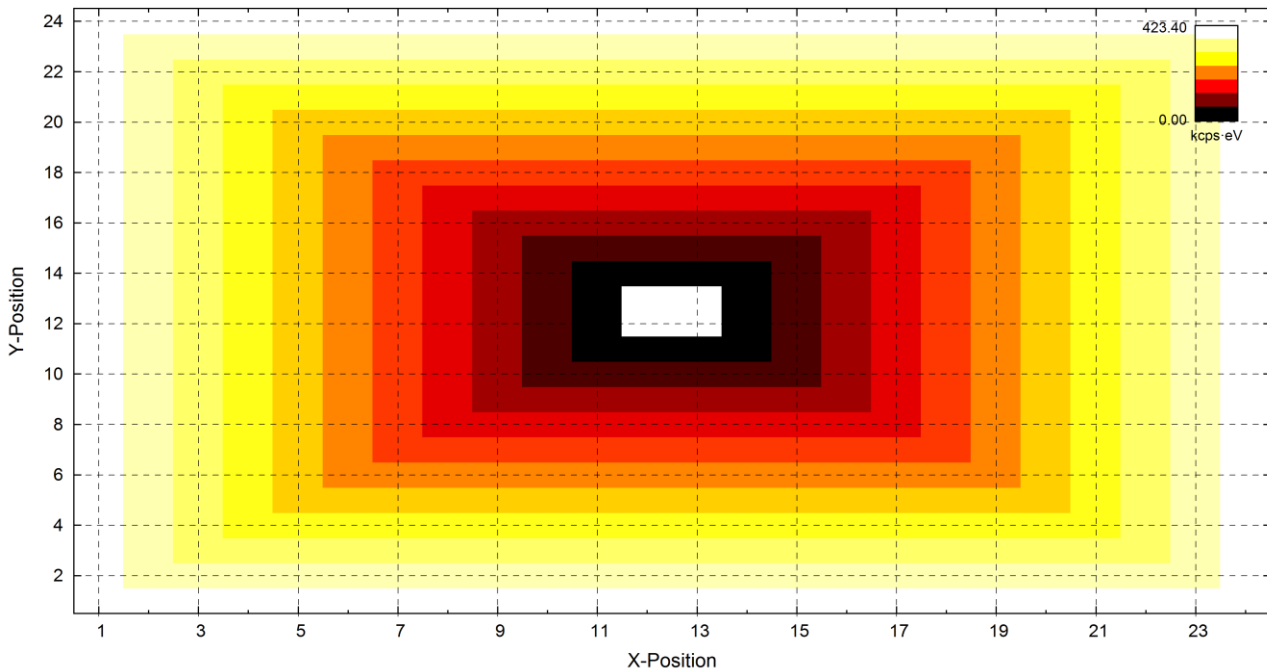


Fig. 34. Example of a presentation 'XY 3D Colour Profile' of a test profile of SiO_2 and Si with UNIFIT 2023, the plot was created using UNIFIT and then inserted as graph into Word document via copy and paste, the maxima (white) of the Si-peak areas are shown in the centre and edges, the plot corresponds with Fig. 32, project: Unifit_2023_User_Files\test spectra\Test35-AreaScan-Si2p-24x24.ufp, window 580

The user must accept the following conditions:

- using of the same arrangement of the analysed peaks,
- the number of additional and existing data points has to be the same.

Steps for quantification (see also example 10):

1. Select and load the regions to be used for quantification,
2. subtract an appropriate background from each peak,

3. load a set of sensitivity factors or Sigma values and the used transmission function with [Quantification - Concentration – Load Sens. Fact./Sigma Values] and [Quantification - Concentration – Load Transmission Function],
4. [Quantification - Concentration] activates a dialogue for selecting the windows which should be used for quantification,
5. select the appropriate windows and press ,
6. the quantification table will be opened, peak names and the sensitivity factors may be edited, the normalized peak areas and atomic concentrations may be recalculated with .

A complete analysis including a parameter plot of a parameter dependent measurement is given in Unifit_2023_User_Files\examples\XPS\Angle_Resolved_Measurement_Si.ufp, Example 11 below describes the generation of a parameter plot from an automatically recorded angle resolved measurement of Si. The measurement is saved as VAMAS format. By contrast example 12 shows the parameter plot of three standard measurements of stepwise oxidized GaAs saved in three projects.

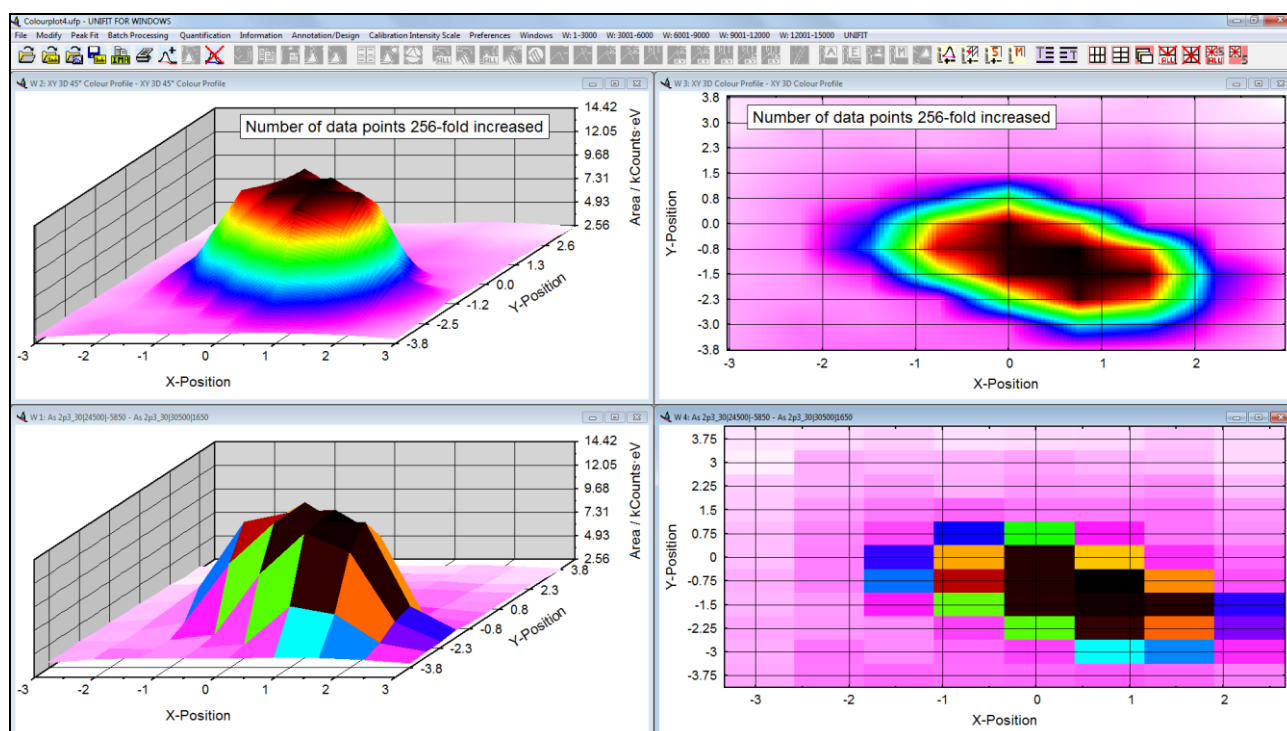


Fig. 35 Screen shot of XY 3D Colour Profiles of the GaAs component of a multipoint measurement of a sputter depth profile of GaAs, left and right bottom: plot of the measuring points, left and right top: the number of points was 256-fold increased, project: Unifit_2023_User_Files\examples\Specials\Colourplot4.ufp

The command ALT-a or ALT-s saves the concentration result (name, energy (always in KE), quantification (in %, last column)) of exactly two elements. The extension of the files is *.pai and can be loaded using the sub-routine 3.9.1.4 or 3.9.4. The intensity ratio is settled to 1.

Note: It is necessary to subtract (or calculate in case of a fittable background) a background function from each peak before quantitative determination. If the spectrum was differentiated, then the peak area is substituted by the peak-to-peak values. A mixing of integral and peak-to-peak values into the quantification routine is not permitted.

Example 11: Calculate the content in [at.%] of carbon, oxygen, sulphur and nitrogen from a survey spectrum recorded with the VG ESCA3 spectrometer:

1. Start UNIFIT,
2. select the number of displayed spectra with [Windows – Hide/Show Standard Windows], the dialogue 'Hide Standard Windows' is opened, select 'Show All Standard Windows' and press , select the displaying of all measurement points with [Preferences – Display – Graphs Standard Windows/Wagnerplot] and 'Plot Option Dots/Squares/Crosses...], select 'All',
3. open the file `Unifit_2023_User_Files\examples\XPS\sulphur_study\example.tap` with [File – Open Spectra - XPS – ESCA3 (*.TAP)],
4. select 'Survey' in the 'Select Spectra' dialogue and confirm with ,
5. select the Shirley background for the right-mouse button operations with [Modify – Calculate Background – Shirley] and activate 'Bckgr. XPS-Quant. Right Mouse Button', leave the dialogue with , if 'Bckgr. XPS-Quant. Right Mouse Button' is grayed then leave the dialogue with , go to point 7,
6. press [Right-Mouse Button - Original/Accept Preferences],
7. generate a cascade arrangement with [Windows – Cascade],
8. make a charge correction of 1.7 eV with [Modify – Charge Correction Active Window],
9. start a automatic peak identification and annotation with [Right-Mouse Button – Automatic Peak ID], after a short calculation time the peak annotations of C 1s, O 1s, S 2s, S 2p, N 1s appear,
10. extract the peaks by setting of two reduction-marker lines and pressing [Right-Mouse Button – Extract Peak for XPS Quantification (Twin)/ Shirley Background] (the operations of that call are: reduction, satellite subtraction, background subtraction, transfer of the annotation label to the windows title),
11. the energy ranges defined using the reduction-marker lines are: O 1s: 540.1 – 524.1, N 1s: 407.3 – 392.1, C 1s: 294.5 – 277.7, S 2p: 174.5 – 156.9
12. four new windows are generated with the names: O 1s, N 1s, C 1s and S 2p,
13. select [Quantification – Concentration] and select the window O 1s, N 1s, C 1s and S 2p, confirm with ,
14. table 'Concentration' appears containing the names, background-free areas, defined sensitivity factors, values of the defined transmission function appears in the quantification table,
15. load correct Sigma-Aluminium Scofield factors 'AlScofld.sen' and transmission function 'ESCALAB220_TWIN_SAE150_10EP.TRM' and re-calculates with , leave the submenu with .

3.6.2 Thickness Estimation 1 (ERXPS)



[Quantification – Thickness Estimation 1] allows the estimation of film thickness using the comparison of the normalized intensities of two photoelectron lines at different energies. Firstly, the normalized intensities have to be calculated with the menu point [Quantification – Concentration]. The calculation of the film thickness d is carried out by equation (103). The sensitivity factors of both lines used for the thickness estimation has to be defined in such a way that the quantification of these two lines without film ($d = 0$) results in a concentration ratio of 50%/50%. The *IMFP* of the film has to be defined manually. The film-thickness analysis can be saved in projects (see also 'Unifit_2023_User_Files\test spectra\Test20-Film-Thickness.ufp', 'Unifit_2023_User_Files\test spectra\Test20-Film-Thickness_Result.ufp' and the example 'Unifit_2023_User_Files\examples\Film_Thickness_Estimation_1.ufp').

Example 12: A quantitative analysis of the measurement *Si_angle_resolved_measurement.vms* saved in the directory *Unifit_2023_User_Files\examples\XPS\Angle_Resolved_Measurement_Si* should be performed. A parameter plot of the normalized peak areas of the two Si components (Si and SiO₂), the O 1s-peak area and the C 1s-peak area shall be created.

1. Start UNIFIT,
2. set [Preferences – Fit Procedure - Product] and [Preferences – Fit Parameter/XAS-Background Parameters – Absolute], select the number of displayed spectra with [Windows - Hide Standard Windows], the dialogue 'Hide Standard Windows' is opened, select 'Show all Standard Window' and press ,
3. load *Si_angle_resolved_measurement.vms* with [File - Open Spectra - XPS – VAMAS (*.VMS;*.NPL)],
4. select the C 1s spectra in ,Select Blocks',
5. load all C 1s spectra with and in ,Select Spectra',
6. activate window 20 and define the energy range from 289 eV to 282 eV (see 3.3.6.5)
7. subtract a Shirley background (see 0),
8. subtract a Shirley background in all windows with [Batch Processing – Batch Processing] and pressing and press , and confirm the batch processing in the message box with ,
9. activate the quantification table with [Quantification - Concentration] and and , confirm the question 'Should the peak names of the quantification table be changed?' with , the quantification table appears, load the file *AlScofld.sen* by pressing ,
10. load the transmission function *ESCALAB220_TWIN_SAE150_10EP.TRM* by pressing the button ,
11. calculate the normalized areas from the C 1s peak by pressing ,
12. open the dialogue 'Parameter Plot' by clicking select ,Batch Parameter' for the X-axis and ,Norm.Area (Components)' for the Y-axis and create a plot of the C 1s peak by pressing , (see also Fig. 40),
13. close the quantification dialogue and close all C 1s standard windows with [Windows – Close all Standard Windows], do not save the project,
14. load all O 1s peaks with ,File - Select Blocks' and ,Select Spectra',
15. subtract from all O 1s peaks a Shirley background with [Modify – Calculate background – Shirley] and [Batch Processing – Batch Processing (see points 6 - 8)],
16. create the quantification table for O 1s with [Quantification – Concentration] and open the parameter-plot dialogue with ,
17. chose the option ,Add to Plot' and add the normalized peak areas of O 1s to the existing C 1s parameter plot with , close all O 1s standard windows, do not save the project,
18. load all Si 2p peaks with ,Select Blocks 'and ,Select Spectra',
19. activate window 20 and subtract the satellite with [Modify – Subtract Satellite],
20. load the saved fit parameter set *Si2p.par* with [Peak Fit – Load Start Parameters, folder: *Unifit_2023_User_Files\examples\XPS\Angle_Resolved_Measurement_Si*) for fitting the Si 2p peak with two doublets and a fitable background,
21. fit the Si 2p peak of window 20 using five iteration steps two cycles,
22. fit all other Si 2p windows (1 – 19) with [Batch Processing – Batch Processing],
23. create the quantification table of all Si 2p windows with [Quantification – Concentration] and pressing and , open the parameter- plot dialogue with ,
24. add to the parameter plot of the C 1s and O 1s values the normalized peak areas of the two Si 2p components with the option ,Add to Plot' and pressing (see Fig. 64),

26. design and annotate the parameter plot using the submenu ,Annotation/Design' (see 3.8) and the preference point [Preferences – Display - Parameter Plot Display](see Fig. 49).

3.6.3 Thickness Estimation 2 (ARXPS)



This menu point allows the estimation of the thickness of epitaxial films using angle resolved measurements. At first the calibration values of the normalized intensities without a film ($d = 0$) are calculated and saved. The thickness of the film will be estimated using equation (104). The knowledge of the *IMFP* in the film for the used kinetic energy is necessary (see also the test projects 'Unifit_2023_User_Files\test spectra\Test21-Film-Thickness.ufp' and 'Unifit_2023_User_Files\test spectra\Test21-Film-Thickness_Result.ufp').

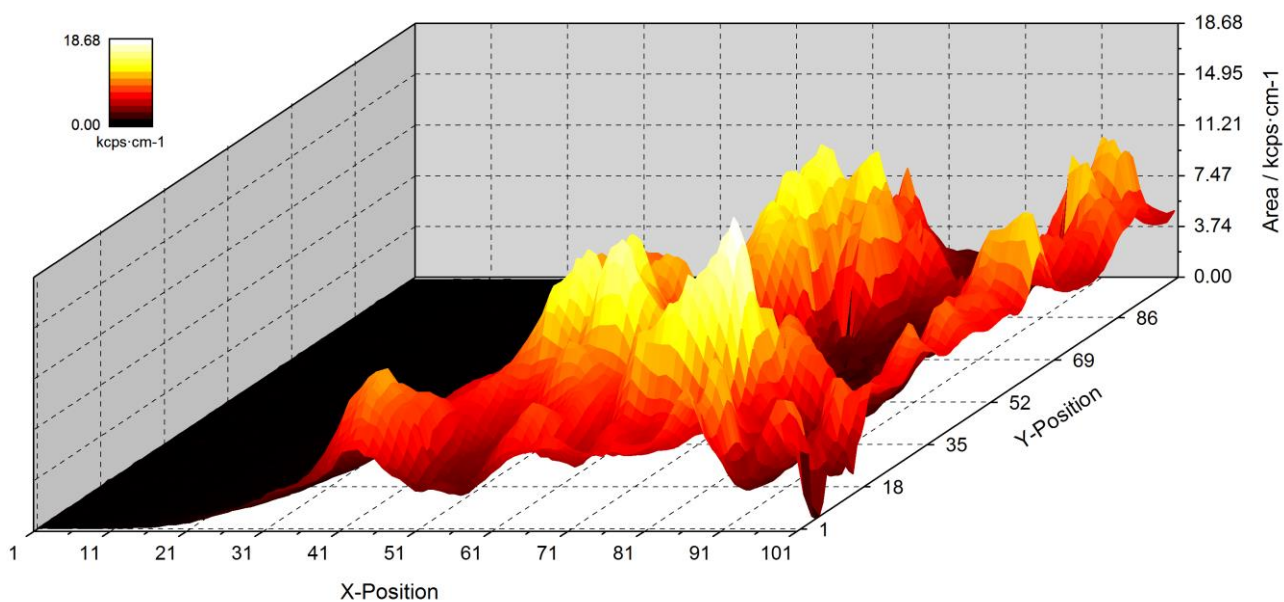


Fig. 36 Example of a presentation 'XY 3D 45° Colour Profile' of a multipoint RAMAN measurement of a Si band with UNIFIT 2023, the plot was created using UNIFIT and then inserted as graph into Word document via copy and paste, the maxima (white) of the Si-peak areas are shown, project: Unifit_2023_User_Files\examples\Colourplot3.ufp and Unifit_2023_User_Files\examples\RAMAN\RAMAN-Si-Mapping-101x101.ufp

3.6.3.1 Calculation/Input of Calibration Values $I'(x^\circ)$ ($d=0$)

This menu point allows the calculation and saving of the normalized intensities at different angles x° of the clean uncovered substrate surface. The intensities can be saved together with the corresponding angles in the folder 'Documents\Unifit_2023_User_Files\film' (see also 'Unifit_2023_User_Files\examples\Film_Thickness_Estimation_2_d=0.ufp').

Example 13: The projects *GaAs_1.ufp*, *GaAs_2.ufp* and *GaAs_3.ufp* are stored in the folder *Unifit_2023_User_Files\XPS\examples*. These projects include measurements of oxidized GaAs (ozone treatment for 0s, 10s, 30s). The element concentration of Ga, As, O and C with respect to the oxidation time shall be displayed.

1. Start UNIFIT, activate [Preferences - Open Project with Showing of the Quantification and Film Thickness Table] (is ticked), be sure that window 20 is the first standard window with [Preferences – Setting of Programme Parameters],
2. Load the project *Unifit_2023_User_Files\examples\XPS\GaAs_1.ufp*, after appearance of the quantification table click **Parameter Plot**, the dialogue ,Parameter Plot' will be opened,

3. chose the option ,Create new Plot', for the X-axis ,Fixed Value' and for the Y-axis ,Quant. at.% (Sum Curve)',
4. enter 0 (0 sec Ozone) into the edit field ,Value', close dialogue by pressing , close the quantification table, close all standard windows (parameter plot remains open),
5. Load the project **Unifit_2023_User_Files\examples\XPS\GaAs_2.ufp**, after appearance of the quantification table click , the dialogue ,Parameter Plot' will be opened,
7. chose the option ,Add to Plot', enter 10 (10 sec Ozone) into the edit field ,Value', close dialogue by pressing (the plot will be extended by the new four values), close the quantification table, close all standard windows (parameter plot remains open),
8. Load the project **Unifit_2023_User_Files\examples\XPS\GaAs_3.ufp** in the currently used Unifit programme (do not execute an additional Unifit), after appearance of the quantification table click , the dialogue ,Parameter Plot' will be opened,
9. chose the option ,Add to Plot', enter 30 (30 sec Ozone) into the edit field ,Value', enter into the edit field ,X-axis (with unit)' ozone / s, close dialogue by pressing (the plot will be extended by the new four values), close the quantification table,
10. design and annotate the parameter plot using the submenu ,Annotation/Design' and the preference point [Preferences - Display – Parameter Plot Display], change the legend annotation to As2p3, C1s, Ga2p3 and O1s.

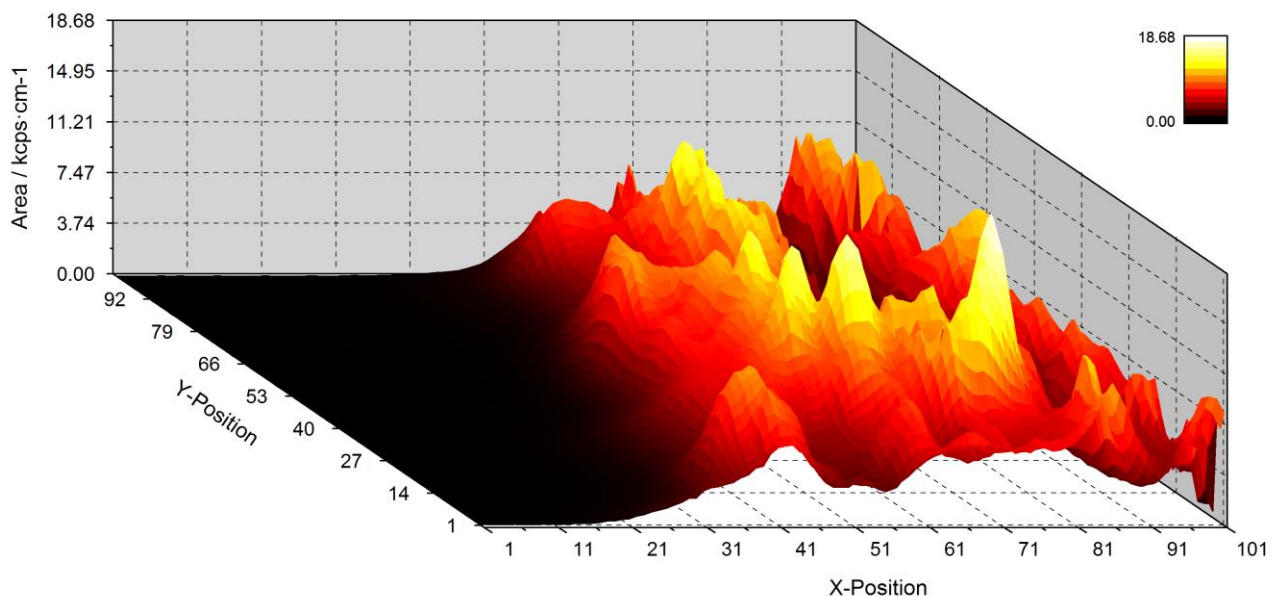


Fig. 37 Example of a presentation 'XY 3D -45° Colour Profile' of a multipoint RAMAN measurement of a Si band with UNIFIT 2023, the plot was created using UNIFIT and then inserted as graph into Word document via copy and paste, the maxima (white) of the Si-peak areas are shown, project: Unifit_2023_User_Files\examples\Colourplot3.ufp and Unifit_2023_User_Files\examples\RAMAN\RAMAN-Si-Mapping-101x101.ufp


3.6.3.2 Calculation of Thickness d with $I'(x^\circ; d=0)/I'(x^\circ; d>0)$

This menu point allows the estimation of the thickness of epitaxial films using angle resolved measurements. The angles x° have to be the same as the saved calibration values. The *IMFP* value of the film is necessary. The used angles of the ARXPS measurement and the saved angles of the calibration values have to be the same (see also Test21.ufp and the example Unifit_2023_User_Files\examples\XPS\Film_Thickness_Estimation_2.ufp).

3.7 Information

This option provides information about the spectrum in the active window, the loaded measurement data or current project.

3.7.1 Acquisition Parameters...

 [Information – Acquisition Parameters...] shows peak name, batch parameter, comment, excitation energy, lens mode, start and end energy, number of steps (points), step width, number of scans (accumulations), time per step (dwell time), analyser mode (CRR – constant retard ratio, CAE – constant analyser energy), the analyser-pass energy, the x- and y-position of the recording point. By pressing the middle mouse button these informations can be displayed, too.

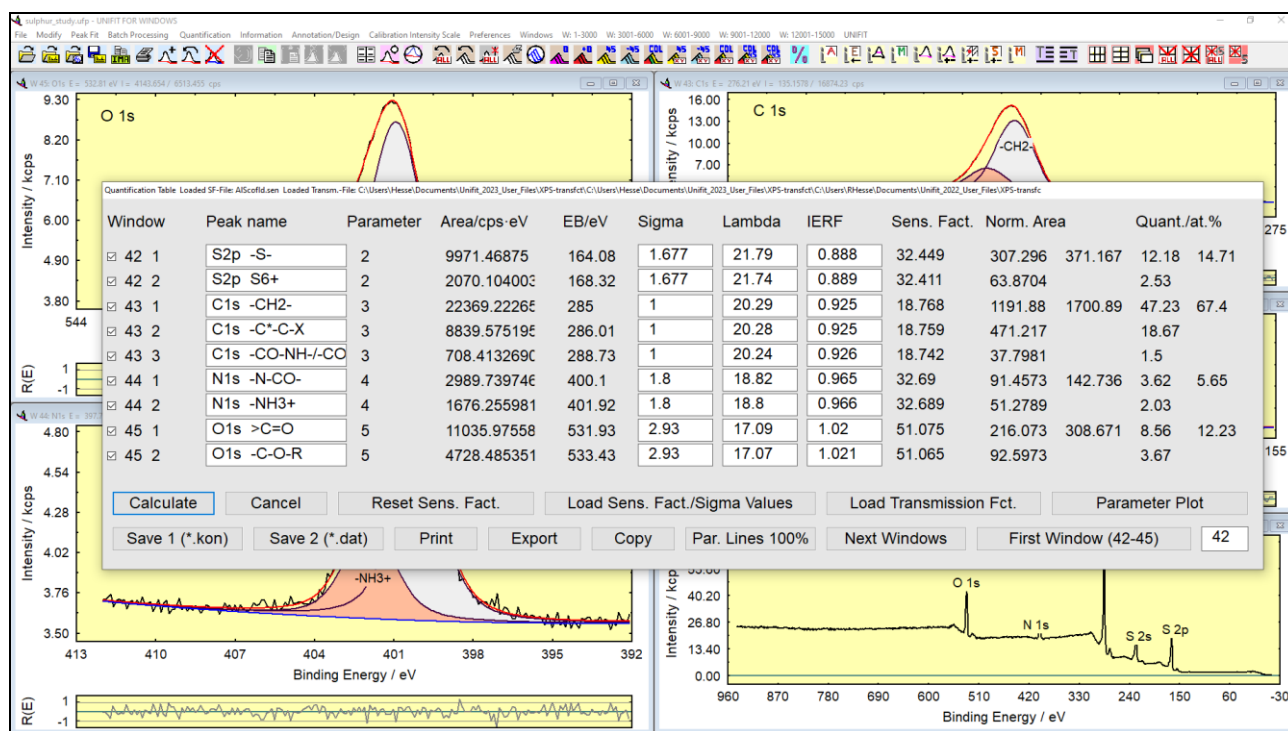




Fig. 38. Screen shot: Dialogue of the quantification of integral values using the sensitivity factor defined by the product of σ , λ and the particular transmission function $T(E)$ ($IERF$) integrated in the software UNIFIT 2023. The dialogue shows the quantification of sulphur, carbon, oxygen and nitrogen, project: Unifit_2023_User_Files\examples\XPS\sulphur_study.ufp


3.7.2 Processing Steps...

 [Information – Processing Steps...] gives the information about the processing steps passed through. The processing steps will be saved in the project files too. The sequence of the steps is not specified.


3.7.3 Charge Correction...

 With [Information – Charge Correction...] the charge corrections of all opened standard windows are shown. If the number of opened standard windows is larger than 100 the charge correction from the active and the next 99 standard windows will be shown.

3.7.4 Quantities Peak Fit...

 With [Information - Quantities Peak Fit] the values χ^2 , χ^{2*} and *Abbe* of the fitted spectra of all windows will be displayed. If the number of opened standard windows is larger than 100 the quantities from the active and the next 99 standard windows will be shown.

3.7.5 Minimum/Maximum

 With [Information – Minimum/Maximum] the intensity minimum and maximum and the corresponding energy of the active window are displayed.

| Peak Name | E_B /eV | Area/cps·eV | Sens. Fact. | Norm. Area | Quant./at.% |
|----------------------|-----------|-------------|-------------|------------|-------------|
| S2p -S- | 164.08 | 9971.6329 | 32.449 | 307.30170 | 12.18 14.71 |
| S2p S6+ | 168.32 | 2070.0950 | 32.411 | 63.870137 | 2.53 |
| C1s -CH2- | 285 | 22369.343 | 18.768 | 1191.8874 | 47.23 67.4 |
| C1s -C*-C-X | 286.01 | 8839.5495 | 18.759 | 471.21646 | 18.67 |
| C1s -CO-NH- / -CO-O- | 288.73 | 708.40255 | 18.742 | 37.797596 | 1.5 |
| N1s -C-N-C- | 400.1 | 2989.7527 | 32.69 | 91.457716 | 3.62 5.65 |
| N1s >N+- | 401.92 | 1676.2438 | 32.689 | 51.278528 | 2.03 |
| O1s =O | 531.93 | 11035.866 | 51.075 | 216.07177 | 8.56 12.23 |
| O1s -O- | 533.43 | 4728.4317 | 51.065 | 92.596332 | 3.67 |

Fig. 39. Image of the quantification table, transferred to the text processing document via the ‘Copy – Paste function’ of UNIFIT and text processing software (e.g. Word), the quantification includes four elements (O 1s, S 2p, C 1s and N 1s), example: Unifit_2023_User_Files\examples\XPS\sulphur_study.ufp, plot corresponds to Fig. 38

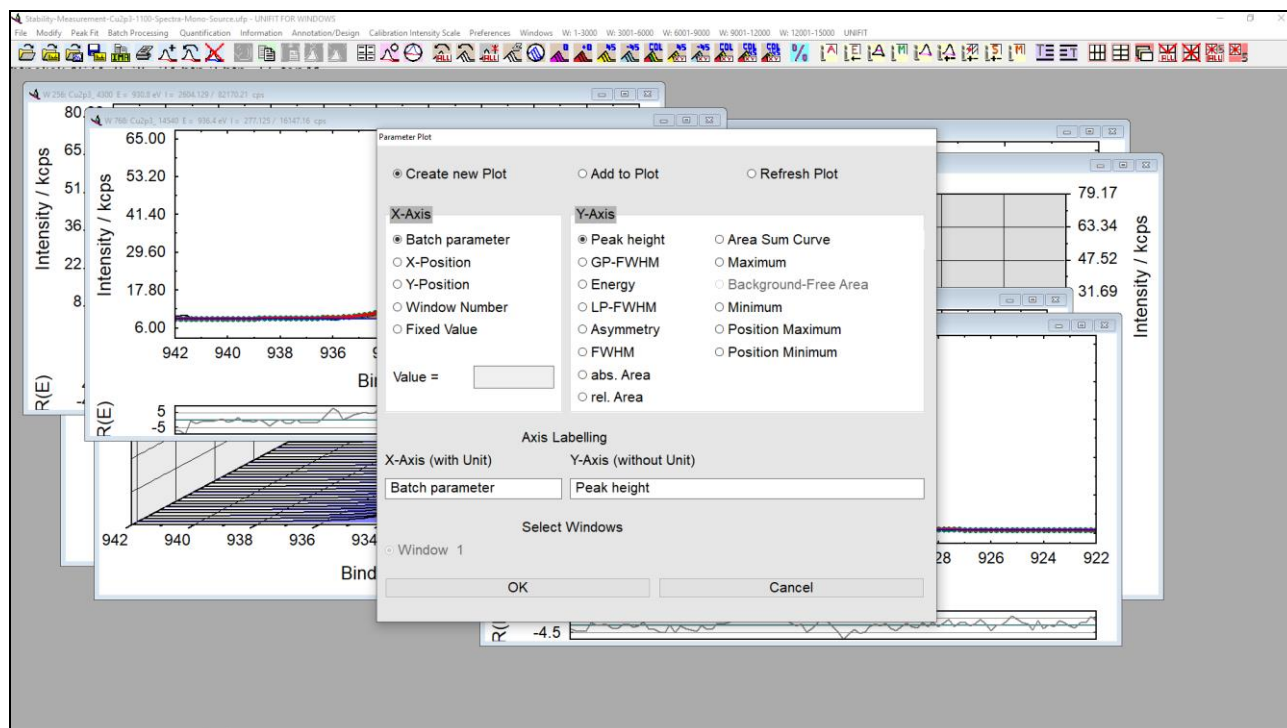


Fig. 40. Screen shot: Dialogue: ‘Plot Fit Parameters/Min/Max/Areas...’

3.7.6 FWHM



With [Information – FWHM] the FWHM of the spectrum, modified spectrum or fitted components of the active window are displayed.

3.7.7 Correction of the Magnetic Field



With [Information – Correction of the Magnetic Field] the value $(I_A(i_2) - I_A(i_1))/(I_n(i_2) - I_n(i_1))$ (important for XMCD) can be displayed ($I_A(i_1)$ - Averaged intensity of modified spectrum of the active window at the low Photon energy side, $I_n(i_1)$ - Averaged intensity of the modified spectrum of all n opened windows at the low Photon energy side, (i_2 - high Photon energy side). If the number of opened standard windows is larger than 100 the correction of the magnetic field from the active and the next 99 standard windows will be shown.

3.7.8 Directory Experiment



This submenu opens a window that contains the directory and the file name used for saving the experimental data.

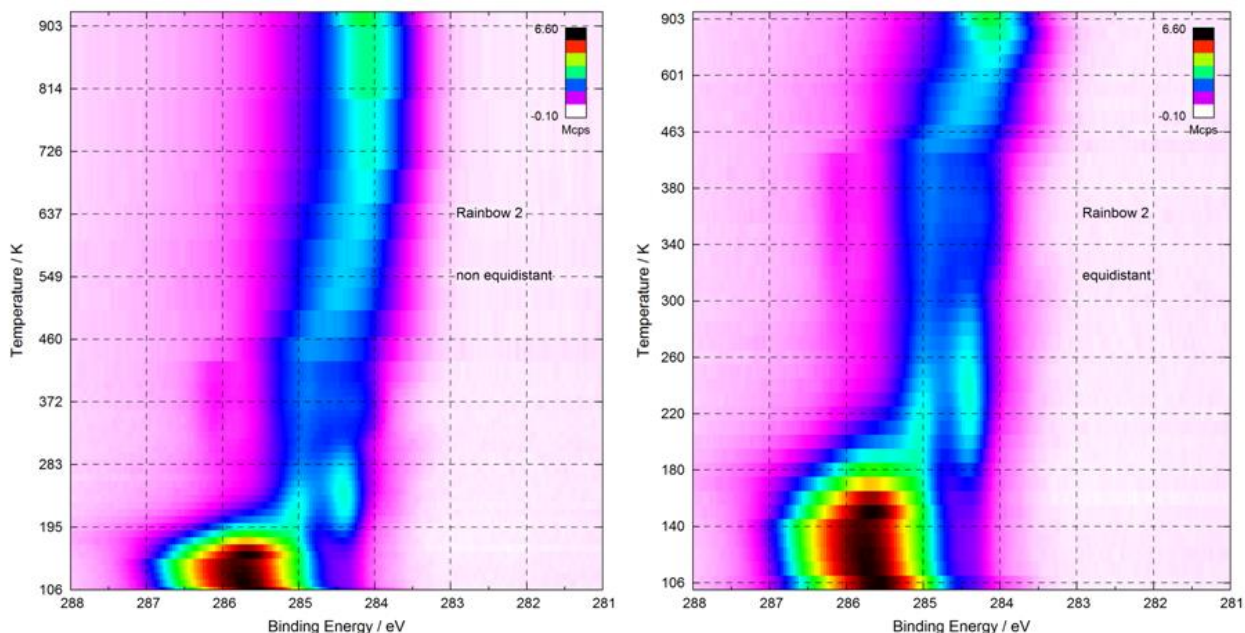


Fig. 41. 3D-Colour Plot (colour profile: Rainbow 2) of Platinum sample covered with Pyridine (C 1s) at different substrate temperatures, left: parameter axis scaled with true experimental values (non-equidistant scaling), right: equidistant parameter steps, project: 'Documents\Unifit_2023_User_Files\examples\Specials\Colourplot_equidistant_non-equidistant_steps.ufp'

3.7.9 Project Comment



This menu point allows to comment the project. Three edit lines may be used for showing and editing the comment.

3.7.10 Identify Lines



The menu item [Information – Identify Lines] was introduced to support the user in the process of identification and perhaps labelling of the XP core level lines and Auger lines of

the elements as well as the chemical species [26, 29, 30].

After activation of the menu item a list box appears, which offers the four following options in 'Select Lines Types':

1. **'All Lines'** shows all lines stored in the file:
'My documents\Unifit_2023_User_Files\lines\Line positions.pos, (see book 'Line Positions and Data Formats – Version 2023', 1),
2. **'Important Lines'** shows the lines marked with a star from the file:
'My documents\Unifit_2023_User_Files\lines\Line positions.pos, (see book 'Line Positions and Data Formats – Version 2023', 1),
3. **'Element Lines'** separates and shows all lines of one element from the file:
'Documents\Unifit_2023_User_Files\lines\Line positions.pos, (see book 'Line Positions and Data Formats – Version 2023', 1),
4. **'Chemical Shift'** shows the lines saved in the files with corresponding names of the chemical components:
'Documents\Unifit_2023_User_Files\lines\Ag 3d5.pos'
'Documents\Unifit_2023_User_Files\lines\Ag (M4N45N45).pos'
...
'Documents\Unifit_2023_User_Files\lines\Zr (M45N23V).pos'
(see book 'Line Positions and Data Formats – Version 2023', 1)

and the options 'Manual' and 'Automatic' in 'Annotation Mode'.

The stored chemical shifts can be opened by selecting the corresponding line with **'All Lines'**, **'Important Lines'** or **'Element Lines'** and clicking the option **'Chemical Shift'**. In case no chemical shifts are stored for the selected peak a message will be displayed.

1. **Manual Annotation:** In case of finding a stored line by moving the mouse via the spectrum in the active window and press the left mouse button, this line will be marked in the List Box. Activating **Annotation** will cause the labelling of the line in the spectrum. The position of the labelling will be chosen automatically by taking into account both the energy and the intensity of the corresponding line. A repositioning may be performed by activating and placing it while pressing the left mouse button.
2. **Automatic Annotation:** The automatic annotation can be optimized by defining three parameters: i) Delta E, ii) Delta I iii) check with main lines. The recommended values are displayed. The main lines can be changed by the user (Documents\Unifit_2023_User_Files\lines\Mainlines.pos).

They will be inserted in the list of spectrum labels and may be modified or deleted by using the call **Spectrum Labelling** or the item [Annotation/Design – Spectrum Labelling]. The chosen option (see above) will be stored automatically and will be reactivated after restart of the programme.

In case the active window includes an Auger spectrum, the Auger lines of the data bank will be displayed only.

3.7.11 Add/Edit/Show Line Positions



The supplied data bank of the line positions was selected from measurements and well-known sources [26, 29, 30]. The data bank can be expanded according to the individual intentions and the research fields of the users.

By activating [Information – Add/Edit/Show Line Position] the user may create a personal data base including the most important chemical shifts for his application (directory: 'Documents\Unifit_2023_User_Files\lines'). After choice of the line of interest all stored chemical shifts will be listed. The element lines are stored in 'Line positions.pos'. Any item may be deleted or edited. As usual, the modified file will be saved by pressing **Save**, **Cancel** exits the

dialogue without saving. An easy way to add a new line is the modification of an existing line. The new file may be saved with a new name using the call **Save as**.

All files in the directory 'Documents\Unifit_2023_User_Files\lines' may also be modified using any ASCII editor (e.g. Word). The format of the insert is: ',space character'+,line position' (binding energy in case of photoemission core levels, kinetic energy in case of Auger lines) ',space character'+,space character'+,labelling of the chemical shift', e.g.: 285.0 -CH2-. The number of inserts is not limited. The file name has to coincide with the corresponding name in the file 'Line positions.pos'.

3.7.12 Identify Auger Parameters



In UNIFIT a data bank of Auger parameters is integrated. With [File – Open Wagner Plot...] a presentation of Auger parameters is available as chemical state plot. With the menu point [Information – Identify Auger Parameters] it is very easy to identify and annotate the points in the chemical state plot.

After activation of the menu item a list box appears, which offers the list of the shown Auger parameters. A stored point can be found by moving the mouse pointer across the Wagner plot in the active window and selecting a point by pressing the left mouse button. The selected data point will be marked automatically in the list box. Activating **Annotation** will cause the labelling of the point in the chemical state plot. The position of the labelling will be chosen automatically by taking into account both the binding energy and the kinetic energy of the corresponding point. A re-positioning may be performed by activating and placing the label while pressing the left mouse button. The label will be inserted in the list of spectrum annotation and may be modified or deleted by using the item [Annotation/Design – Spectrum Labelling] (see Fig. 7).

3.7.13 Add/Edit/Show Auger Parameters



The supplied data bank of Auger parameters was selected from measurements and well-known sources [12, 26, 29, 30]. The data bank can be expanded according to the individual intentions and the research fields of the users.

By activating [Information – Add/Edit/Show Auger Parameters] the user will be enabled to create a personal data bank including the most important Auger parameters for his application (directory: Unifit_2023_User_Files\auger parameters). After the choice of the element of interest all Auger parameters related will be listed. Any item may be deleted or edited. As usual, the modified file will be saved by pressing **Save**. An easy way to add a new Auger-parameter value is the modification of an existing Auger-parameter file. The modified file may be saved with a new name using the call **Save as**. **Cancel** exits the dialogue without saving.

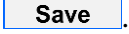


All files in the directory 'Documents\Unifit_2023_User_Files\auger parameters' may also be modified using any ASCII editor (e.g. Word). The format of the insert is: ',space character'+,Auger parameter'+,='+,binding energy of photo line'+,+',kinetic energy of Auger line'+,space character'+,space character'+,name of compound' (e.g.: 726.0=368.2+357.8 Ag).The number of inserts is not limited. The file name has to coincide with the corresponding name in the folder '*\auger parameters*.aup'.

3.7.14 Add/Edit/Show Sensitivity Factors/Sigma Values



The software package UNIFIT includes different data banks of sensitivity factors and ionisation cross-sections for the quantification of XPS and AES data (e.g. Wagner, Scofield). These data banks should be a starting point to create special data sets of the user's spectrometer. The data were extracted from Wagner et al. [9] and Briggs et al [12].




All files with which the name starts with 'Wagner' (e.g. Wagner-XPS-SF.sen, Wagner-AES-PHI700-3kV-Differential.sen) contain empirical data. If these data are used during the quantification, the values of λ and $T(E)$ are settled to unity.

By activating [Information –Add/Edit/Show Sens.Fact./Sigma Values] the user will be enabled to create his personal data bank. The directory 'Documents\Unifit_2023_User_Files\sensitivity factors' will be opened. After the choice of the element of interest all its stored sensitivity factors are listed. Any item may be deleted or edited. As usual, the modified file will be saved by pressing . An easy way to add new factors is the modification of an existing file. The modified file may be saved with a new name using the call .  exits the dialogue without saving. All files in the directory 'Documents\Unifit_2023_User_Files\sensitivity factors' may also be modified using any ASCII editor (e.g. Word). The format of the insert is: ',name of the line'+,='+,sensitivity factor', e.g.: Ag3d3=2.10). The number of inserts is not fixed (see book 'Line Positions and Data Formats – Version 2023', 5.3).

3.7.15 Add/Edit/Show Doublet Data



The software package UNIFIT includes a data bank of doublet data. In this data bank users can find the known intensity ratios and energy difference values of many doublet lines. The data were extracted from Wagner et al. [9] and Briggs et al [12].

By activating [Information –Add/Edit/Show Doublet Data] the directory 'Documents\Unifit_2023_User_Files\settings' will be opened. After the choice of the element of interest all doublet data related will be listed. Any item may be deleted or edited. As usual, the modified file will be saved by pressing . An easy way to add new doublet data is the modification of an existing file. The new file may be saved with a new name using the call .  exits the dialogue without saving.

The files *.dda in the directory Unifit_2023_User_Files\settings may be modified also using an ASCII editor (e.g. Word). The format of the insert is: ',name of doublet'+,='+,intensity ratio'+,/'+,energy difference value', e.g.: Ag3d = 0.666/6.00). The number of inserts is not limited (see book 'Line Positions and Data Formats – Version 2023', 5.5).

3.7.16 Plot Cross Section Lambda·K(T)



This menu point allows the plot of the calculated and stored inelastic electron scattering cross-section $\lambda(E) \cdot K(E, T)$, (E – kinetic energy, T – loss energy) (see Fig. 20, left). The extension of the files is *.cro. The recommended path is *\My documents\Unifit_2023_User_Files\inelastic electron scattering cross-sections.

3.7.17 Information about Main Memory



This menu point gives the information about the usable and currently used main memory by the programme UNIFIT.

3.7.18 AES-Calculation Tool



This menu point allows the calculation of the sensitivity factors of the AES lines. The used equations are suggested by Mroczkowski and Eichman [23] (see also 2.8.).

3.7.19 Add/Edit/Show AES Target Atom Subshell



The software package UNIFIT includes a data bank of the binding energies of the AES target atom sub shells (e.g. the binding energy of Ag M4 for the Auger line Ag (M4N45N45)). The data can be calculated in the UNIFIT sub-menu 3.7.18 using the equations suggested by Mroczkowski and Eichman [23].

By activating [Information – Add/Edit/Show AES Target Atom Subshell] the directory Documents\Unifit_2023_User_Files\lines will be opened. After loading of the file AES-LinePositionsTargetIonisationSubshell.apo the target atom subshell data will be listed. Any item may be deleted or edited. As usual, the modified file will be saved by pressing **Save**. An easy way to add new doublet data is the modification of an existing file. The new file may be saved with a new name using the call **Save as**. **Cancel** exits the dialogue without saving.

The files *.apo in the directory Unifit_2023_User_Files\lines may be modified also using an ASCII editor (e.g. Word). The format of the insert is: ,name of element'+, '+,name of the subshell'+,:'+,binding energy subshell', e.g.: C K:287). The number of inserts is not limited (see book 'Line Positions and Data Formats – Version 2023', 5.6).

3.8 Annotation/Design

This menu item may be used to place comments and line labelling. It can also be applied to the modification of that information that was introduced above in the menu item [Information – line identification]. Additionally, this menu item allows the user to change manually the scaling as well as the start and endpoints of the X-, Y- and Z-axis. The complete design modifications of the spectrum will be included in the printout.

Note: The automatic scaling and annotation of energy, intensity and parameter axis of the corresponding window will be disabled in case of using the manual mode. After a new processing step the automatic scaling is reactivated and the manual formatting is deleted.

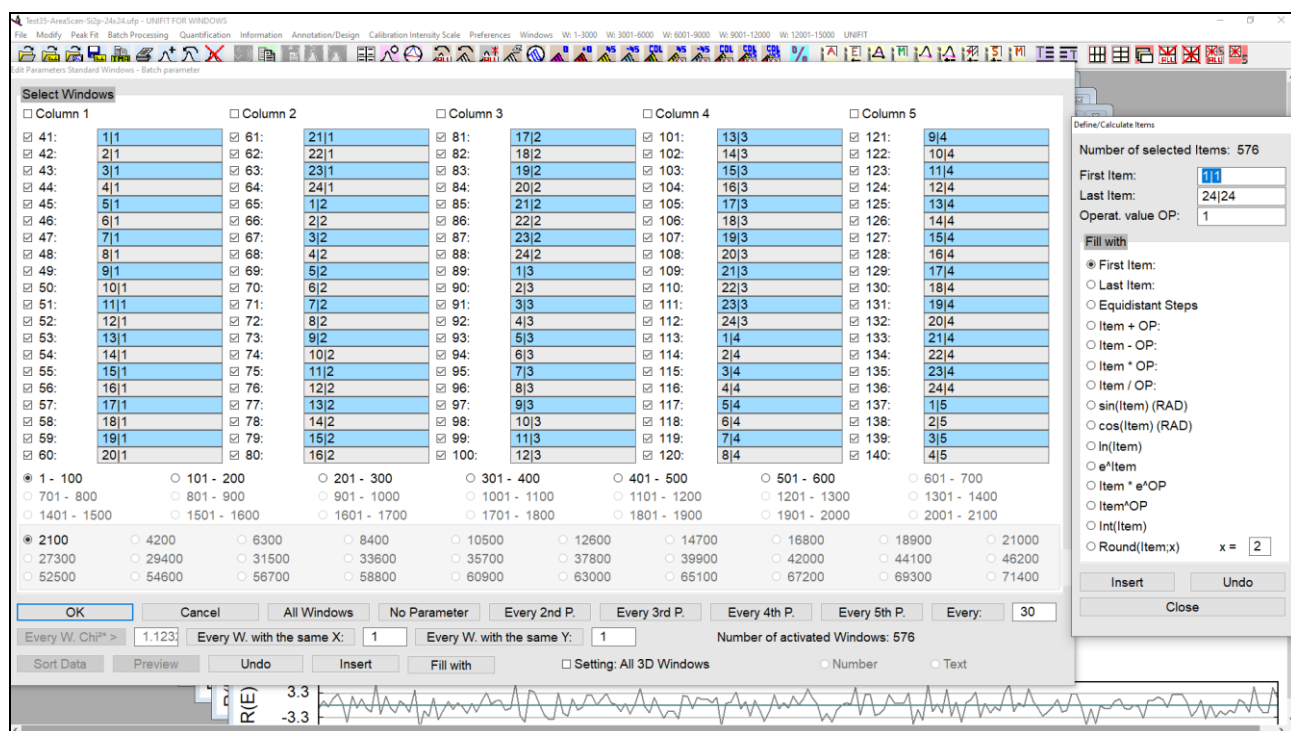


Fig. 43. Screen shot: Edit-parameter dialogue and the Fill-with dialogue for the manipulation of the different parameters of the spectra as well as the batch parameters of the 3D and parameter plots (project: Unifit_2023_User_Files\test spectra\Test35-AreaScan-Si2p-24x24.ufp)

3.8.1 Load Annotation/Design Display Active Window



This menu point allows the loading of the files including design elements, the spectrum title, the annotation and legend for the active window (*.dsg). This software function can be very

helpful in case of the annotation of a set of surveys of similar samples. Only by the active window the new design elements is used.

3.8.2 Load Annotation/Design Display All Windows of the Same Type

This menu point allows the loading of the files including design elements, the spectrum title, the annotation and legend for the active window (*.dsg). The design features and annotations of all windows of the same type (how the active one) are changed.

3.8.3 Load Annotation/Design Display Selected Windows of the Same Type

This menu point allows the loading of the files including design elements, the spectrum title, the annotation and legend for the active window (*.dsg). The design features and annotations of before selected windows of the same type (how the active one) are changed.

3.8.4 Save Annotation/Design Display



This menu point allows the loading of the files including design elements, the spectrum title, the annotation and legend for the active window (*.dsg). This software function can be very helpful in case of the annotation of a set of surveys of the same element.

This menu point allows the saving of the design elements, the spectrum title, the annotation and legend of the active window (*.dsg). The software function can be very helpful in case of the annotation of a set of survey spectra of the same element. The recommended path is 'Documents\Unifit_2023_User_Files\design'

3.8.5 Spectrum Title 1



This sub-menu serves to create the spectrum title and can be opened using the pull down menu or by clicking the right mouse button if the mouse pointer is over a spectrum title of the active window.

Steps:

1. Activate the window including the spectrum to be entitled,
2. activate [Annotation/Design – Spectrum Title 1],
3. introduce the title in an empty edit-field, confirm with , press to leave the menu item,
4. By pressing the dialogue will be closed, the new title is displayed with a small shift in x and y with respect to a former title and the dialogue will be reopened.

The spectrum title can be displayed without a frame, with a simple or a shadow frame. The number of title lines is 100. If the menu point will be opened again an empty edit field appears for writing an additional title line. The titles can be indicated optionally in all window or selected windows. Additionally, the title can be extended by the windows number, the batch parameter or a series number. The x and y position can be defined manually. The dialogue size can be changed by pressing and .

3.8.6 Spectrum Title 2



This menu point serves to create formatted spectrum title (rtf format). The steps and frame options are the same as in 3.8.5. In each spectrum window only one formatted title field can be created. Currently five formats are offered: subscript, superscript, bold, italic, Greek.

This menu point can be used also to insert equations and pictures generated in other software (e.g. Word) via the clipboard. After positioning of the formatted title the text field has the original size of the edit field. The size can be changed by: i) positioning the mouse cursor of the text, ii) pressing

the shift key and iii) the left mouse button and vi) moving the mouse. With the special pop-up call the resizing can be activated and deactivated, too.

The title format of the presetting can be transferred to the marked text by pressing **Format Title Annotation**. With the button **Delete** the current text or picture may be deleted. The size of an inserted picture can be changed in the edit field (clicking with the mouse of the picture). The x and y position as well as the weight and height of the text field can be defined manually.

3.8.7 Spectrum Labelling 1



This sub-menu serves to create the comments and annotations inside the spectrum and can be opened using the pull down menu or by clicking the right mouse button if the mouse pointer is over the spectrum label of the active window.

Steps:

1. activate the window including the spectrum to be labelled,
2. activate [Annotation/Design – Spectrum Labelling 1],
3. introduce the comment in an empty edit-field, confirm with **OK**, press **Cancel** to leave the menu item.
4. By pressing **OK Plus New Labelling** the dialogue will be closed, the new annotation is displayed with a small shift in x and y with respect to a former annotation and the dialogue will be reopened.

The comments and labelling of the lines may be removed by deleting the corresponding information from the edit-field. The number of annotations is 100. If the menu point will be opened again an empty edit field appears for writing an additional labelling. The labelling can be indicated optionally in all window or selected windows. Additionally, the label can be extended by the windows number, the batch parameter or a series number. The x and y position can be defined manually. The dialogue size can be changed by pressing **-DS** and **DS+**.

3.8.8 Spectrum Labelling 2



This menu point allows the labelling of spectra with a formatted text or inserting of pictures or equations. The operation procedure is the same as described in point 3.8.5. Special frames are not available.

3.8.9 Legend/Select Curves



This menu point allows the showing of a legend for plots and can be opened using the pull down menu or by clicking the right mouse button if the mouse pointer is over the spectrum legend of the active window. The Labelling of the different curves may be changed. For the representation of the legend 25 positions are possible in the window. With **OK** the settings will be accepted. **Cancel** leaves the menu without saving the changed settings. A first viewing of the changes gives the command **Preview**. **Original** reactivates the original setting. The legend may be activated and reactivated by using the option 'Show Legend'.

In case of standard windows the legend shows the spectrum, the background, the components, the sum curve and the residual concerning the processing steps. The separate viewing of these curves is not possible.

In case of parameter plots each curve may be presented or left out optionally. An automatic rescaling does not take place. With the call **Create Sum Curve** the sum of the selected curves can be calculated and displayed additionally (e.g. the sum of all oxides).

In case of an active colour-profile window the option 'Show Legend' allows the displaying of a colour-scaling bar at different positions.

3.8.10 Plot Energy/Wavenumber Axis/Plot X-axis

E In order to modify the title, the tick labelling, the start and endpoints as well as the scaling of the energy/wavenumber axis (XY 3D plots: X-axis) this menu item may be used. In addition, a zero line and grid lines can be plotted. The form, shape and colour of the grid lines are selected with [Preferences – Display - Axis/Lines/Text Display...]. As usual, the modified design will be accepted by pressing **OK**, **Cancel** exits the dialogue without changing the design. By pressing **Preview** the modifications can be shown, **Original** reactivates the original setting. The option 'Setting: All Std. Windows' transfers the modifications to all other standard windows with the same recording conditions. A fix number of decimal places of the tick labelling can be chosen. The chosen setting will be saved as preferences if the check box 'Save as Preferences' is ticked.

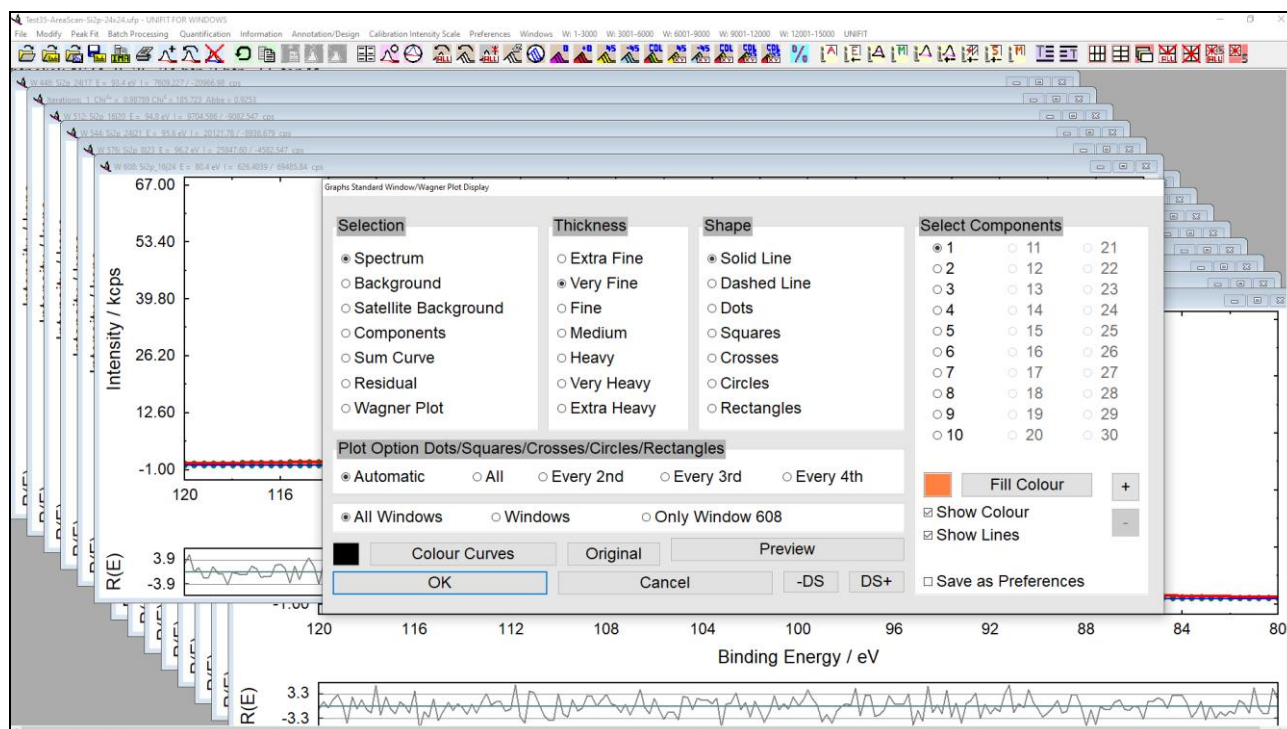


Fig. 42. Screen shot: Dialogue for setting the shape, thickness and colour of all curves displayed on the screen, setting of the fill colour of the components of the peak fit (Graphs Display)

3.8.11 Plot Intensity Axis

I In order to modify the title, the tick labelling, the start and endpoints as well as the scaling of the intensity axis the menu item [Annotation/Design – Plot Intensity Axis] may be used. In addition, zero lines and grid lines can be plotted. The form, shape and colour of the grid lines are selected with [Preferences – Display - Axis/Lines/Text Display...]. As usual, the modified design will be accepted by pressing **OK**, **Cancel** exits the dialogue without changing the design. By pressing **Preview** the modifications can be shown, **Original** reactivates the original setting. The option 'Setting: All Std. Windows' transfers the modifications to all other standard windows with the same recording conditions. The scaling, the start and endpoints of the intensity axis will only be transferred, if 'Scaling for all Windows' is activated. With 'Labelling of Scale Lines' the labelling of the ticks can be deactivated.

In case of windows presentations 'Plot 3D Waterfall 0°' and 'Plot 3D Waterfall 0° Plus' the offset, the separation distance of the lines and the stretching factor can be defined by the user. An additional zero line can be plotted into 'Standard Windows', 'Parameter plot' and 'Plot 3D Waterfall

0°'. The Y-axis of the presentation 'Parameter Plot' can be rescaled optionally in at.% by 'Normalization to %'. A fix number of decimal places of the tick labelling can be chosen. The chosen setting will be saved as preferences if the check box 'Save as Preferences' is ticked.

3.8.12 Plot Parameter Axis/Plot Y-axis



The parameter axis of all five 3D plots, the parameter plot and the Y-axis of the five XY 3D plots integrated in the programme UNIFIT can be designed using this menu item. In addition, a zero line and grid lines can be plotted. The form, shape and colour of the grid lines are selected under [Preferences – Display - Axis/Lines/Text Display...]. The option 'Non-equidistant Scaling' allows the scaling of the parameter axis using the true experimental parameter steps and values (see Fig. 41). The option 'Setting: All 3D Windows' transfers the modifications to all other 3D windows with the same recording conditions. With 'Labelling of Scale Lines' the labelling of the ticks can be deactivated. A fix number of decimal places of the tick labelling can be chosen. The chosen setting will be saved as preferences if the check box 'Save as Preferences' is ticked.

3.8.13 Edit Parameters Standard Windows/Edit Batch Parameters 3D Window/Edit Batch Parameters Parameter Window



Regarding the activated window (standard, 3D window or parameter window) the title of this menu point switch form [Annotation/Design – Edit Parameters Standard Windows], [Annotation/Design – Edit Batch Parameters 3D Window], [Annotation/Design – Edit Batch Parameters Parameter Window] or vice versa.

The submenu call [Annotation/Design – Edit Parameters Standard Windows] allows manually changes or calculation of the acquisition parameters peak name, batch parameter, comment, lens mode, analyser mode, pass energy, x position, y position, dwell time and number of accumulations of standard windows. If the start energy, end energy or step width are modified then a new spectrum by using an interpolation routine are generated.

[Annotation/Design – Edit Batch Parameters 3D Window] and [Annotation/Design – Edit Batch Parameters Parameter Window] allows the manual changes or calculation of the batch parameters of the activated 3D or parameter window. The option 'Setting: All 3D Windows' transfers the modifications to all other 3D or parameter windows.

For the parameter plot the parameter values are always arranged from the left to the right with rising values. The parameter steps are equidistant if the parameter values are no numbers. The option 'Text' must be selected in that case.

The selection of the items can be carried out by clicking with the left mouse button or using eight special options:

1. All windows,
2. no window,
3. every 2nd window,
4. every 3rd window,
5. every 4th window,
6. every 5th window,
7. every n -th window (n can be defined by the user),
8. every window with a larger χ^2 * than a defined value,
9. every windows with the same defined X position,
10. every windows with the same defined Y position,
11. all items of a column.

The selection procedure starts from the first selected item.

The changed parameter values may be tested with . The option allows the sorting of the displayed curves with respect to the parameter values. leaves this sub-

programme without changes and **OK** accepts the new values of all selected windows. External data for using as parameter names can be transferred to the selected edit fields with the copy function of the external programme (e.g. Origin, Word or Editor) and **Insert**. **Undo** writes the primary values in the selected fields. The function **Fill with** opens an additional dialogue and allows the extensive manipulation of the data using thirteen options (see Fig. 43). The first and last selected values can be defined freely. A defined value (OP) can be used for different mathematically operations. The fill options for the marked fields are:

1. First item,
2. last item,
3. equidistant steps,
4. item+OP,
5. item-OP,
6. item*OP,
7. item/OP,
8. sin(item) (RAD),
9. cos(item) (RAD),
10. ln(item),
11. e^(item),
12. item*e^OP,
13. item^OP,
14. Int(item),
15. Round (Item; x), (x - number of decimal places, variable).

If the x or y positions or the batch parameters were changed or selected then the programme-internal peak names can be changed optionally (see 3.2.24).

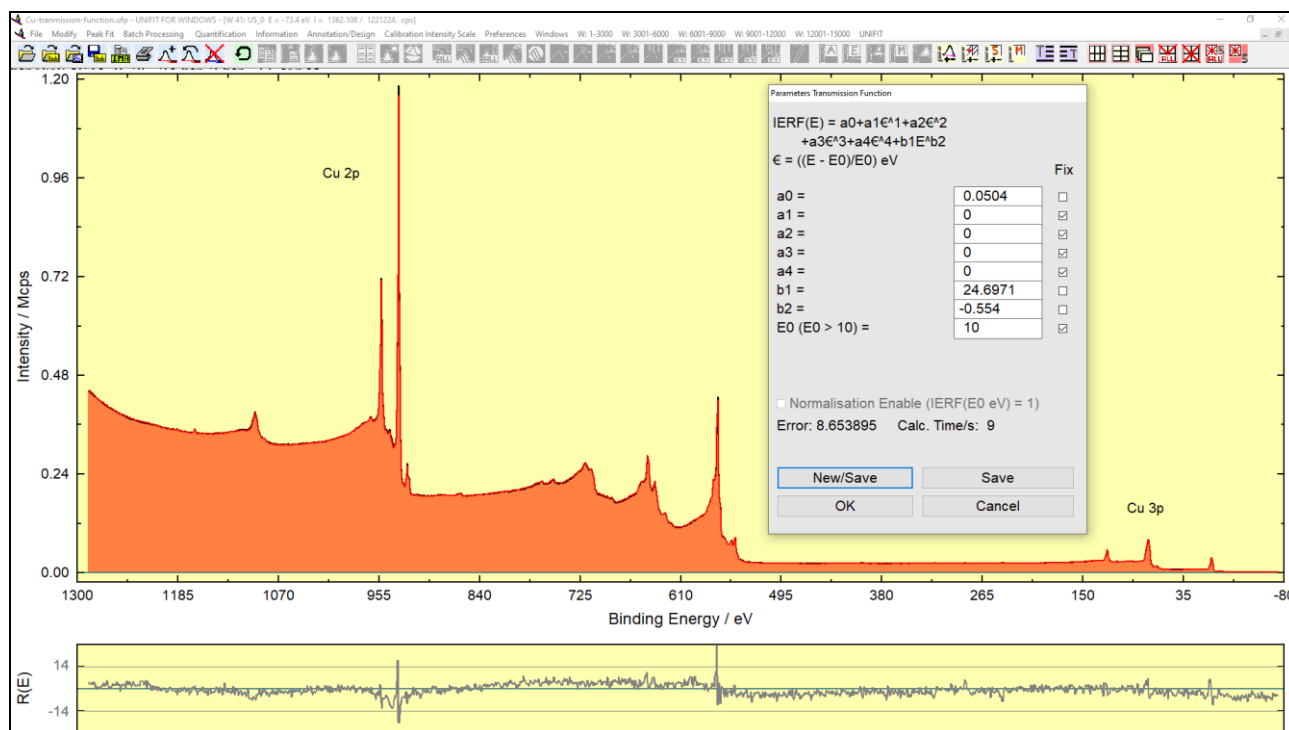



Fig. 44. Screen shot: Measured survey spectrum (black) and reference spectrum (red) of Cu, dialogue box for the input of the starting parameter for fitting by variation of $T(E)$, project: Unifit_2023_User_Files\examples\XPS\Cu_transmission_function.ufp

3.8.14 Marker Lines

 The menu point ‚Marker Lines’ supports the additional display of up to fifteen lines. Five line types are available. The line form, line strength and colour can be defined in [Preferences - Display - Axis/Lines/Text Display]. A movement marker can be activated by pressing the shift key and moving the mouse or with the pop-up menu. With the help of this marker the lines can be positioned by the mouse. Inside the marker the number of the marker line is displayed.

3.9 Calibration Intensity Scale

This sub-routine enables the user to determine the transmission function of the spectrometer in two different ways [19]. The resulting functions can be saved, printed, and applied in the concentration analysis routine. Examples for Au, Ag and Cu recorded with the spectrometer ESCALAB220iXL for AlK α -standard excitation, 50 eV pass energy and XL-Lens are saved under:

Unifit_2023_User_Files\examples\XPS\Calibration_Intensity_Au.ufp

Unifit_2023_User_Files\examples\XPS\Calibration_Intensity_Ag.ufp

Unifit_2023_User_Files\examples\XPS\Calibration_Intensity_Cu.ufp.

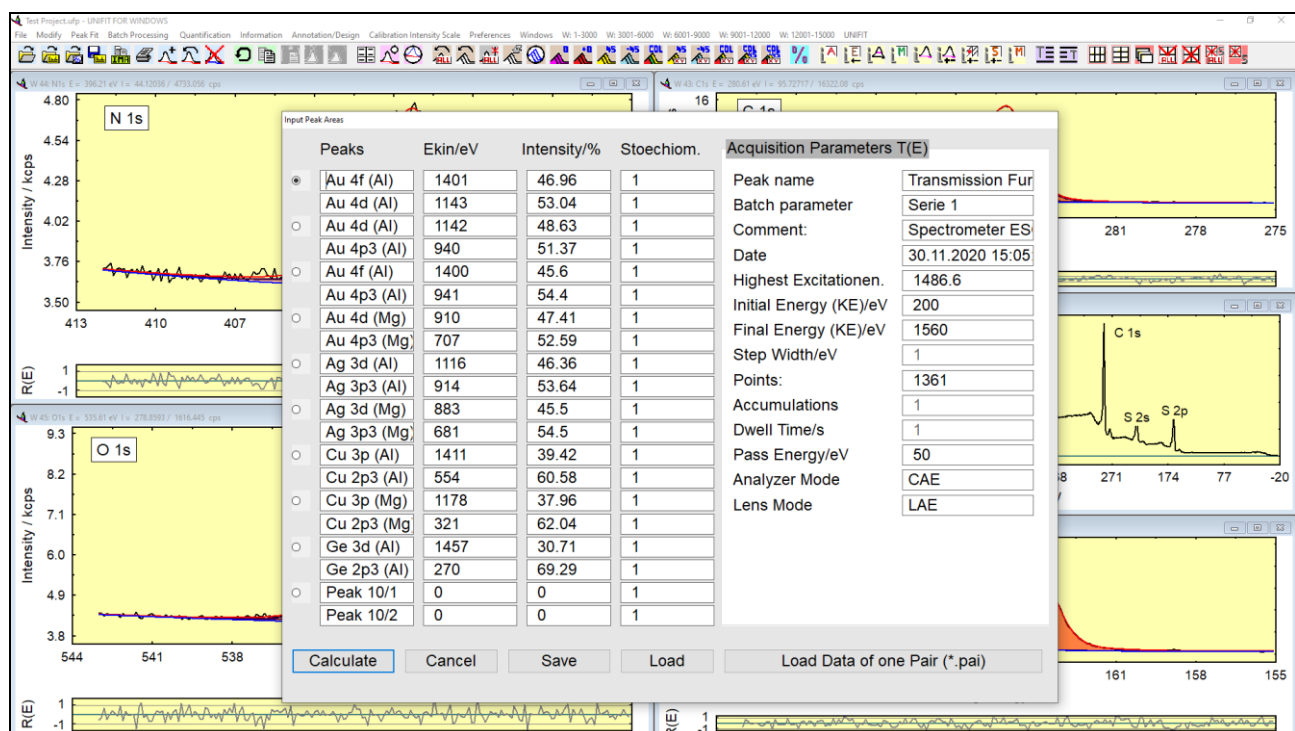


Fig. 45. Screen shot: Dialogue ‘Calculation Transmission Function using Peak Pairs’, input data for the estimation of the transmission function $T(E)$ using reference-peak pairs, example IL C₇H₁₃F₆N₃O₄S₂

3.9.1 Load Reference Spectrum

[Calibration Intensity Scale - Load Reference Spectrum] is one way to determine the transmission function $T(E)$. To use this part of the programme, a survey spectra of Au, Ag and Cu must be measured first using a defined format:

Excitation energy: AlK α (1486.6 eV), 15 kV, 20 mA or corresponding settings of mono source

Pass energy: arbitrary, >20 eV

Step width: 1eV

Start energy (E_{Kin}): 1560 eV

End energy (E_{Kin}): 200 eV

Dwell time: arbitrary, 0.3 s, recommended

Accumulations: arbitrary, 3, recommended

Analysing mode: FAT

Exact energetic calibration of the spectrometer is presupposed.

After the measured survey spectra of Au, Ag, or Cu were read into UNIFIT, the corresponding “true” reference spectra can be added by [Calibration Intensity Scale - Load Reference Spectrum - Au twin, Ag twin, Cu twin, Au mono, Ag mono, Cu mono].

3.9.1.1 Au Twin

When selecting this option, the gold spectra will be loaded as reference. A new window opens automatically allowing to choose the start parameter for the fit of the transmission function $T(E)$ (Fig. 44). Each parameter may be fixed. The fit process is initiated by clicking **OK**, while **Save** will store the achieved transmission function. Press **New/Save** to redraw the function with modified and saved parameters, and **Cancel** to leave this menu. “Normalization enable” normalizes the function $T(E)$ at E_0 (recommended $E_0 = 1000$ eV) to the intensity 1. This should only be activated after reaching a good fit. The normalization is only available if all other parameters are fixed. For the fit of the survey spectra, even some thousand iteration steps may be needed.

Following the calculation of the transmission function for Au, Ag, and Cu, these three functions can be added to each other by clicking [Modify - Spectrum Operation - Addition...] and multiplied by 0.33 by [Modify - Spectrum Manipulation - Correct Intensity]. This procedure will result in a standardized $T(E)$ -function. Further optimization of the function can be performed using [Calibrate Intensity Scale – Fit/Show Parameter Transmission Function].

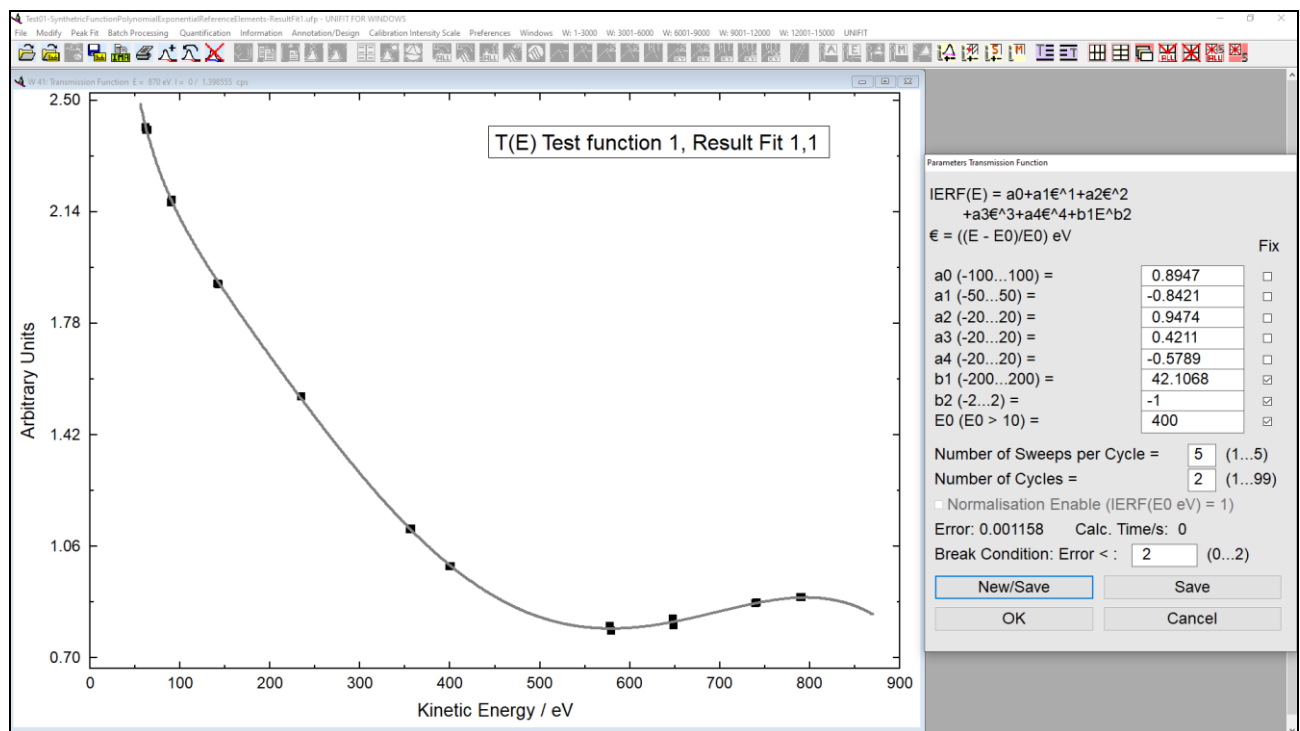


Fig. 46. After pressing **OK** and the selection of the transmission function in the dialogue ‘Select Spectra’ the normalized input data and the $T(E)$ function are plotted in one window. The dialogue ‘Parameters Transmission Function’ appears for the definition of the fit condition.

3.9.1.2 Ag Twin

By making this selection, the reference spectrum of Ag excited with Al twin is loaded.

3.9.1.3 Cu Twin

By making this selection, the reference spectrum of Cu excited with Al twin is loaded.

3.9.1.4 Au Mono

By making this selection, the reference spectrum of Au excited with Al mono is loaded.

3.9.1.5 Ag Mono

By making this selection, the reference spectrum of Ag excited with Al mono is loaded.

3.9.1.6 Cu Mono

By making this selection, the reference spectrum of Cu excited with Al mono is loaded.

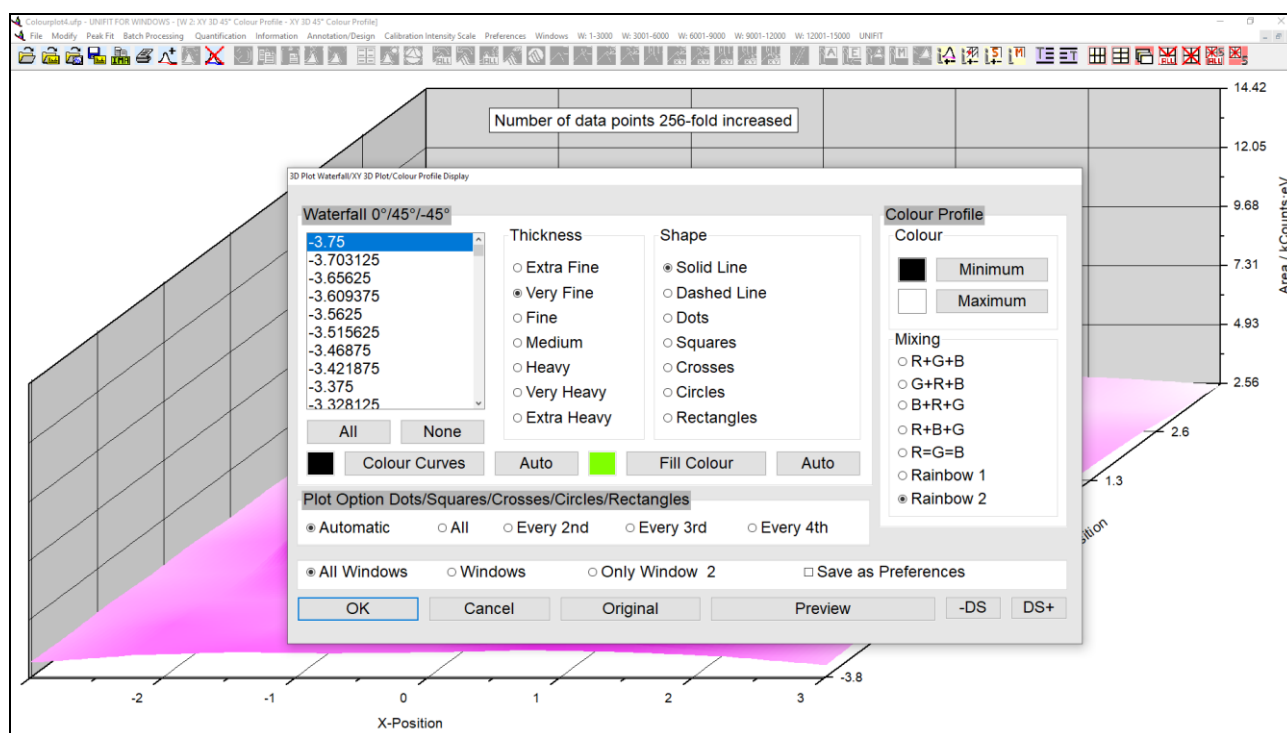


Fig. 47. Screen shot: Dialogue '3D Plot Waterfall/XY 3D Plot/Colour Profile Display' for setting the shape, thickness, and colour and fill colour of the 0°, 45° und -45° as well as the minimum and maximum colour and mixing mode of the colour profile

3.9.2 Fit/Show Parameters Transmission Function

After loading the transmission function $T(E)$ with [Calibrate Intensity Scale - Plot Transmission Function] (Unifit_2023_User_Files\XPS-transfct*.trm), the parameters of $T(E)$ can be displayed

here. If the arithmetic average $T_M(E) = \frac{\sum_{i=1}^n T_i(E)}{n}$ is used, then the parameters can be fitted again.

The dialogue is also displayed using the calculation with peak pairs. All eight fit parameters can be fixed or fitted. **Save** stores (*.trm) the transmission function. **Cancel** closes this menu. 'Normalization enable' normalizes the intensity of the function $T(E)$ at $E = E_0/eV$ to unity. This

option is only available if all other parameters are fixed. The more parameters are left variable the longer the calculation of $T(E)$ will take.

3.9.3 Calculate Transmission Function using Peak Pairs

The **second** way to evaluate the transmission function $T(E)$ can be performed here. As described in 2.6.2 the relative areas (given in percentage) of selected calibration lines are used. The input data are:

1. Peak name (e.g. Au 4f, Cu 2p3)
2. Kinetic energy (E_{kin}/eV)
3. Intensity (in %, the sum of the intensities of one pair must be 100%)
4. Stoichiometry (the number of atoms of the elements in the molecule, e.g. the reference element Au: pair Au 4f and Au 4d: Au 4f = 1 and Au 4d = 1, the reference compound IL $C_7H_{13}F_6N_3O_4S_2$: pair C 1s and F 1s: C 1s = 7, F 1s = 6, pair F 1s and N 1s: F 1s = 6, N 1s = 3, ...)

It is not necessary to enter all calibration lines. Additionally, the acquisition parameters of the measurements have to be defined. The number of accumulations, the dwell time and the step width is settled to one and fixed. The first call shows the data of an example of using the reference elements Au, Ag and Cu. The spectrometer was an ESCALAB 220 iXL. Figure 45 shows the input dialogue using measurements of a IL reference compound.

Press to leave this menu. will store all data of the dialogue and reads saved data (*.dat). The command loads the saved *.pai-files. The pai-files includes the names, energies (KE) and the intensity ratios of two XPS peaks (one pair, see 3.6.1). will open the dialogue 'Select Spectra' and with selection of the spectrum 'Transmission Function' and a new window plots the normalized input data and the $T(E)$ function. Additional, the input dialogue for the definition of the eight $T(E)$ parameters appears. Each parameter can be fixed or adjusted during the fit. The 'Number of Sweeps per Cycle' defines the accuracy of the parameters and the 'Number of Cycles' gives the number of iterations. Additionally, a break condition of the calculated error can be defined (see Fig. 46). saves the redefined parameters and the plot of the $T(E)$ function is refreshed. Press to start the fit of $T(E)$. During the fit a progress bar, the error, the number of the cycle and the number of the sweep of the current cycle are displayed.

3.9.4 Display Peak Pairs of the Transmission Function

After reloading of a UNIFIT project including a calculation of $T(E)$ using reference-peak pairs the input data may be displayed. A changing of the input parameters is not possible.

3.9.5 Plot Transmission function

Calculated and saved transmission functions (*.trm) can be displayed and compared here (Unifit_2023_User_Files\XPS-transfct*.trm). The excitation energy, start- and end-energy and the information of the spectrometer setting can be changed. The number of accumulations, the dwell time and step width is fixed to one. To show the individual parameters of the transmission function use [Calibration Intensity Scale – Fit/Show Parameter Transmission Function].

3.10 Preferences

With the sub-menu [Preferences] the user is able to define individual settings for working with UNIFIT. Not only graphical elements of the programme, but also mathematical methods of the fit routine can be influenced here. It is recommended to change the preferences immediately after initiating the programme, but it is also possible to do this during the processing. Changes in [Preferences – Fit Procedure] and [Preferences – Fit Parameters/XAS-Background Parameters],

however, have no effect on open windows. This way it is possible to simulate one and the same spectrum once with product and once with convoluted functions in two different windows and to compare the results. In the same way results with absolute and relative parameters can be obtained simultaneously.

The sub-points [File - Original/Accept Preferences] and [Batch Processing – Original/Accept Preferences all Windows] assign changed presetting to the active window or to all open windows.

The preferences will be saved as Unifit_2023_User_Files\presetting\presetting.set when quitting the programme and loaded automatically during re-start.

3.10.1 Load Preferences...

With [Preferences – Load Preferences...] one of the saved user defined preferences (*.SET) can be selected from a list box and loaded into the programme. Two preference files are delivered by the UNIFIT developer. The first recommended preference (Presetting_Image_Export.set) should be used if the operator wants to create presentations directly with UNIFIT. The second preferred presetting (Presetting_Monitor_Working.set) should be taken especially for monitor working. If a preference files is loaded and spectra windows are already opened the setting of the programme parameters (3.10.1), the toolbar (3.10.4), the language (3.10.8), the Y-axis (3.10.18), the X-axis (0) and the number of hidden standard windows (3.11.8) will not be changed. If a project is loaded the spectra windows get all settings saved in that project.

3.10.2 Save Presetting/Setting of the Active Window...

This menu point enables to save the preferences of the currently activated window in 'Documents\Unifit_2023_User_Files\presetting*.set'.

3.10.3 Setting the Programme Parameters...

Clicking [Preferences – Setting of Programme Parameters...] displays the dialogue for the definition of the maximal number of the seven general programme parameters:

- a) Peak-fit components (1...30),
- b) XAS background steps as well as XPS background functions (3...9),
- c) presentable curves inside the 'Plot 3D Waterfall Presentations' (100...300),
- d) presentable fitted spectra inside the 'Plot 3D Waterfall Plus Presentation' (7...21),
- e) presentable curves inside the 'Parameter Plot' (10...30),
- f) presentable parameter steps inside the 'Parameter Plot_' (30...50,000)
- g) number of the first standard window (1...101).

This menu point permits the optimal adaption of the programme UNIFIT to the power of the used computer system. The maximal number of the seven general programme parameters can be changed only if no spectrum window was opened, yet. If the operator has planned to create ten parameter plot or 3D windows, the number of the first standard window should be eleven. In order to optimise the usage of the main memory the parameter plot windows or the 3D presentation windows can be created using the windows with the numbers 1 to 100 only. and change only the first six parameters (a - f).

3.10.4 Toolbar

Clicking [Preferences – Toolbar] displays a toolbar additional to the pull-down menu. In general, the function of the icons is identically with the menu options. In case of differences it is mentioned in the manual (see the corresponding paragraph).

3.10.5 Modify Toolbar

With [Modify Toolbar] the user can create an individual toolbar. The user can choose the icons shown in the toolbar. The size of the icons is variable.

3.10.6 Text Dialogues

With [Text Dialogues] the user can choose the form, size and colour of the dialogue text.

3.10.7 Text Table Export

UNIFIT 2023 permits the export of the quantification tables as image file. With this menu point the text font and size can be changed. The maximum size is 14.

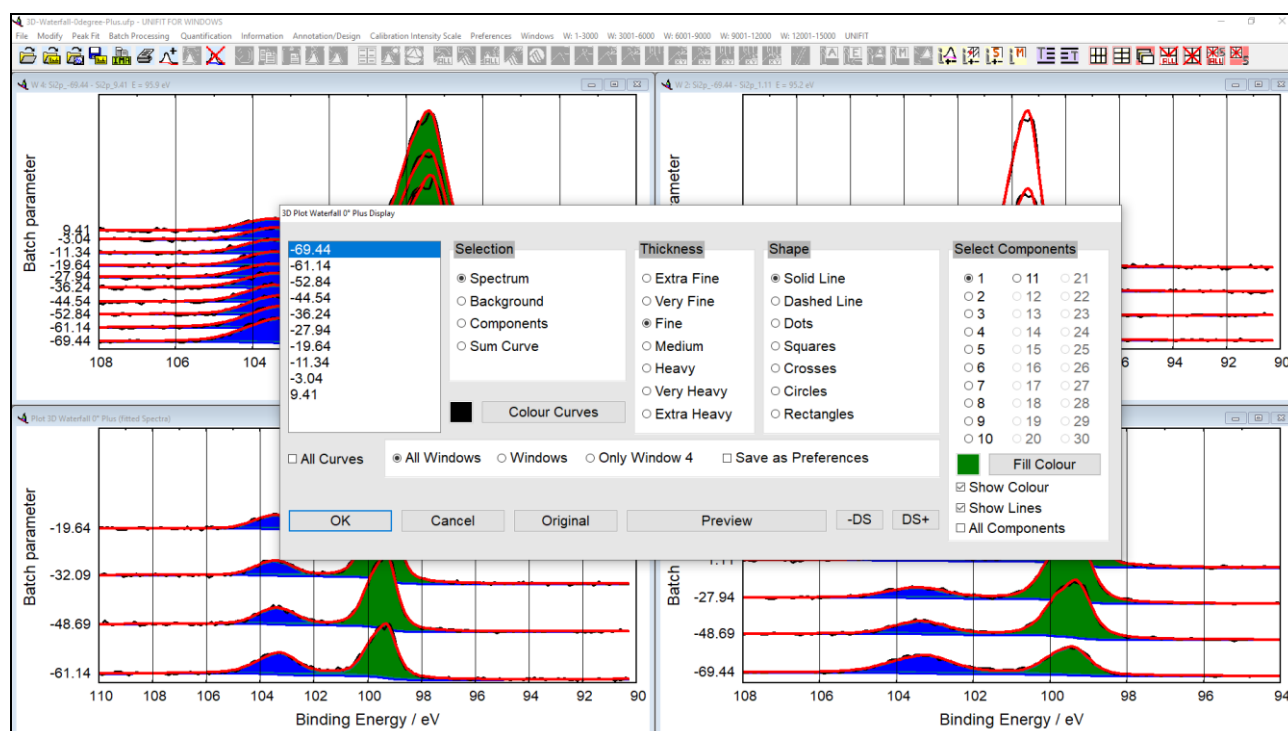


Fig. 48. Screen shot: Dialogue for setting the shape, thickness, and colour and fill colour of the components of fitted spectra plotted using the '3D Plot Waterfall Plus 0° Display'

3.10.8 Language

This menu allows the choice of the language of the programme design including printing and data export. The information is stored in `*\Unifit2023\language\language.set`.

3.10.8.1 German

With the selection of [Preferences - Language – German] the complete programme design including printing and data export may be done in German language.

3.10.8.2 English

With the selection of [Preferences - Language – English] the complete programme design including printing and data export may be done in English language.

3.10.9 Decimal Character Display/Printer/Graphic Export

This menu allows the choice of the decimal character (point or comma) for the display presentation of the spectra, for the printing out using UNIFIT and for the graphic export (window presentations and tables).

3.10.10 Save project automatically

With this menu point the automatic saving of backups of the projects can be activated and deactivated. The storage time is variable.

3.10.11 Open Project with Showing of the Quantification and Film Thickness Table

This menu point defines the loading of projects with or without the showing of saved quantification and film thickness tables.

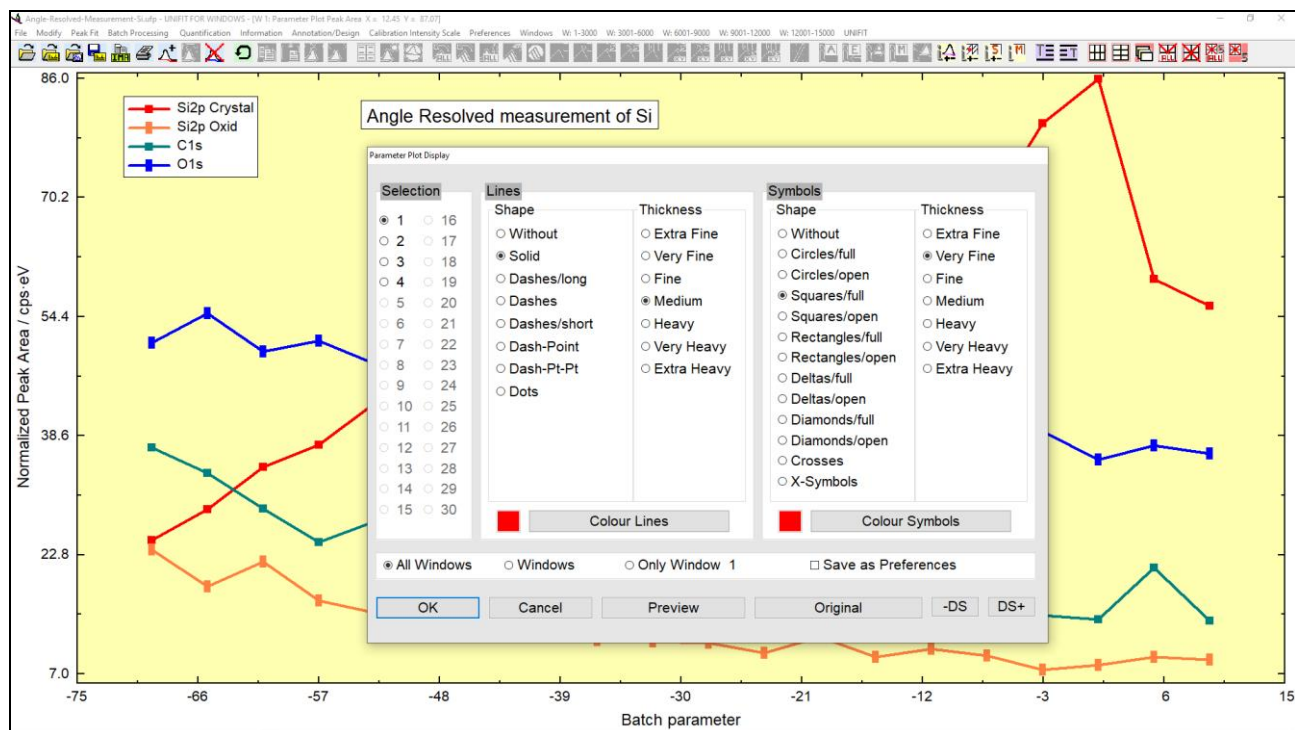


Fig. 49. Screen shot: Dialogue for setting the colour, shape and thickness of the parameter plot displayed on the screen

3.10.12 Export Data

This option was installed to adapt the UNIFIT data export format to requirements of other programmes.

3.10.12.1 Decimal Character

'Point' or 'Comma' can be selected for decimal character. A tick marks the present setting.

3.10.12.2 Delimitation

'Semicolon', 'Comma', 'Tabulator', or 'Space' can be selected for column delimiter. A tick marks the present setting.

3.10.13 Import

This point allows the control of input options of measurement data.

3.10.13.1 VAMAS (*.VMS;*.NPL)

Different options for the input of data using the VAMAS format are available:

1. Reading of the intensities.
2. Reading of the 1. corresponding variables.
3. Formation of sum spectra with all blocks of each spectral region.
4. Normalization of the data by the first corresponding variables.

3.10.13.2 ScientaSES-Spectra (*.TXT)

Different options for the input of data using the ScientaSES format are available:

1. Formation the sum spectrum of all slices.
2. Each slice gives a separate spectrum.

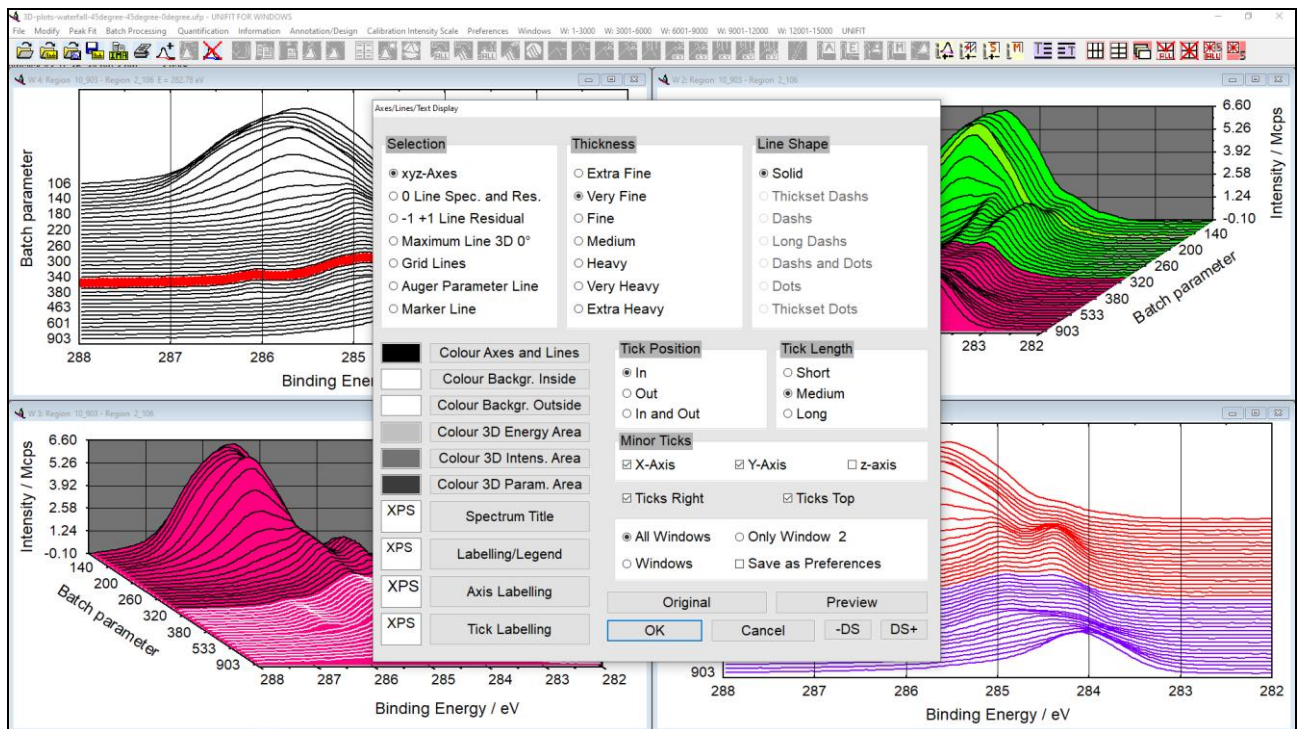


Fig. 50. Screen shot: Dialogue for setting the shape, thickness and colour of all displayed axes, lines and characters

3.10.13.3 SPECS Prodigy (*.XY)

Different options for the input of data using the SPECS Prodigy format are available. Reading options are:

1. Intensities,
2. Rin current.
3. TEY data.
4. Mirror current.

Operation options during the reading procedure are:

1. Create a sum curve of separate stored scans
2. Normalization of intensities with the ring current.

3.10.14 Resolution Image Export/Copy

The export/copy resolution of the presentations of the active window can be selected stepwise (six levels: monitor resolution, 400, 600, 800, 1000, 1200 dpi). The maximum resolution can be used with computers having a main memory of 1 GByte or more.

3.10.15 Points to Average

With [Preferences – Points to Average] a dialogue box will be displayed showing the current value for the *number of points to average* over for:

1. Calculation of start and end points for background determination in [Modify – Calculate Background] (see 3.3.5).
2. Calculation of n^{th} derivative of the spectrum in [Modify – Differentiation] (see 3.3.10),
3. Calculation of smoothed spectrum in [Modify – Smoothing] (see 3.3.14).
4. Normalization of the spectra [Modify – Normalization] (see 3.3.18)

An odd number between 1 and 19 can be selected and confirmed with (or the setting can be left unchanged with).

3.10.16 Threshold Multiplier of Spike Correction...

The operator can manually define the threshold multiplier (recommended value: 20) and the largest number of spikes (in %, recommended value: 5) in the spectra before a automatically spike correction is started (see 3.5.4). The theoretical basic is given in 2.9. Optionally the spectra modified using the Laplace operator can be displayed.

3.10.17 X-axis

This option allows the presentation of the spectra in two different energy scales.

3.10.17.1 XPS: Binding Energy/XAS: Photon Energy/AES: Kinetic Energy/RAMAN: Wavenumber

By choosing the option [Preferences - XPS: Binding Energy/XAS: Photon Energy/AES: Kinetic Energy] the XP spectra will be displayed with respect to the binding energy, the XA spectra with respect to the photon energy and the Auger electron spectra with respect to the kinetic energy. The current option is ticked.

3.10.17.2 XPS: Kinetic Energy/XAS: Photon Energy/AES: Kinetic Energy/RAMAN: Wavenumber

By choosing the option [Preferences - XPS: Kinetic Energy/XAS: Photon Energy/AES: Kinetic Energy] the XP spectra will be displayed with respect to the kinetic energy, the XA spectra with respect to the photon energy and the Auger electron spectra with respect to the kinetic energy. The current option is ticked.

3.10.18 Y-axis

This option allows the presentation of the spectra in two different intensity scales.

3.10.18.1 Counts

By choosing this option the intensities will be displayed in counts (true values). The current option will be ticked. Areas after background subtraction or peak fit intended for quantitative analysis are given in cps·eV independent of the Y-axis preferences.

3.10.18.2 Counts per Second

By choosing this option the intensities will be displayed in cps (true values divided by the number of scans and dwell time). The current option will be ticked. Areas after background subtraction or peak fit intended for quantitative analysis are given in cps·eV independent of the Y-axis preferences.

3.10.19 Display

Because the suitable monitor setting must not be suitable also for printing out (e.g. dark background) the setting of the monitor and printer was created separately. An individual setting can be also assigned to every window. While opening this dialogue the settings of the active window are indicated. The new settings can be saved as preferences if the check box 'Save as Preferences' is ticked.

3.10.19.1 Graphs Standard Window/Wagner Plot Display

With [Preferences – Display - Graphs Standard Window/Wagner Plot Display] the user is able to define the shape, thickness, colour of all displayed curves of the standard windows and Wagner plot. Additionally, the fill colour of the component curves may be defined. The fill colour of the 3D-plots may be selected, too (see Fig. 42). The dialogue can be opened using the pull down menu or by pressing the right mouse key if the mouse pointer is inside the coordinate system.

3.10.19.2 3D Plot Waterfall/XY 3D Plot/Colour Profile Display

This menu point permits the definition of the form, colour, and thickness and fill colour (Waterfall 45° and -45° (see Figure 47), XY 3D Plot 45° and -45°) for:

- a) all selected curves of the active window,
- b) all curves of the active window,
- c) all selected curves of all windows,
- d) all curves of all windows.

The following options are available for the '3D Colour Profile' and 'XY 3D Colour Profile':

A: Definition of the minimum and maximum colour as well as the superposition procedure of the colours,

1. R + G + B (768 colour steps)
2. G + R + B (768 colour steps)
3. B + R + G (768 colour steps)
4. R + B + G (768 colour steps)
5. R = G = B (256 brightness steps)

B: Minimum and maximum colour fixed (black and white):

6. Rainbow 1 (1536 colour steps)
7. Rainbow 2 (1792 colour steps).

confirms the settings and with the menu can be left without changing. allows a quick check of the new settings and goes back to the old settings. All settings can be defined for the activated window or all opened windows. The dialogue can be opened using the pull down menu or by pressing the right mouse key if the mouse pointer is inside the coordinate system.

3.10.19.3 3D Plot Waterfall 0° Plus Display

This menu point allows the separate definition of the form, colour, and thickness of fitted spectra (spectrum, sum curve, background function and component curves (see Figure 48)) for:

- a) all selected curves of the active window,
- b) all curves of the active window,

- c) all selected curves of all windows,
- d) all curves of all windows.

Additionally, the fill colour of each component curve can be defined separately. Optionally, all component curves can be plotted with or without lines and with and without fill colours. All component curves can be displayed with and without lines and fill colours. confirms the settings and with the menu can be left without changing. allows a quick check of the new settings and recreates the old settings. All settings can be defined for the activated window or all opened windows. Two to ten fitted spectra can be displayed. The dialogue can be opened using the pull down menu or by pressing the right mouse key if the mouse pointer is inside the coordinate system.

3.10.19.4 Parameter Plot Display

The original symbols and lines used for the parameter plot (see 3.5.7 and 0) may be changed with this menu point. The colour, shape and thickness of the curves may be varied (see Fig. 49). All settings can be defined for the activated window or all opened windows. The dialogue can be opened using the pull down menu or by pressing the right mouse key if the mouse pointer is inside the coordinate system.

3.10.19.5 Axes/Lines/Text Display

This menu item and the chapters 3.7.11, 0 and 3.10.19 are the central design tools to create presentations for exporting images via copy or export. Seven shapes and thicknesses and any colours for styling the lines are prepared (see Fig. 50). With [Preferences – Display - Axes/Lines/Text Display] the user is able to define the four different characters (spectrum title, spectrum labelling, axes labelling, tick labelling). The user may choose optionally three different tick lengths (short, medium, long) and three different tick positions (in, out, in & out). Additionally, to the major ticks minor ticks can be selected. Ticks on the right and top axis may also be shown. Two different colours inside and outside the coordinate system can be chosen. The choice is confirmed by , the dialogue can be left without changes by clicking . With the changes can be shown without saving and activates the previous settings. The dialogue can be opened using the pull down menu or by pressing the right mouse key if the mouse pointer is outside the coordinate system on the side without axis labelling.

3.10.20 Printer

With the dialogues in that menu point the user can define the presentation features of the printing out directly using UNIFIT. All dialogues are slightly different from comparable monitor settings. The new settings can be saved as preferences if the check box 'Save as Preferences' is ticked. This menu point is disabled if the pull down menu 3.10.21 'Monitor Setting ==> Printer Setting' is ticked. In this case, the printing out from UNIFIT is like the design of the monitor.

3.10.20.1 Graphs Standard Window/Wagner Plot Printer

[Preferences – Printer - Graphs Standard Windows/Wagner Plot Printer] allows the configuration of the curves for printout directly from UNIFIT. The menu handling is nearly the same as in chapter 3.10.19.1. with exception of the button . This button transfers the monitor setting to the printer setting.

3.10.20.2 3D Plot Waterfall/XY 3D Plot/Colour Profile Printer

[Preferences – Printer - 3D Plot Waterfall/XY 3D Plot/Colour Profile Printer] allows the configuration of the curves for printout directly from UNIFIT. The menu handling is nearly the

same as in chapter 3.10.19. with exception of the button **Monitor Setting >>> Printer Setting**. This button transfers the monitor setting to the printer setting.

3.10.20.3 3D Plot Waterfall 0° Plus Printer

[Preferences – Printer - 3D Plot Waterfall 0° Plus Printer] allows the configuration of 21 fitted spectra for printout directly from UNIFIT. The menu handling is nearly the same as in chapter 3.10.18.1 with exception of the button **Monitor Setting >>> Printer Setting**. This button transfers the monitor setting to the printer setting.

3.10.20.4 Parameter Plot Printer

[Preferences – Printer - Parameter Plot Printer] allows the configuration of the curves for printout directly from UNIFIT. The menu handling is nearly the same as in chapter 3.10.19.4 with exception of the button **Monitor Setting >>> Printer Setting**. This button transfers the monitor setting to the printer setting.

3.10.20.5 Axes/Lines/Text Printer

[Preferences – Axis/Lines/Text Printer] allows the configuration of the curves for printout directly from UNIFIT. The menu handling is nearly the same as in chapter 3.10.19.5 with exception of the button **Monitor Setting >>> Printer Setting**. This button transfers the monitor setting to the printer setting.

Note: A dark monitor background setting is comfortable for monitor working, but a dark printing background is not suitable in many cases!

3.10.21 Display Setting ==> Printer Setting

The activation of this menu point (ticked) puts the design setting of the printing out directly from UNIFIT like the monitor setting of the selected windows. The menu point 3.10.20 will be disabled.

3.10.22 Presetting Printer

This sub-menu offers five options for the definition of the printing out of the spectra:

- Window plus Acquisition Parameters
- Wagner-Pöot Window plus Auger Parameters
- Window plus Fit Parameters
- Window plus Quantification Table
- Two Windows on One Page or On the Half Page.

The quantification table (if available) is printed out after the printing of the windows.

3.10.23 Create and Save Unifit Project Backup Files

The activation of this menu point (ticked) create and save backup files of the Unifit projects. This menu point should be deactivated using more than 1000 standard windows.

3.10.24 Satellite Selection

The option serves for a detailed definition of different energy shifts and intensity ratios for X-ray satellites excited with different sources. Functions can be modelled. The parameters of the satellite curves are saved quitting the programme.

3.10.24.1 Al...

This menu point allows the definition of the intensity and energy parameters of the AlK α excitation. The parameters of the satellite curves are saved leaving the programme.

3.10.24.2 Mg...

This menu point allows the definition of the intensity and energy parameters of the MgK α excitation.

3.10.24.3 Source3...

This menu point allows the definition of the intensity and energy parameters of a special source. The source name and the source energy can be defined by the user.

3.10.24.4 Source4...

This menu point allows the definition of the intensity and energy parameters of a special source. The source name and the source energy can be defined by the user.

3.10.25 Load/Define Transmission Function

This option allows the loading and new definition of transmission functions (IERF). The analytical form to describe the transmission function is given in 2.6.

3.10.26 Fit Procedure

Three different mathematical routines for simulation of the experimental spectra are included in the programme code. The selected option will be ticked. The fit procedure affected closed windows or opened windows without peak fit.

3.10.26.1 Product

[Preferences – Fit Procedure - Product] chooses the product model of Lorentzian and Gaussian functions.

3.10.26.2 Sum

[Preferences – Fit Procedure - Sum] chooses the sum model of Lorentzian and Gaussian functions.

3.10.26.3 Convolution

[Preferences – Fit Procedure - Convolution] chooses the Voigt profile of Lorentzian and Gaussian functions.

Note: A change of the fit procedure does not affect windows already fitted.

The following example demonstrates how to use the different fit procedures.

Example 14: The S 2p signal of the ESCA3 file *example.tap* in the folder *Unifit_2023_User_Files\examples\XPS\sulphur_study* has to be fitted with a product function in window 21 and with convolution in window 22. C 1s, displayed in window 20 serves as charge correction to the reference value of 285.0 eV. Because of non-monochromatized excitation, a satellite subtraction is necessary. S 2p is described as doublet with an intensity ratio $I_{S2p1/2} : I_{S2p3/2} = 1 : 2$, an energetic separation of 1.2 eV and the same line shape and width for both peaks.

1. Start UNIFIT,
2. select [Preferences – Fit Procedure – Product] ('Product' will be ticked),

3. select [Preferences – Fit Parameters/XAS-Background Parameters/XPS-Background Parameters (INHOM) – Absolute] ('Absolute' will be ticked),
4. select [Preferences - Tougaard-Background Calculation - Homogeneous Samples],
5. select [Preferences - Y-axis - Counts per Second],
6. select [Windows - Hide Standard Windows], the dialogue 'Hide Standard Widows' will be opened, choose 'Show all Standard Windows' and press ,
7. be sure that the number of the first standard window is 20 and the maimal numer of peak-fit components is large than two with [Preferences – Setting of Programme Parameters...],
8. set number of points to average over in [Preferences – Points to average] to 3,
9. select **Unifit_2023_User_Files\examples\XPS\sulphur_study\example.tap** with [File – Open Spectra – XPS - ESCA3 (*.TAP)] and confirm with ,
10. select C 1s and S 2p in the dialogue box 'Select Spectra' and display them with ,
11. switch window C 1s active and determine the binding energy of the intensity maximum with [Information – Min/Max] (286.7 eV),
12. shift energetic scales by 1.7 eV with [Batch Processing – Charge Correction all Windows],
13. switch window S 2p active,
14. by selecting [Modify – Subtract Satellite], the excitation satellites will be displayed; subtract them with ,
15. select [Peak Fit – Fit Background XPS (HOM)] and set:

| | | |
|---------------------------|------|---------|
| a-Parameter | 600 | unfixed |
| b-Parameter | 1 | unfixed |
| c-Parameter | 0 | fixed |
| d-Parameter | 0 | fixed |
| Shirley Factor | 0 | fixed |
| B-Parameter | 5732 | unfixed |
| C-Parameter | 1643 | unfixed |
| C'-Parameter | 0 | fixed |
| D-Parameter | 0 | fixed |
| T ₀ -Parameter | 0 | fixed |

 (i.e. the background will be calculated and fitted with constant, linear, and Tougaard parts and the so-called 'Universal Inelastic Electron Scattering Cross-Section'), display the background with and confirm the settings with ,
16. with [Peak Fit – Manual Input of Start Parameters – Doublet Peaks...], set 'Doublet' to 2 and confirm with ,
17. the dialogue box 'Min/Max Parameters Doublet' appears – confirm values with ,
18. the dialogue 'Fit Parameters Doublet/Product/Absolute' will be opened – fill it with the following settings (variable = no tick; fixed = tick)
 - a) by entering the values through the keyboard or
 - b) by pressing Alt-Y or left mouse button to accept the position of the mouse pointer in the display for energy (Position) and intensity (Peak height) start parameters of the S 2p_{3/2} peak. Energetic distance (1.2 eV) and intensity ratio (2:1) between doublet components are saved in a data base and will be used for calculation of energy and intensity start parameters of the S 2p_{1/2} peak automatically,

| | | Doublet1 | Fix | Doublet2 | Fix |
|-------------|-------|----------|-----|----------|-----|
| Peak height | Peak1 | 3000 | | 500 | |
| | Peak2 | 1500 | X | 250 | X |
| L-G Mixing | Peak1 | 0.5 | | 0.5 | |
| | Peak2 | 0.5 | X | 0.5 | X |
| Position/eV | Peak1 | 164 | | 167.8 | |

| | | | | | |
|-----------|-------|-------|---|-----|---|
| | Peak2 | 165.2 | X | 169 | X |
| FWHM/eV | Peak1 | 2 | | 2 | |
| | Peak2 | 2 | X | 2 | X |
| Asymmetry | Peak1 | 0 | X | 0 | X |
| | Peak2 | 0 | X | 0 | X |

confirm with (the start parameters are saved in **Unifit_2023_User_Files\examples\XPS\sulphur_study\BE_start.PAR**, too),

19. [Peak Fit – Iteration] calculates components, sum curve and background with the setting given in 16. The dialogue box ‘Input Number of Iterations’ appears. Set the number of iterations per cycle to 22 and the number of cycles to 2 and confirm with .
20. ‘Stop Iterations’ shows the end of the fit procedure. Click for displaying the results,
21. the parameters for later as **TEST.PAR** in **Documents\Unifit_2023_User_Files\examples\XPS**, leave the dialogue box with and the peak fit (fitting procedure with product function is complete),
22. for comparison to the second fit procedure select [Preferences – Fit Procedure – Convolution],
23. select S 2p in [File – Select Spectra] and confirm with : S 2p is displayed in window 3,
24. subtract satellite (see 3.3.6.2),
25. load **Documents\Unifit_2023_User_Files\examples\XPS\TEST.PAR** with [Peak Fit – Load Start Parameters] and confirm with .
26. confirm parameters in ‘Fit Background XPS’ with .
27. change the max value of the GP width for both doublets in ‘Min/Max Fit Parameters Doublet’ from 1 to 5 and confirm with .
28. confirm [Fit Parameters Doublet/Convolution/Absolute] with .
29. define with ‘Input Number of Iterations’ the numbers as 22 and 2 and confirm with , the iteration starts,
30. after 44 iteration cycles the fit procedure in ‘Stop Iterations’,
31. print both results with [File – Print] by selecting the S 2p windows in the dialogue box ‘Select Window to Print’ and starting the print with .

3.10.27 Fit Parameters/XAS Background Parameters/XPS Background Parameters (INHOM)

This option allows the use of absolute or relative fit parameters for the peak fit, the XAS step background fit and the fit background XPS (INHOM) (parameters of the Tougaard background for inhomogeneous samples). Both options use also different fit routines. Therefore, the convergence behaviour does not have to be the same. The currently active option will be ticked.

3.10.27.1 Absolute

[Preferences – Fit Parameters/XAS Background Parameters/XPS Background Parameters (INHOM) - Absolute] activates the using of absolute parameters for the peak fit, the XAS step background and the XPS background for inhomogeneous samples.

3.10.27.2 Relative

[Preferences – Fit Parameters Fit Parameters/XAS Background Parameters/XPS Background Parameters (INHOM) - Relative] activates the using of relative fit parameters for the peak fit, the XAS step background and the XPS background for inhomogeneous samples.

Note: A change of this fit parameter option does not affect open windows already fitted before.

3.10.28 Tougaard-Background Calculation

The option allows the changing of the calculation of the Tougaard background.

3.10.28.1 Homogeneous Samples

The option [Preferences – Tougaard-Background Calculation - Homogeneous Samples] should be activated in case of XPS measurements of homogeneous samples. One Tougaard background is calculated for the complete spectrum (see 2.1.1.5 and 2.1.1.7.1).

3.10.28.2 Inhomogeneous Samples

The option [Preferences – Tougaard-Background Calculation - Inhomogeneous Samples] should be activated in case of XPS measurements of laterally inhomogeneous samples. Different Tougaard-background functions may be defined and calculated iteratively by using the peak-fit component. The number and the sequence of Tougaard-background functions and the number of peak-fit components have to be the same (see 2.1.1.7.2).

3.10.29 Batch Processing

This option allows modifying the batch processing routine.

3.10.29.1 Load Original Spectra

If this option [Preferences - Load Original Spectra] is ticked (activated), then the original spectrum of each standard window is loaded before the batch processing steps are carried out. If a manually or an automatically spike correction is carried out before, this option has to be deactivated.

3.10.29.2 Input Number of Iterations

With the setting [Preferences – Batch Processing – Input Number of Iterations] the user can define the number of iterations and cycles of the peak fit during batch processing.

3.10.30 Calculation of Errors

This menu point defines the procedure of the calculation of the fit parameters. The calculation routines are different for both possibilities: 'Iterative' or 'Matrix Inversion'. Therefore, the results of calculation of these two options must not be the same. The currently active option will be ticked.

3.10.30.1 Iterative

[Preferences – Calculation of Errors - Iterative] selects the iterative method for the calculation of the fit-parameter errors.

3.10.30.2 Matrix Inversion

[Preferences – Calculation of Errors – Matrix Inversion] selects the procedure 'Matrix Inversion' for the calculation of the fit-parameter errors.

3.10.31 Fit-Parameter Errors

3.10.31.1 Absolute

With that menu point the fit-parameter errors will be shown using absolute values. The currently active option will be ticked.

3.10.31.2 Relative

With that menu point, the fit-parameter errors will be shown using relative values. The currently active option will be ticked.

3.11 Windows

This submenu contains options to rearrange the windows. Additionally, the windows can be activated directly.

3.11.1 Side by Side



[Windows - Side by Side] arranges all open windows side by side on the whole area of the parent window 'Unifit for Windows'. The windows are not sorted by the window numbers.

3.11.2 On Top of Each Other



[Windows - On Top of Each Other] arranges all open windows on top of each other on the whole area of the parent window 'Unifit for Windows'. The windows are not sorted by the window numbers.

3.11.3 Cascade



[Windows - Cascade] arranges the windows as cascade using increasing window numbers. The number of lowermost window is one.

3.11.4 Automatic Resize Deactivated

[Windows - Automatic Resize Deactivated] deactivates the automatic resize function after a new arrangement of the windows with the functions 3.11.1, 3.11.2 and 3.11.3.

3.11.5 Automatic Resize Image Windows Deactivated

[Windows - Automatic Resize Image Window Deactivated] deactivates the automatic resize function after a new arrangement of the image windows with the functions 3.11.1, 3.11.2 and 3.11.3.

3.11.6 Previous



[Windows - Previous] activates the previous window. The previous window does not necessarily have a number one smaller than the active one.

3.11.7 Next



[Windows - Next] activates the next window. The next window is not necessary the window with a number one higher as the active one.

3.11.8 Hide/Show Standard Windows



With [Windows - Hide/Show Standard Windows] the number of visible or hidden standard windows can be defined. These programme option allows the processing of large number of spectra (e.g. larger than 400). The processing time will be strongly reduced and the handling of the windows may be optimized by hiding of a well defined number of standard windows.

3.11.9 Hide/Show Standard Windows (manual)



With [Windows - Hide/Show Standard Windows (manual)] the number of visible or hidden standard windows can be defined manually.

3.11.10 Size/Position



[Window - Size/Position] permits the manual setting of the size (height and width) and the position of the active window. X and Y length of the coordinate system of the active window can optionally also be assigned. The new window parameters can be transferred on all other opened windows.

3.11.11 Change Windows Numbers



[Windows - Change Windows Numbers] permits this exchange of the window numbers of two standard windows. This function allows the arrangement of the windows in the correct order for future parameter presentations.

3.11.12 Show Windows Video Sequence



[Windows - Show Windows Video Sequence] permits the generation and displaying of video sequences of standard, 3D and parameter plot windows. Only displayed windows (not hidden) can be used. Before the video sequence is started the dwell time (in seconds) of the frames can be defined. The windows size and position as well as the intensity scaling of the selected windows can be adjusted (see example 15).

Example 15: This example illustrates a generation of a short windows-video sequence of a sputter depth profile (SDP) multipoint measurement with ten sputter steps. The 990 As 2p_{3/2} spectra of the ESCALAB-SDP multipoint measurement (one multipoint measurement has 99 spectra (area: 11x9 points)) are saved in the file *As2p3-SDP-AreaScan-SAXL150-Open-Open.avg* in the folder *'Unifit_2023_User_Files\examples\XPS\As2p3-SDP-MultiPointMeasurement-WindowsVideoSequence'*. Every 128th window is displayed. A peak fit of all spectra using the fit mode product, absolute parameters and two components (one component for the As oxides and one component for the GaAs and As species) has to be carried out. After the peak fit of all standard windows the 'XY 3D Plot 45°' and 'XY 3D Colour Profile' plots of the component areas of the multipoint measurements of every sputter step are generated. The 'XY 3D Plot 45°' and 'XY 3D Colour Profile' plots can be displayed as windows-video sequence. The result is saved in the project: *As2p3-SDP-MultiPointMeasurement-WindowsVideoSequence.ufp*.

1. Start UNIFIT,
2. select [Preferences – Fit Procedure – Product] ('Product' will be ticked),
3. select [Preferences – Fit Parameters/XAS-Background Parameters/XPS-Background Parameters (INHOM) – Absolute] ('Absolute' will be ticked),
4. select [Preferences - Tougaard-Background Calculation - Homogeneous Samples] (Homogeneous Samples will be ticked),
5. select [Preferences - Y-axis - Counts per Second],
6. select [Preferences - Setting of Programme Parameters], Maximal Number of Peak Fit Components: 5, Maximal Number of Presentable Curves Inside 'Plot 3D Waterfall': 300, Number of the First Standard Window: 41, and press ,
7. select [Windows - Hide Standard Windows], the dialogue 'Hide Standard Widows' will be opened, choose 'Show Every 128th Standard Windows' and press ,

8. *select **Unifit_2023_User_Files\examples\XPS\As2p3-SDP-MultiPointMeasurement-WindowsVideoSequence\As2p3-SDP-AreaScan-SAXL150-Open-Open.avg** with [File – Open Spectra – XPS - ESCALAB/K-ALPHA Avantage (*.AVG)] and confirm with* ,
9. *select all As2p3 spectra in the dialogue box 'Select Spectra' and display them with* ,
10. *every 128th standard window is displayed,*
11. *the x recording positions are optimized (from -3 to 3) with [Annotation/Design - Edit Parameters Standard Windows], the dialogue 'Selection Acquisition Parameters' is opened, select 'x-Position', the dialogue 'Edit Parameters Standard Windows - x-Position' is opened, select , open the operation routine and do the following operations: subtraction with 24500, division by 1000, subtraction with 3, (window 41: -3, windows: 42: -2.25, window 139: 3: window 140: -3,...), close the 'Fill with' dialogue, and* ,
12. *the y recording positions are optimized (from -3.75 to 3.75) with [Annotation/Design - Edit Parameters Standard Windows], the dialogue 'Selection Acquisition Parameters' is opened, select 'y-Position', the dialogue 'Edit Parameters Standard Windows - y-Position' is opened, select , open the operation routine and do the following operations: addition with 5850, division by 1000, subtraction with 3.75, (window 41: -3.75, window 42: -3.75 window 139: 3.75: window 140: -3.75,...), close the 'Fill with' dialogue, and* ,
13. *activate window 256,*
14. *satellite correction with [Modify - Subtract Satellite] and* ,
15. *load the start parameters of window 256 with [Peak Fit - Load Start Parameters], folder: **Unifit_2023_User_Files\examples\XPS\As2p3-SDP-MultiPointMeasurement-WindowsVideo-Sequence\As2p3-Window256.par**,*
16. *confirm the fit-background parameters with* , *confirm the Min/Max-values with* , *confirm the fit parameters with* ,
17. *carry out 22 iteration steps in window 256 (Number of Iterations per cycle: 11, Number of Cycles: 2), close the dialogue 'Stop Iterations?' with* ,
18. *carry out a peak fit of all standard windows with {Batch Processing - Batch Processing}, batch processing windows selection dialogue is opened, select all windows, start the batch processing with close the batch processing information (Satellite Subtraction, Add background, Peak Fit) with* ,
19. *create the 'XY 3D Plot 45°' plots of the first peak-fit component of all ten multipoint measurements with [Batch Processing - XY 3D Plot 45°], the windows selection dialogue is opened, select all 99 spectra of the first multipoint measurement (windows 41 - 139), and* , *activate a standard window,*
20. *the curve selection dialogue is opened, select 'Area Component 1' and 'Numbers of the 3D Plots': 10, and* *ten 'XY 3D Plot 45°' plots are generated and displayed in the windows 1 - 10,*
21. *repeat points 19 and 20 using component 2 (oxides), the 'XY 3D Plot 45°' plots of component 2 are displayed in windows 11 - 20, activate a standard window,*
22. *generate in windows 21 - 30 'XY 3D Colour Profile' plots of component 1, activate a standard window,*
23. *generate in windows 31 - 40 'XY 3D Colour Profile' plots of component 2,*
24. *start the windows video sequence of component 1 with [Windows - Show Windows Video Sequence], the windows selection dialogue 'Show Windows Video Sequence' is opened,*
25. *select windows 1 - 10, and* ,
26. *the dialogue 'Show Windows Video Sequence' is opened, the setting should be: Frame-Dwell Time: 2, all options activated,*
27. *start the windows-video sequence of the windows 1 - 10 with* ,

28. *repeat points 24 - 27 for showing the video sequences of the windows 11 - 20, 21 - 30 and 31 - 40.*
29. *The image export as well as the generation of animated-gif files is described in the example 3.*

3.11.13 Close All Windows



[Windows – Close All Windows] closes all opened windows, the fit parameters will be deleted and the control flags will be resettled. The spectrum names in the dialogue [File – Select Spectrum] are preserved. Before closing of the windows the saving of the current project is available.

3.11.14 Close Windows



[Windows – Close Windows] closes opened windows (see 3.11.13). Before the windows will be closed the windows can be selected using a special sub-menu.

3.11.15 Close All Standard Windows



[Windows – Close all Standard Windows] closes all opened standard windows, the fit parameter will be deleted and the control flags reset. The spectrum names in the dialogue [File – Select Spectra] are preserved. Before closing of the standard windows the saving of the current project is available.

3.11.16 Close Standard Windows



[Windows – Close Standard Windows] closes opened standard windows (see 3.11.15). Before the standard windows will be closed the standard windows can be selected using a special sub-menu.

3.12 W: 1 - 3000

This menu point permits the direct activation of windows from number 1 up to 3000. The number of the currently activated window is ticked.

3.13 W: 3001 - 6000

This menu point permits the direct activation of windows from number 3001 up to 6000. The number of the currently activated window is ticked.

3.14 W: 6001 - 9000

This menu point permits the direct activation of windows from number 6001 up to 9000. The number of the currently activated window is ticked.

3.15 W: 9001 - 12000

This menu point permits the direct activation of windows from number 9001 up to 12000. The number of the currently activated window is ticked.

3.16 W: 12001 - 15000

This menu point permits the direct activation of windows from number 12001 up to 15000. The number of the currently activated window is ticked. Spectra windows with a number higher than 15000 can be activated and displayed using the commands described in 3.11.8 and 3.11.9.

3.17 UNIFIT

The call [UNIFIT - Info] provides information about the actual version number, the revision code, the currently used Windows version and the address of the author, the invoice number, the form of the licence (company, work group or single licence), the name and the address of the owner of the licence.

4 Examples

4.1 Problem: Analysis of an n-type GaAs (100) surface oxidized by UV-ozone

The chemical composition, the thickness of the ultrathin over layer of the oxidation products and the carbon contamination of a GaAs (100) surface after oxidation by UV-ozone treatment were determined by XPS. The corresponding projects are;

Unifit_2023_User_Files\examples\XPS\GaAs_Ozone.ufp,

Unifit_2023_User_Files\examples\XPS\GaAs_Ozone_As.ufp,

Unifit_2023_User_Files\examples\XPS\GaAs_Ozone_Ga.ufp.

The **measurements** were performed using an X-ray photoelectron spectrometer VG ESCALAB 220 iXL with a monochromatic $AlK\alpha$ source and the lens mode LAXL (magnetic lens underneath the sample). The charge correction (-0.2 eV) for the GaAs samples was estimated with $C\ 1s = 285.0$ eV. The instrument was operated in the CAE mode (constant ΔE) at pass energies of 50 eV (for survey spectrum) and 10 eV for the single spectra Ga 3d, As 3d, Ga $2p_{3/2}$, As $2p_{3/2}$, O 1s and C 1s.

The **survey spectrum** in Figure 51 shows the peaks of Ga 3d, As 3d, Ga $2p_{3/2}$, As $2p_{3/2}$, O 1s and C 1s as well as the Auger transitions of Ga and As in the range of the binding energies E_B between 50 and 530 eV.

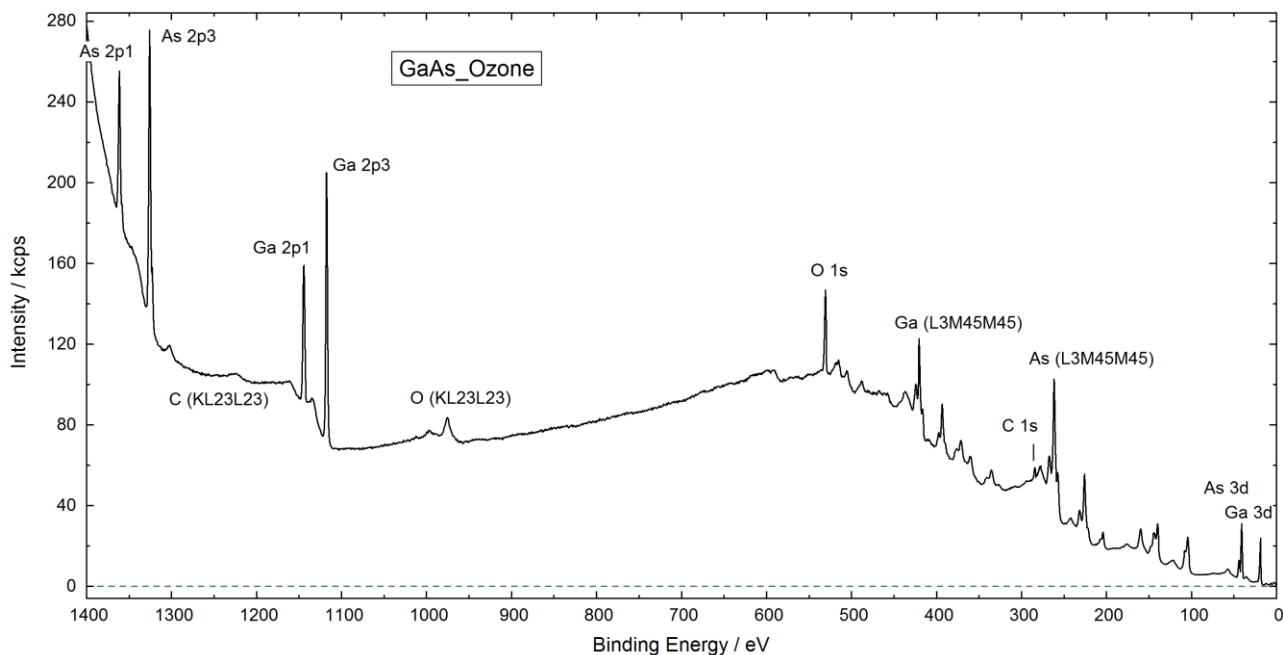
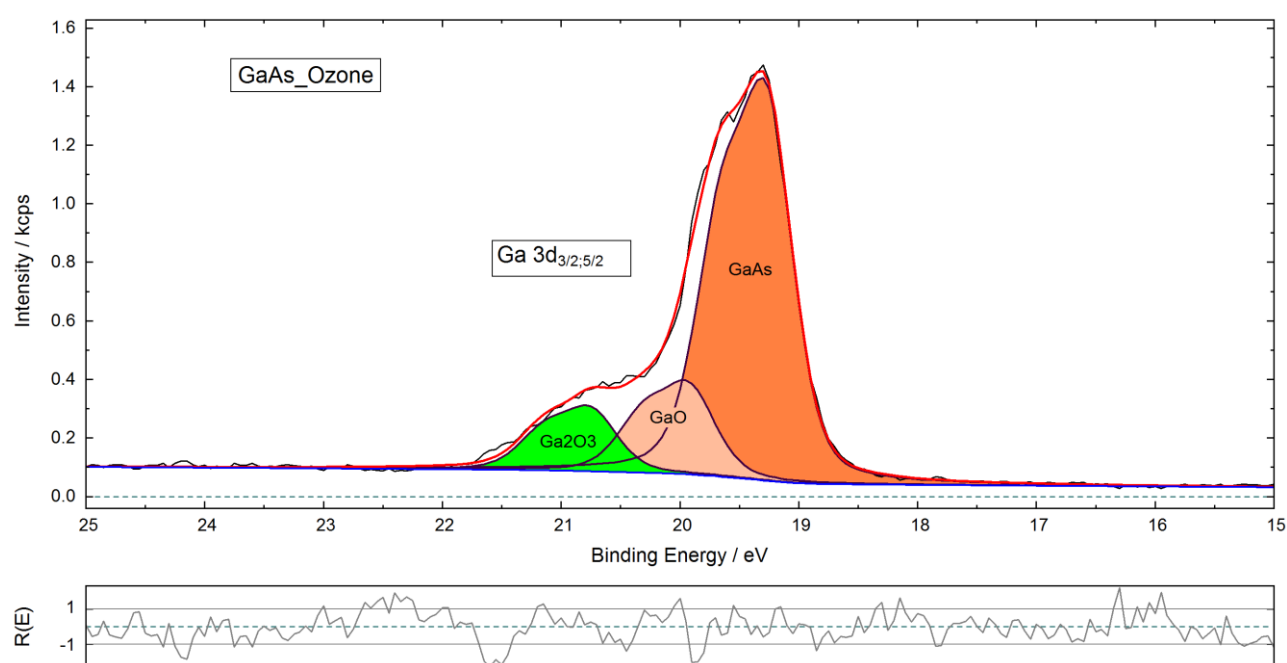


Fig. 51. Survey spectrum of GaAs treated with ozone, copied from UNIFIT, inserted into this text processing document, project: Unifit_2023_User_Files\example\XPS\GaAs_Ozone.ufp, window 7

The intensities of Ga $2p_{3/2}$, Ga 3p, As $2p_{3/2}$, As 3p, O 1s and C 1s were determined from the fitted **single spectra**. The model function was generated by the sum of Gaussian G and Lorentzian L functions. The fit parameters, such as peak height and peak position, were set free. The L-G mixing ratio and the FWHM of the first component peak were set free and the other component peaks were fixed relatively to the first one. The spectral background was described using a polynomial and a Shirley background. The fittable background parameters were calculated parallel to the peak fit. The fit of the $2p_{3/2}$ and 3d peaks of Ga and As displays different chemical species of Ga and As. The Ga

oxidation products of GaAs are identified as GaO and Ga₂O₃. The As oxidation products of GaAs were As, AsO, As₂O₃ and As₂O₅ (see also [31]). The C 1s components were –CH₂–, –C*H₂-O- and –C-O- (project: Unifit_2023_Usr_Files\example\GaAs_Ozone.ufp, window 3). The O 1s peak could be fitted using two oxide components (project: Unifit_2023_Usr_Files\example\GaAs_Ozone.ufp, window 6). The plot of the fitted Ga and As spectra together with the table of fit parameters is shown in Figure 52, 53, 54 and 55.

The peak areas ‘Norm. Area’ are corrected with the sensitivity factors and were used to calculate the **quantification results (at.%)** shown in the quantification tables 1 and 2 for the fitted 3d or the 2p_{3/2} spectra of Ga and As (Figs. 56 and 57). The calculation based on the assumption that the sample is homogeneous. The atom-% ratio of Ga/As is always larger than 1.0, resulting from an As loss at the surface. Different results in tables 1 and 2 depend on different λ values for 2p_{3/2} and 3d peaks of Ga and As. Due to the smaller λ values for the 2p_{3/2} peaks the results are more surface sensitive.



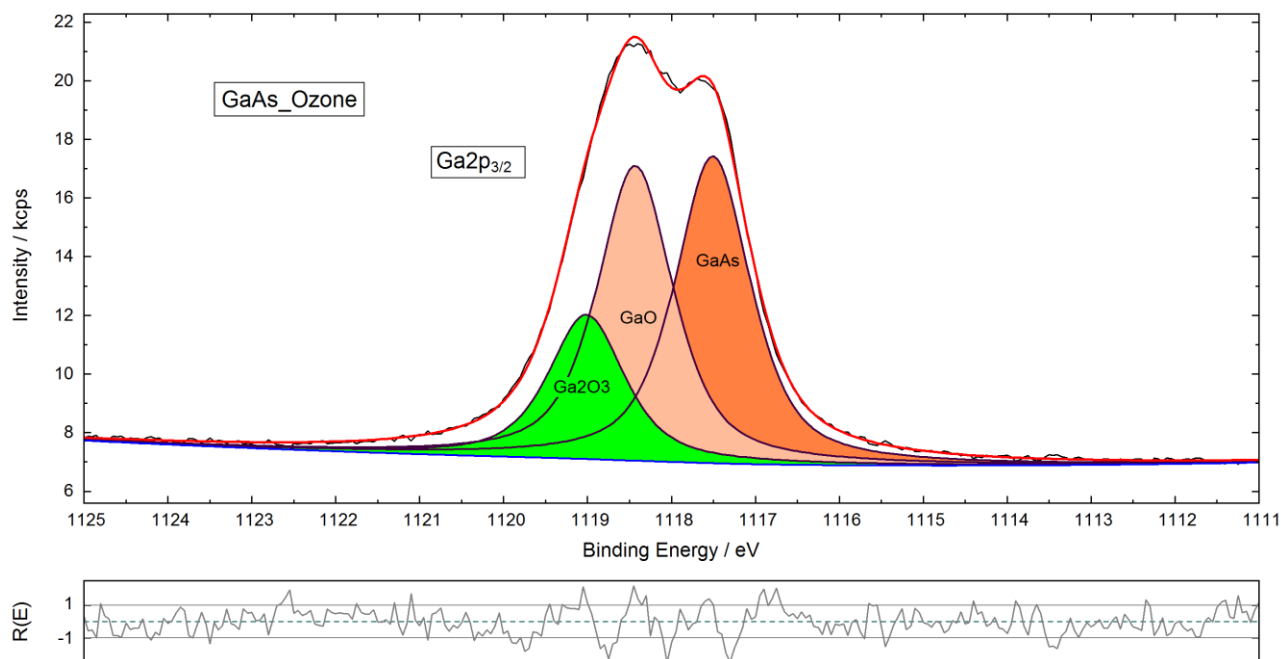
| Doublet name | Peak height/ cps | L-G Mixing | Position/ eV | FWHM/ eV | abs. Area/ cps·eV | rel. Area/ % |
|--------------------------------|---------------------|------------|-----------------|-------------|----------------------|-----------------|
| GaAs | 1178.4 | 0.31858 | 19.2603 | 0.51074 | 727.8 | 42.94 |
| | 0.666 | 1 | 0.4 | 1 | 484.83 | 28.61 |
| GaO | 0.23341 | 1 | 0.6548 | 1 | 169.93 | 10.03 |
| | 0.666 | 1 | 0.4 | 1 | 113.17 | 6.68 |
| Ga ₂ O ₃ | 0.16427 | 1 | 1.4805 | 1 | 119.56 | 7.05 |
| | 0.666 | 1 | 0.4 | 1 | 79.59 | 4.7 |

Fig. 52. Fit of the Ga 3d spectrum and table of fit parameters of the GaAs sample treated with ozone (copied from UNIFIT, inserted into this text processing document), project: Unifit_2023_User_Files\examples\XPS\GaAs_Ozone_Ga.ufp

For estimation of the **thickness of the thin overlayer** the method ERXPS (Energy Resolved XPS, see 2.7.1) was used [22]. The different attenuation of the substrate intensities of Ga 3d and Ga 2p_{3/2} photoelectrons or of As 3d and As 2p_{3/2} photoelectrons allows to estimate the overlayer thickness d with (103). Instead of the λ values with $\lambda \approx 0.103 E^{0.745}$ (124) we used the more reliable effective attenuation length of the photoelectrons L_{ave} of Powell and Jablonski [32]: $L_{ave}(\text{Ga } 2p_{3/2}) = 8.06 \text{ \AA}$,

$L_{\text{ave}}(\text{Ga } 3d) = 25.64 \text{ \AA}$, $L_{\text{ave}}(\text{As } 2p_{3/2}) = 4.77 \text{ \AA}$ und $L_{\text{ave}}(\text{As } 3d) = 25.30 \text{ \AA}$. We assumed that the overlayer consists of the oxidation products of GaAs covered with carbon contamination ($-\text{CH}_2-$ and $-\text{C-O}-$).

The different d values estimated using the GaAs component of the Ga and the As peaks ($d = 9.03 \text{ \AA}$ and 10.92 \AA , Figures 58 und 59) could be caused by a non ideal layer structure. As a result, we have rounded the estimated values of the overlayer (together with the carbon contamination) on the GaAs substrate to $d \approx 10 \text{ \AA}$. The thickness of the carbon contamination was determined with the same method. However, here we have to use all components of the fitted Ga or As spectra. We found a thickness of $d \approx 2 \text{ \AA}$.



| Peak name | Peak height/ cps | L-G Mixing | Position/ eV | FWHM/ eV | abs. Area/ cps·eV | rel. Area/ % |
|-----------|---------------------|------------|-----------------|-------------|----------------------|-----------------|
| GaAs | 10477 | 0.65359 | 1117.507 | 1.06993 | 15083 | 41.15 |
| GaO | 0.96056 | 1 | 0.9245 | 1 | 14488 | 39.52 |
| Ga2O3 | 0.47005 | 1 | 1.5074 | 1 | 7085 | 19.33 |

Fig. 53. Fit of the Ga $2p_{3/2}$ spectrum and table of fit parameters of the GaAs sample treated with ozone (copied from UNIFIT, inserted into this text processing document), project: Unifit_2023_User_Files\examples\XPS\GaAs_Ozone_Ga.ufp.

As supplement of the investigation the position of the **valence-band edge** of the sample was determined (see 2.5.3). For modelling this edge the convolution of the square root and the Gaussian function is used. We used the FWHM of the Gaussian peak of 0.45 eV determined by the peak fit of As and Ga single lines with a G-L convolution model function. The valence-band edge was determined to 0.89 eV (Fig. 60) using a curve fit. The energy band gap 1.42 eV indicates an n-type semiconductor.

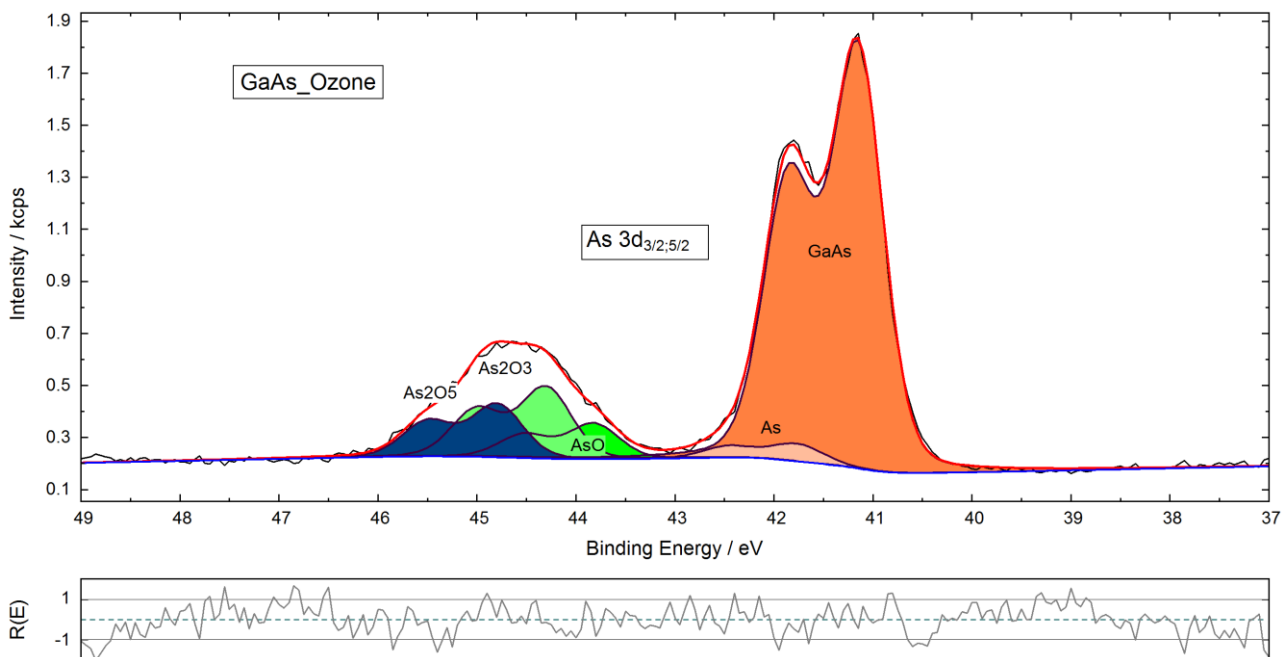
4.2 Problem: Study of Forward Scattering of a Silicon Single Crystal Covered with Natural Oxide Layer

Si 2p, O 1s, and C 1s spectra were recorded at 20 different polar angles (angle perpendicular to the sample surface = 0° , step 4.25°) with ESCALAB 220iXL spectrometer. The signals were recorded using a standard Mg $K\alpha$ source. Batch processing of UNIFIT was used for evaluation of spectra

(time to get a graph ready for presentation: 5 min). Two doublets were chosen for the simulation of Si2p (Fig. 61). O 1s and C 1s were fitted by singlet peaks (Fig. 62 and 63). These presentations were designed and exported with UNIFIT and then inserted in this test processing document.

The parameter plot function of UNIFIT is demonstrated in Fig. 64 using normalized peak areas of the different signals. The decreasing carbon intensity to smaller polar angles giving larger photoelectron escape depths is due to the contamination layer covering the sample.

In contrast to the carbon and oxide layer signals (SiO_x and O 1s) the intensity of elemental Si clearly fluctuates due to diffraction effects in the single crystal lattice depending on the angle.



| Doublet name As3d | Peak height/ cps | L-G Mixing | Position/ eV | FWHM/ eV | abs. Area/ cps·eV | rel. Area/ % |
|----------------------|---------------------|------------|-----------------|-------------|----------------------|-----------------|
| GaAs | 1595 | 0.18728 | 41.1532 | 0.60368 | 1106 | 42.14 |
| | 0.666 | 1 | 0.7 | 1 | 737 | 28.08 |
| As | 0.0416998 | 1 | 0.6092 | 1 | 46.16 | 1.76 |
| | 0.666 | 1 | 0.7 | 1 | 30.75 | 1.17 |
| AsO | 0.0850055 | 1 | 2.6674 | 1 | 94.11 | 3.58 |
| | 0.666 | 1 | 0.7 | 1 | 62.65 | 2.39 |
| As2O3 | 0.17037 | 1 | 3.1487 | 1 | 188.57 | 7.18 |
| | 0.666 | 1 | 0.7 | 1 | 125.51 | 4.78 |
| As2O5 | 0.12703 | 1 | 3.6413 | 1 | 140.54 | 5.35 |
| | 0.666 | 1 | 0.7 | 1 | 93.52 | 3.56 |

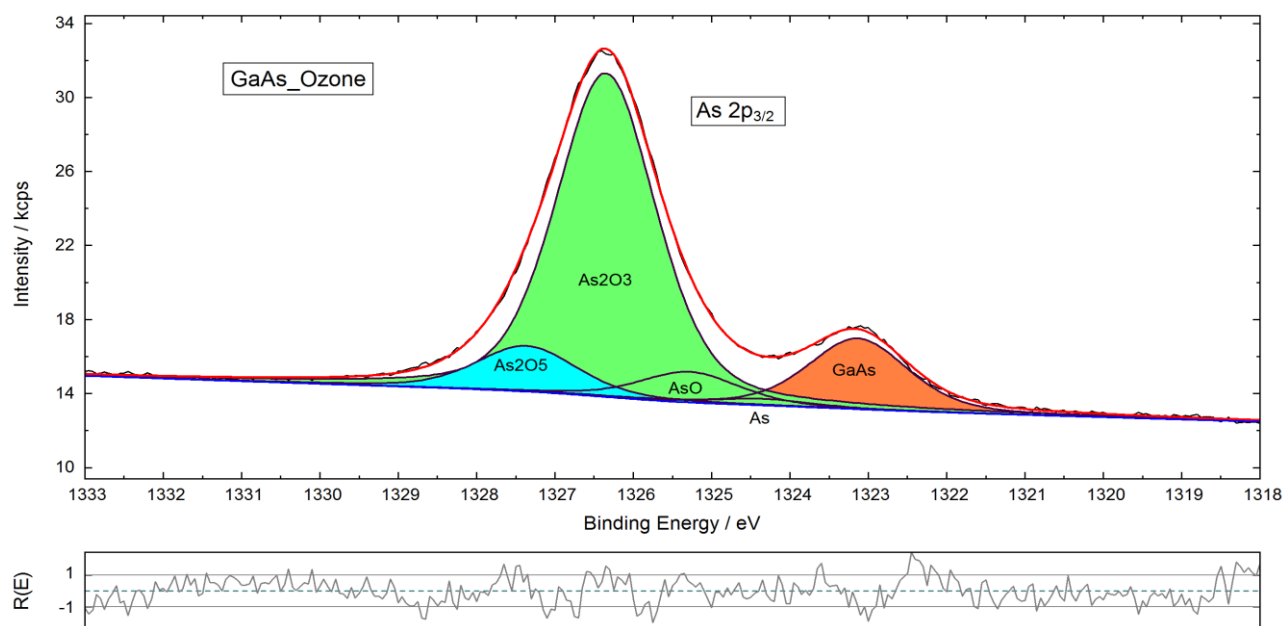
Fig. 54. Fit of the As 3d spectrum and table of fit parameters of the GaAs sample treated with ozone (copied from UNIFIT, inserted into this text processing document), project: Unifit_2023_User_Files\examples\XPS\GaAs_Ozone_As.ufp.

4.3 Problem: Fit of an X-Ray absorption spectrum of Iron Oxide on Barium Titanate

At BESSY II X-Ray absorption spectra of Iron Oxide (Fe_xO_y) on Barium titanate (001) (Project: Unifit_2023_User_Files\examples\XAS\XAS_Peak_Fit_FeOxideOnBa.ufp) have been

measured in order to study the magnetic properties of thin layers of this material. Therefore, 20 ML of iron have been deposited on Barium titanate. Afterwards this layer was oxidized for 15 minutes at 400 °C and $5 \cdot 10^{-6}$ mbar. The measurement geometry was set for in-plane studies which means that the sample was at grazing incidence (50° distorted towards the beam). The spectra were recorded in total electron yield (TEY) measuring the sample current (Fig. 65). The signal was normalized to the mirror current (the reference signal for the intensity normalization) at the last focusing mirror.

A fit of the data has been performed using UNIFIT in order to gain a better understanding of the absorption spectrum and hence a better understanding of the electronic structure of the sample. The total time needed preparing the final graphs for presentations yielded 10 minutes. All graphs have been generated using UNIFIT. Afterwards they were copied from UNIFIT and pasted to text processing software (Fig. 66).



| Peak name | Peak height/ cps | L-G Mixing | Position/ eV | FWHM/ eV | abs. Area/ cps·eV | rel. Area/ % |
|-----------|---------------------|------------|-----------------|-------------|----------------------|-----------------|
| GaAs | 3827.6 | 0.36864 | 1323.1321 | 1.50457 | 6971 | 14.79 |
| As | 0.0948023 | 1 | 1.2 | 1 | 662.53 | 1.41 |
| AsO | 0.43408 | 1 | 2.1521 | 1 | 3036 | 6.44 |
| As2O3 | 4.5719 | 1 | 3.2178 | 1 | 31962 | 67.79 |
| As2O5 | 0.64706 | 1 | 4.2318 | 1 | 4517 | 9.58 |

Fig. 55. Fit of the As $2p_{3/2}$ spectrum and table of fit parameters of the GaAs sample treated with ozone (copied from UNIFIT, inserted into the text processing document), project: Unifit_2023_User_Files\examples\XPS\GaAs_Ozone_As.ufp.

In the beginning of the fit a double step background has been generated. In doing so the positions of the steps were fixed to the energies of the absorption maxima. One needs to consider that these step positions are not always located at the absorption maxima. However, the deviation is comparably small so that it was not taken into account. In addition the ratio of the step heights from $L_3:L_2$ had to be fixed at 2:1. The step width was arbitrarily set to a value of 2 eV.

As shown in Fig. 65 the iron L edge in iron oxide shows some distinct features. First of all there is a shoulder at the L_3 edge at lower photon energies (position 1, Fig. 65). However, the splitting at the L_2 edge is more pronounced (position 2, Fig. 65). These features can be seen in all ferrites and some other iron oxides [33].

Altogether eight singlet peaks have been used to fit the spectrum. The model function was generated by a convolution of Gaussian and Doniach-Sunjic functions (in case of symmetric lines the Doniach-Sunjic function is identical with the Lorentzian function). In the end there were only symmetric lines. During the iteration of the singlet peaks the background was fitted as well.

| Peak name | E_B /eV | Area/cps·eV | Sens. Fact. | Norm. Area | Quant./at.% | |
|---------------|-----------|-------------|-------------|------------|-------------|-------|
| As3d GaAs | 41.15 | 1843.5211 | 29.675 | 62.123711 | 19.78 | 28.17 |
| As3d As | 41.76 | 76.904170 | 29.675 | 2.5915474 | 0.83 | |
| As3d AsO | 43.82 | 156.75868 | 29.679 | 5.2818049 | 1.68 | |
| As3d As2O3 | 44.3 | 314.07627 | 29.721 | 10.567486 | 3.37 | |
| As3d As2O5 | 44.79 | 234.06125 | 29.709 | 7.8784630 | 2.51 | |
| C1s -CH2- | 284.81 | 476.89422 | 16.983 | 28.080682 | 8.94 | 12.05 |
| C1s -C*H2-CO- | 285.69 | 116.71223 | 16.995 | 6.8674456 | 2.19 | |
| C1s -C-O- | 286.55 | 48.921701 | 16.986 | 2.8801189 | 0.92 | |
| Ga3d GaAs | 19.26 | 1212.6340 | 17.631 | 68.778520 | 21.9 | 30.62 |
| Ga3d GaO | 19.92 | 283.09135 | 17.623 | 16.063743 | 5.12 | |
| Ga3d Ga2O3 | 20.74 | 199.14655 | 17.641 | 11.288847 | 3.6 | |
| O1s Peak 1 | 531.25 | 4229.7028 | 52.358 | 80.784270 | 25.73 | 29.17 |
| O1s Peak 2 | 532.35 | 566.09865 | 52.377 | 10.808153 | 3.44 | |

Fig.56. Quantification table of the fitted single spectra of As 3d, Ga 3d, C 1s and O 1s (copied from UNIFIT, inserted into the text processing document)

| Peak name | E_B /eV | Area/cps·eV | Sens. Fact. | Norm. Area | Quant./at.% | |
|---------------|-----------|-------------|-------------|------------|-------------|-------|
| As2p3 GaAs | 1323.13 | 6970.8794 | 719.73 | 9.6853551 | 3.56 | 23.98 |
| As2p3 As | 1324.33 | 662.52922 | 721.69 | 0.9180221 | 0.34 | |
| As2p3 AsO | 1325.28 | 3035.7365 | 722.61 | 4.2010369 | 1.54 | |
| As2p3 As2O3 | 1326.35 | 31962.059 | 722.52 | 44.236797 | 16.25 | |
| As2p3 As2O5 | 1327.36 | 4516.5402 | 723.73 | 6.2406425 | 2.29 | |
| C1s -CH2- | 284.81 | 476.89422 | 16.983 | 28.080682 | 10.32 | 13.9 |
| C1s -C*H2-CO- | 285.69 | 116.71223 | 16.995 | 6.8674456 | 2.52 | |
| C1s -C-O- | 286.55 | 48.921701 | 16.986 | 2.8801189 | 1.06 | |
| Ga2p3 GaAs | 1117.51 | 15082.503 | 472.63 | 31.911659 | 11.72 | 28.47 |
| Ga2p3 GaO | 1118.43 | 14488.265 | 473.15 | 30.620741 | 11.25 | |
| Ga2p3 Ga2O3 | 1119.01 | 7085.2954 | 473.30 | 14.969735 | 5.5 | |
| O1s Peak 1 | 531.25 | 4229.7028 | 52.358 | 80.784270 | 29.68 | 33.65 |
| O1s Peak 2 | 532.35 | 566.09865 | 52.377 | 10.808153 | 3.97 | |

Fig. 57. Quantification table of the fitted single spectra of As 2p_{3/2}, Ga 2p_{3/2}, C 1s and O 1s (copied from UNIFIT, inserted into the text processing document)

In case of iron oxide (Fe_xO_y) or even magnetite (Fe_3O_4) such a peak fit becomes inevitable because of hidden orbital magnetic moments. These moments are revealed at the iron L₂ edge only with fitting the single components [34]. Furthermore, the chemical environment of the single iron species within the spinell can be pointed out. Primarily it is possible to tell the difference between octahedral and tetrahedral coordination of the iron species.

However, XAS peak fitting is just at its beginning making further experiments absolutely essential. The results and parameters of the fitting approach are shown in Figs. 66 and .

4.4 Problem: Estimation of the position and size of the sputter crater using SiO₂

The position and size of the sputter crater of the spectrometer ESCALAB 220 iXL shall be estimated. Two multipoint (area) scans of the untreated and sputtered sample (26x26 recording points) were carried out.

The spectrometer setting was:

- Lens mode: SmallAreaXL 150, Aperture Field of View: 5, Aperture Objective Lens: 7,
- Pass energy: 50 eV,
- excitation: Al twin anode, 1486.6 eV
- step width: 0.2 eV,
- initial and final energy: 93 and 110 eV,
- number of scans: 2,
- step width X- and Y-axis: 0.2 mm.

The project names are 'Unifit_2023_User_Files\examples\Si2p_AreaScan_26x26.ufp' and 'Unifit_2023_User_Files\examples\XPS\Si2p_AreaScan_26x26_AfterSputtering.ufp'. During the measurement the X-ray source switched off.

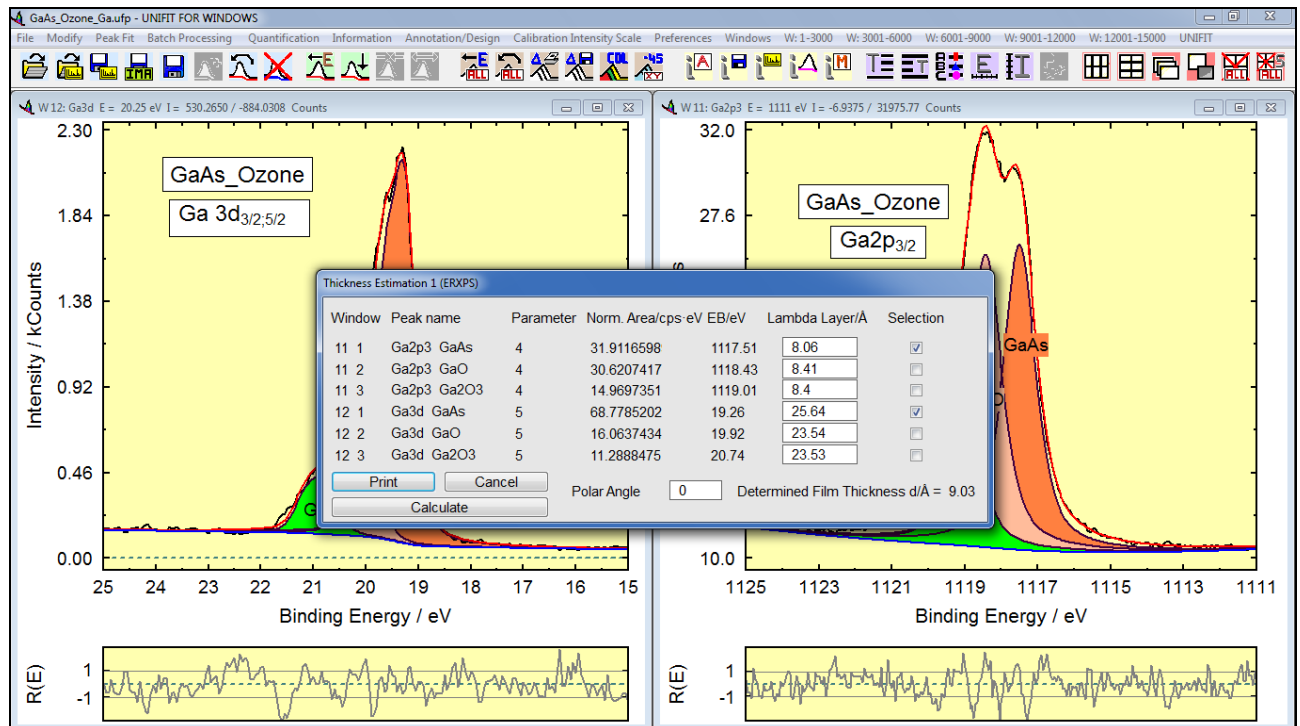


Fig. 58. Screen shot: Dialogue of the Thickness Estimation 1 of the GaAs overlayer from the fitted singlet peaks Ga 2p_{3/2} and Ga 3d (screen shot), project: Unifit_2023_User_Files\examples\XPS\GaAs_Ozone_Ga.ufp

The x and y positions were changed using the UNIFIT parameter editing sub-routine. The x and y positions of standard measurements were defined to x = 0 and y = 0. Because the pass energy was very large two singlet peaks (Si and SiO₂) were chosen for the peak fit of the Si2p signal. After the peak fit the peak areas of the Si and SiO₂ component were presented with respect to the x and y recording position using the 'XY 3D Plot 45°' (see Fig. 68, 69 and 71) and 'XY 3D Plot -45°' (see Fig. 72). Different directions of the y position scale were used. Additionally 3D colour profiles of the fit results were created (see Fig. 70 and 73). The parameter plot function of UNIFIT is demonstrated in Figure 74 using the peak height of the two fitted components.

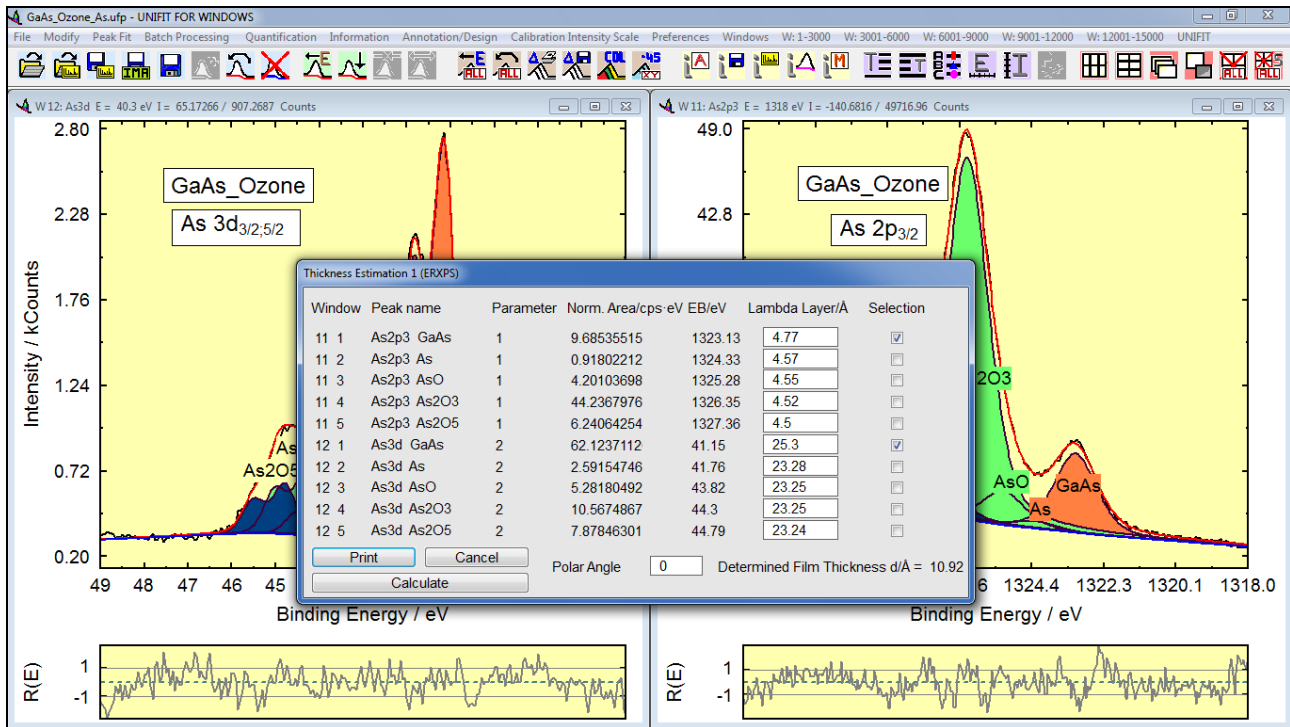


Fig. 59. Screen shot: Dialogue of the Thickness Estimation 1 of the GaAs overlayer from the fitted singlet peaks As 2p_{3/2} and As 3d (screen shot), project: Unifit_2023_User_Files\examples\XPS\GaAs_Ozone_As.ufp.

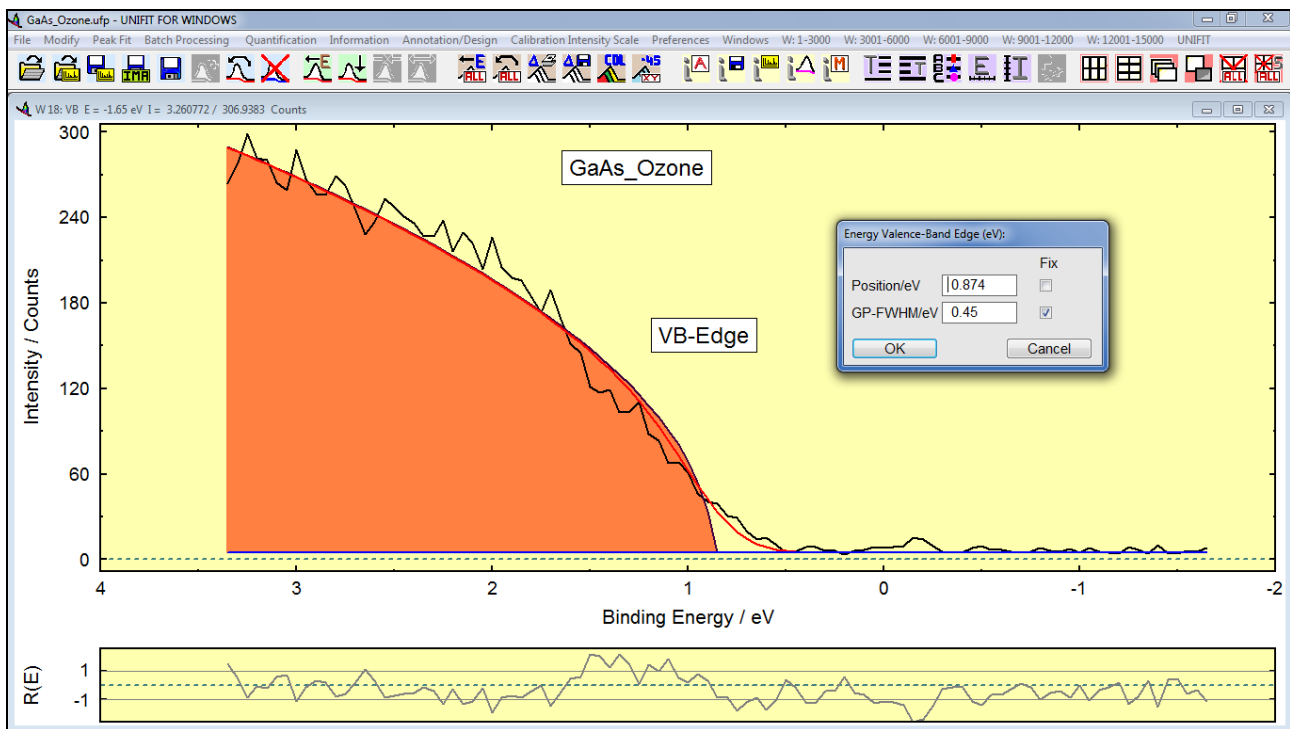


Fig. 60. Screen shot: Dialogue of the determination of the valence-band edge position of the ozone treated GaAs (model function: convolution of square root and Gaussian functions $SQR(E)*G(E)$) (screen shot), project: Unifit_2023_User_Files\examples\XPS\GaAs_Ozone.ufp, window 8

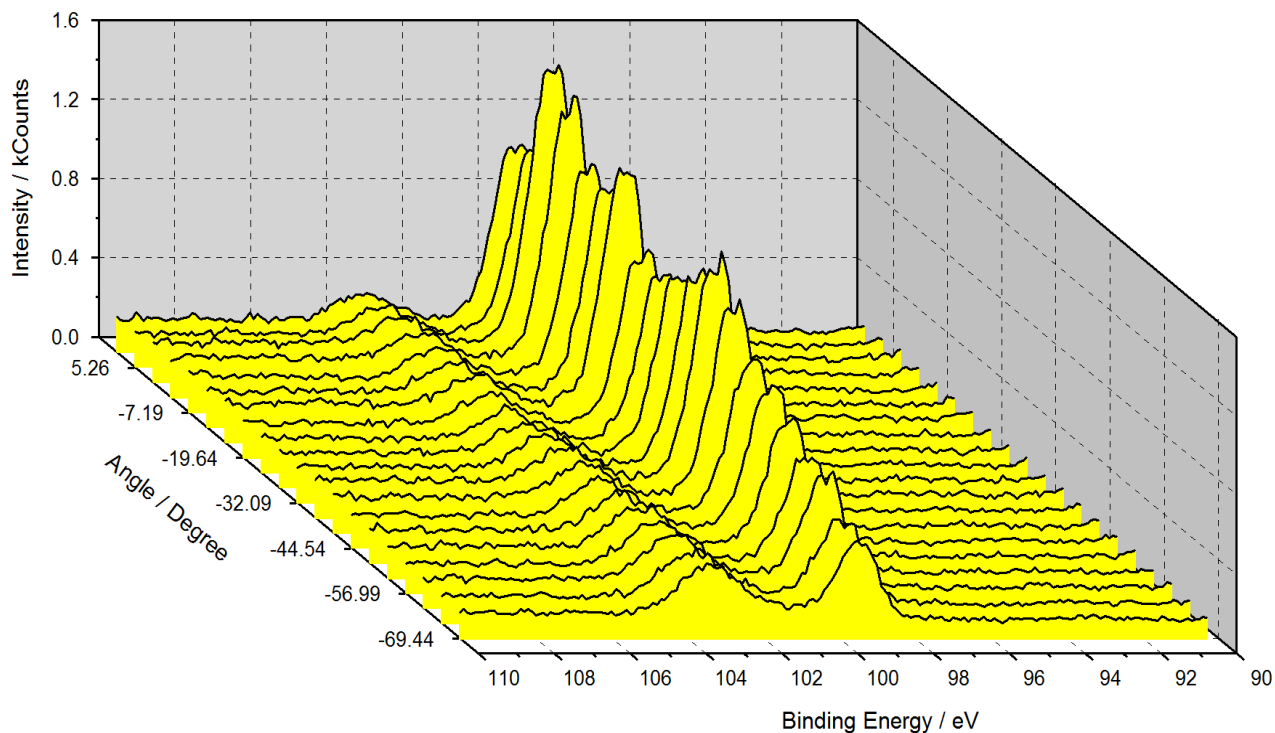


Fig. 61. 3D waterfall -45° plot of angle-dependent collected Si 2p spectra from naturally oxidized exited Si wafer, presentation created using UNIFIT and inserted in this document as graphic, project: Unifit_2023_User_Files\examples\XPS\Angle_Resolved_Measurement_Si.ufp

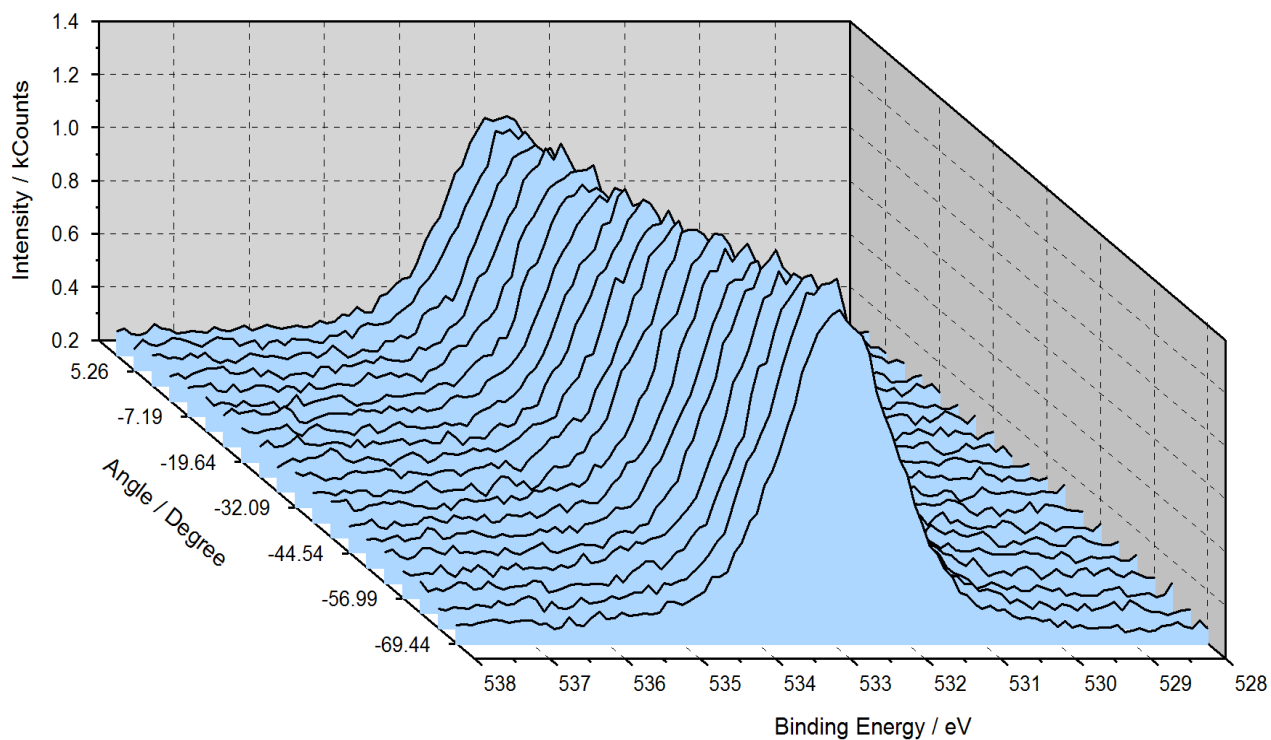


Fig. 62. 3D waterfall -45° plot of angle-dependent collected O 1s spectra from naturally oxidized Si wafer, presentation created using UNIFIT, exported and inserted in this document as graphic, project: Unifit_2023_User_Files\examples\XPS\Angle_Resolved_Measurement_Si.ufp

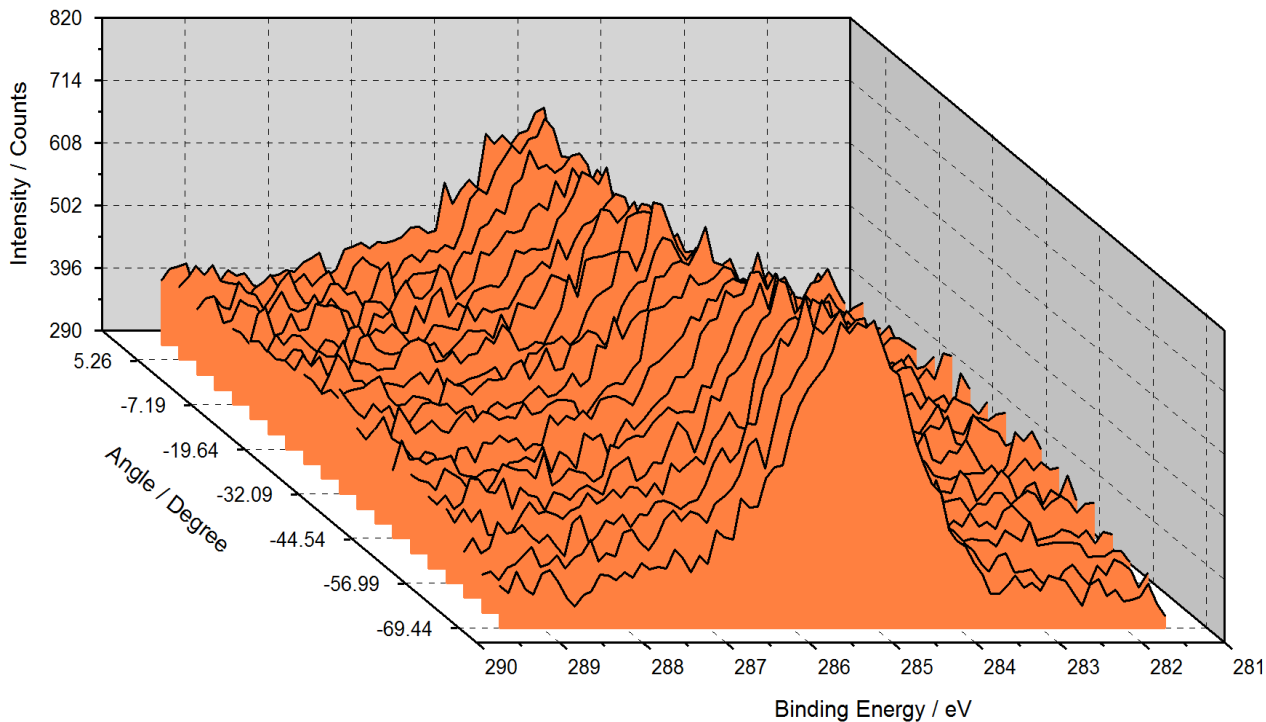


Fig. 63. 3D waterfall -45° plot of angle-dependent collected C 1s spectra from naturally etched Si wafer, presentation created using UNIFIT, exported and inserted in this document as graphic, project: Unifit_2023_User_Files\examples\XPS\Angle_Resolved_Measurement_Si.ufp

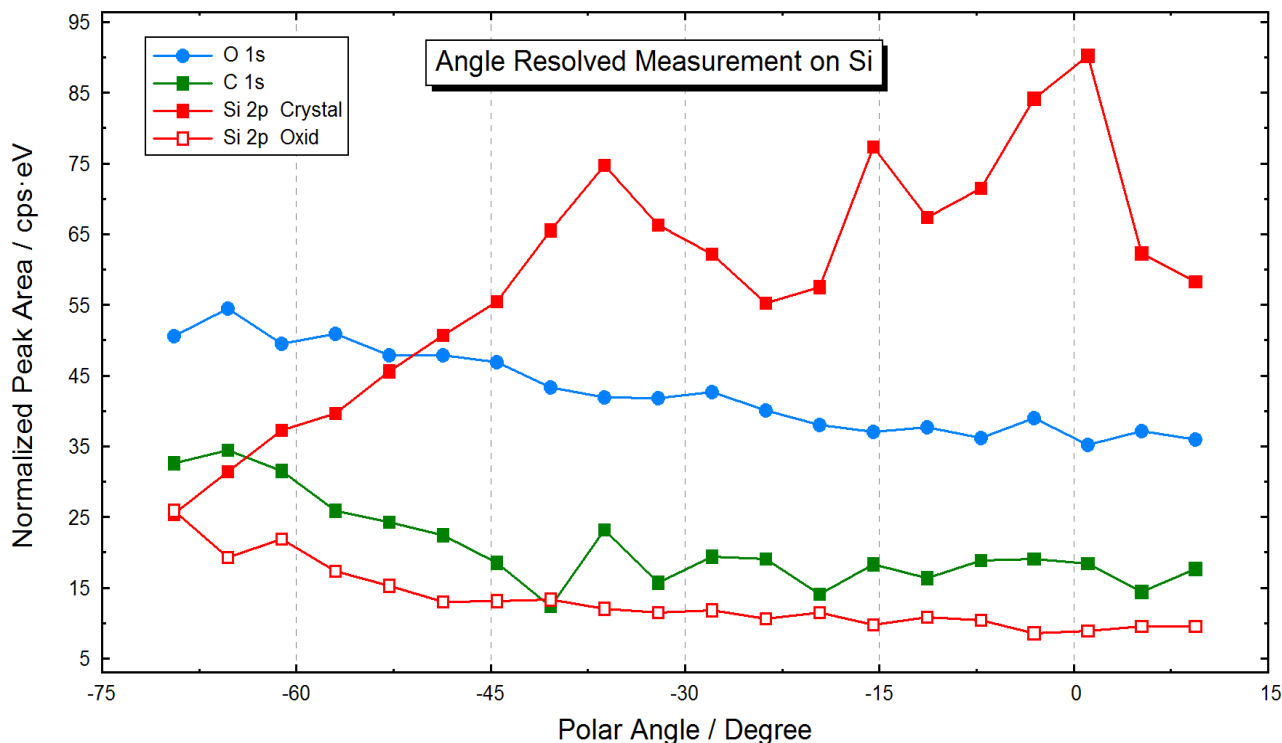


Fig. 64. Normalized peak areas of Si 2p (Si and SiO₂), O 1s and C 1s depending on the polar angle (parameter plot), graph created with UNIFIT and inserted in this document, project: Unifit_2023_User_Files\examples\XPS\Angle_Resolved_Measurement_Si.ufp

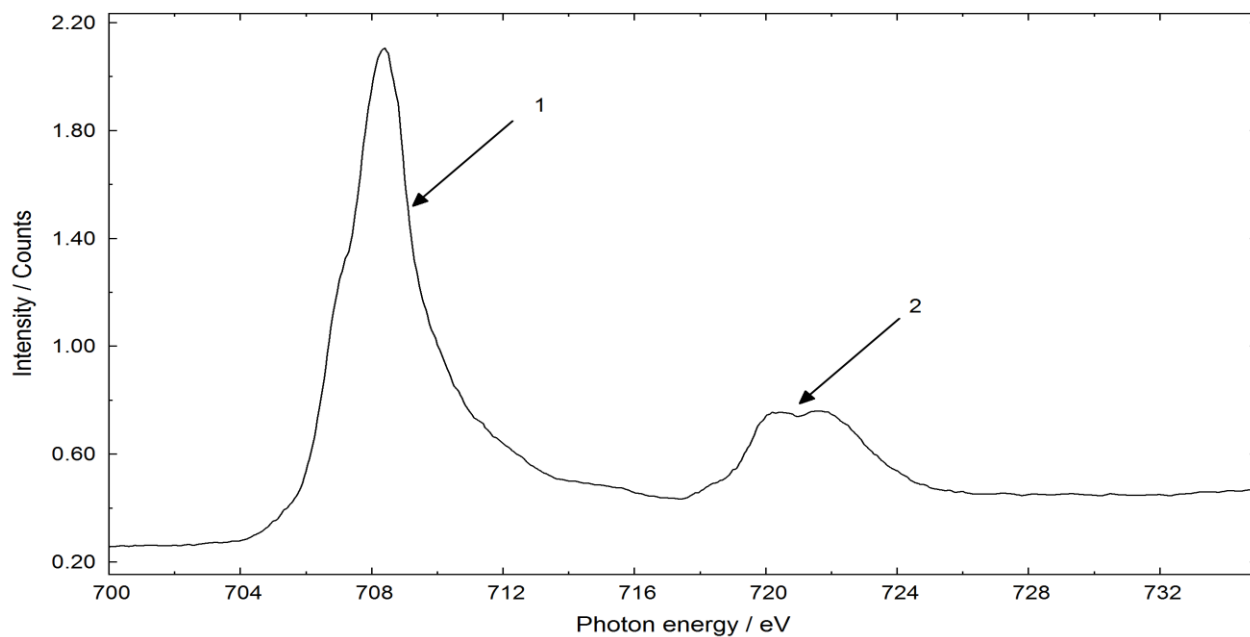
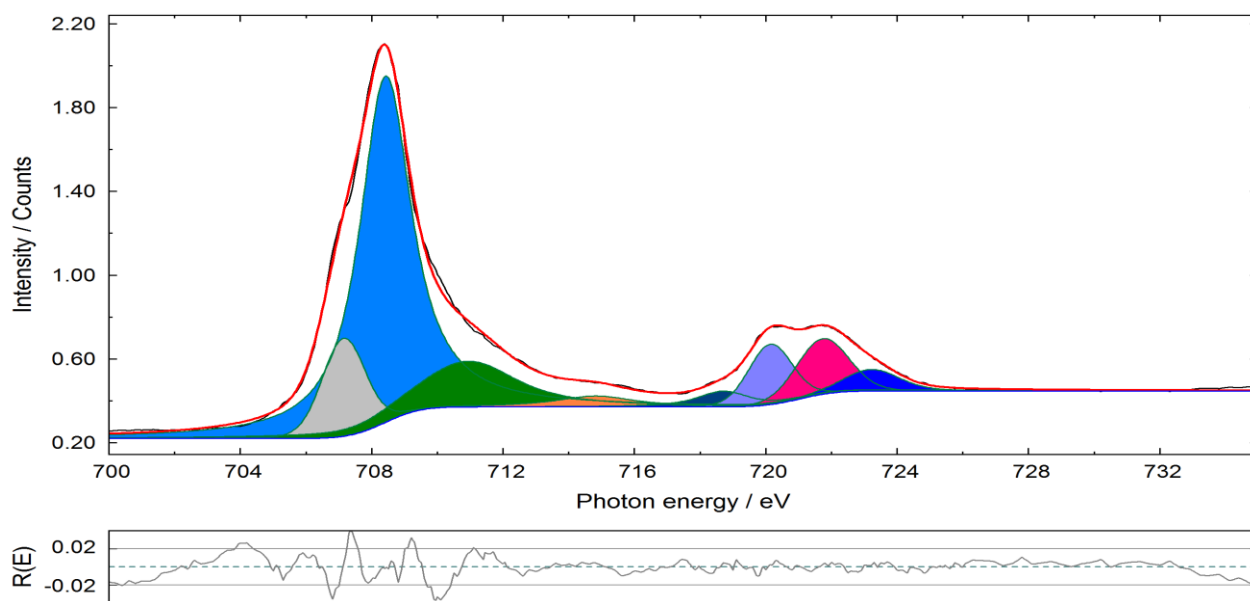


Fig. 65. Absorption spectrum of the Fe-L_{2,3} edge of Fe_xO_y, 1: L₃ edge, 2: L₂ edge, project: Unifit_2023_User_Files\examples\XAS\XAS_Peak_Fit_FeOxideOnBa.ufp



| Peak name | Peak height/ Counts | GP-FWHM/ eV | Position/ eV | LP-FWHM/ eV | abs. Area/ Counts·eV | rel. Area/ % |
|-----------|------------------------|----------------|-----------------|----------------|-------------------------|-----------------|
| 1030_1 | | | | | | |
| Peak 1 | 1.65363 | 0.57206 | 708.4076 | 1.69646 | 4.5266 | 55.77 |
| Peak 2 | 0.46788 | 1.46701 | 707.1417 | 0.16965 | 0.808 | 9.96 |
| Peak 3 | 0.21825 | 1.50931 | 710.9437 | 2.82362 | 1.0558 | 13.01 |
| Peak 4 | 0.052275 | 0.42855 | 714.8172 | 2.83131 | 0.2239 | 2.76 |
| Peak 5 | 0.07552 | 0.75919 | 718.7093 | 1.58078 | 0.2065 | 2.54 |
| Peak 6 | 0.28782 | 1.47432 | 720.1335 | 0.16965 | 0.5001 | 6.16 |
| Peak 7 | 0.2651 | 1.78133 | 721.7191 | 0.16965 | 0.547 | 6.74 |
| Peak 8 | 0.10346 | 1.61872 | 723.2149 | 0.6579 | 0.2482 | 3.06 |

Fig. 66. Peak fit of the L edge XAS signal of Fe in Fe_xO_y using UNIFIT and the table of the calculated fit parameters (absolute)

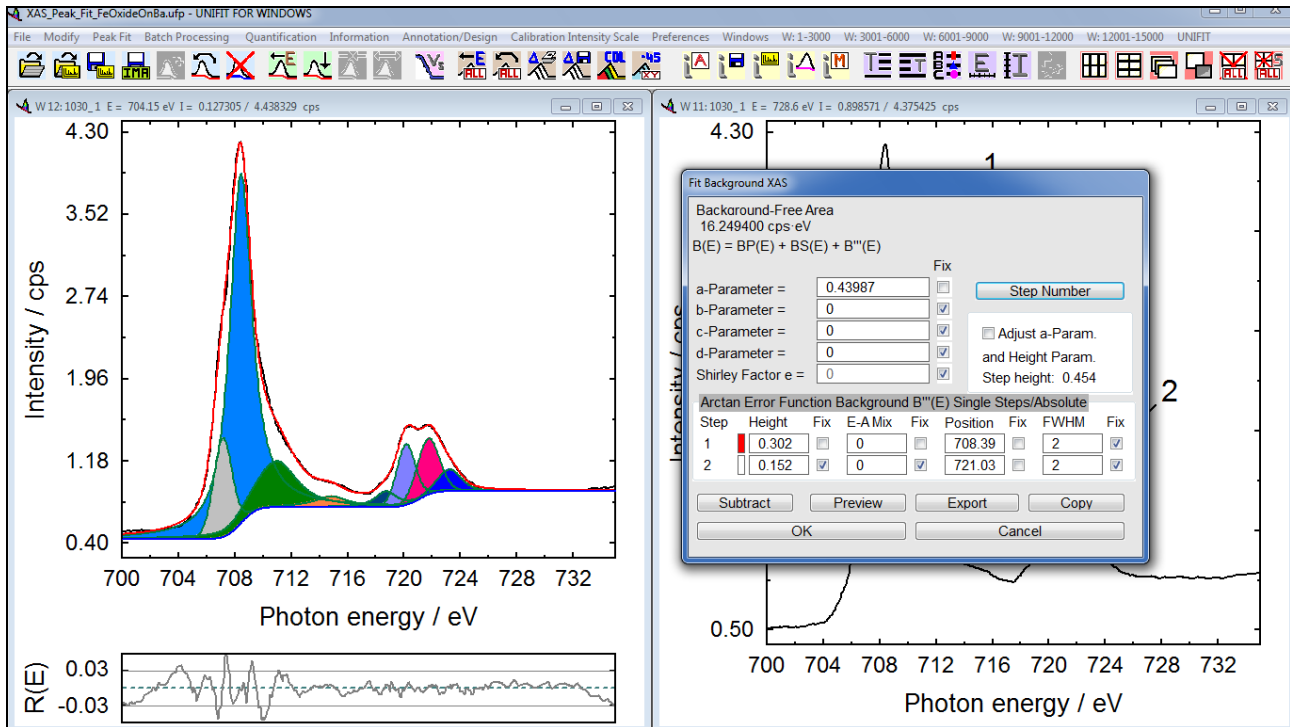


Fig. 67. Screen shot: Parameters of the absorption edge background (relative) of Fe in Fe_xO_y

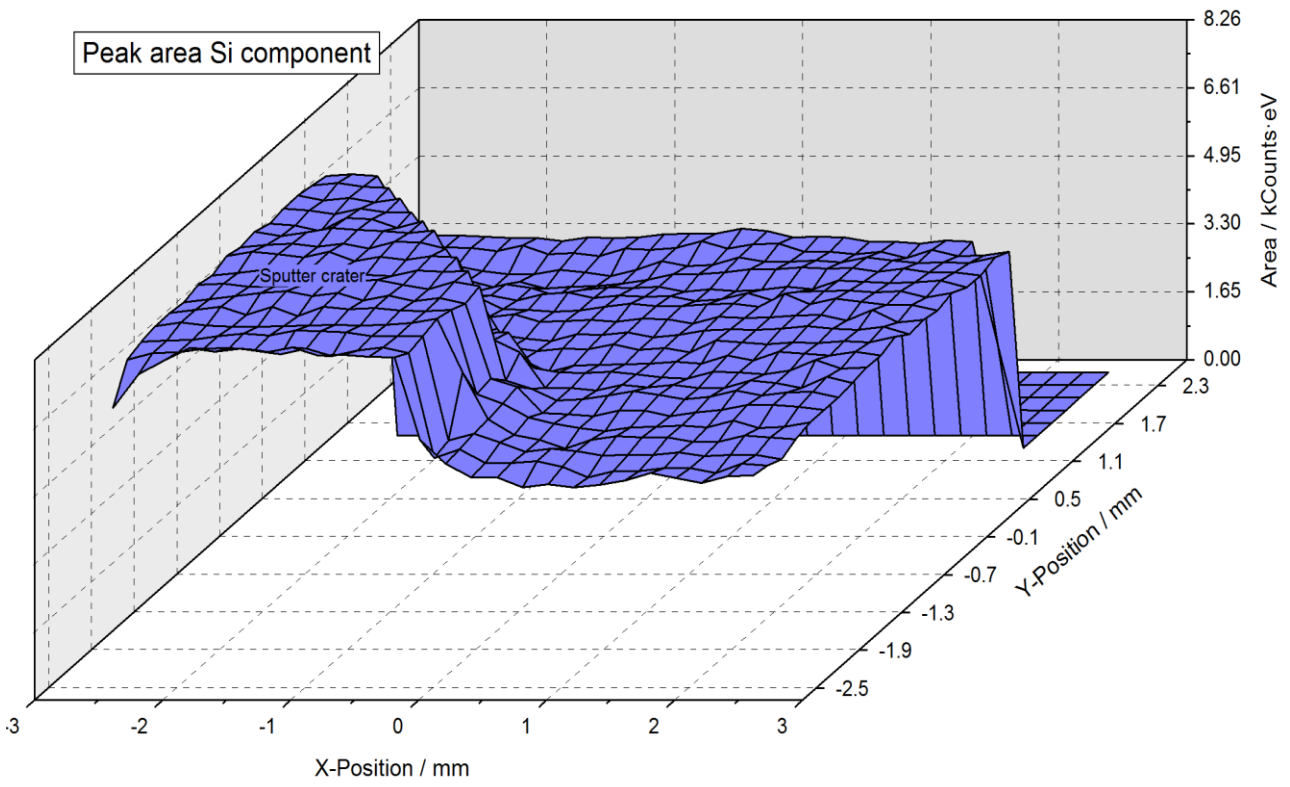


Fig. 68. 'XY 3D Plot 45°' of the fitted Si component of Si 2p (Si/SiO₂), the removed oxide layer of the sputter crater results in higher intensities of the Si substrate signal (in front on the left side)

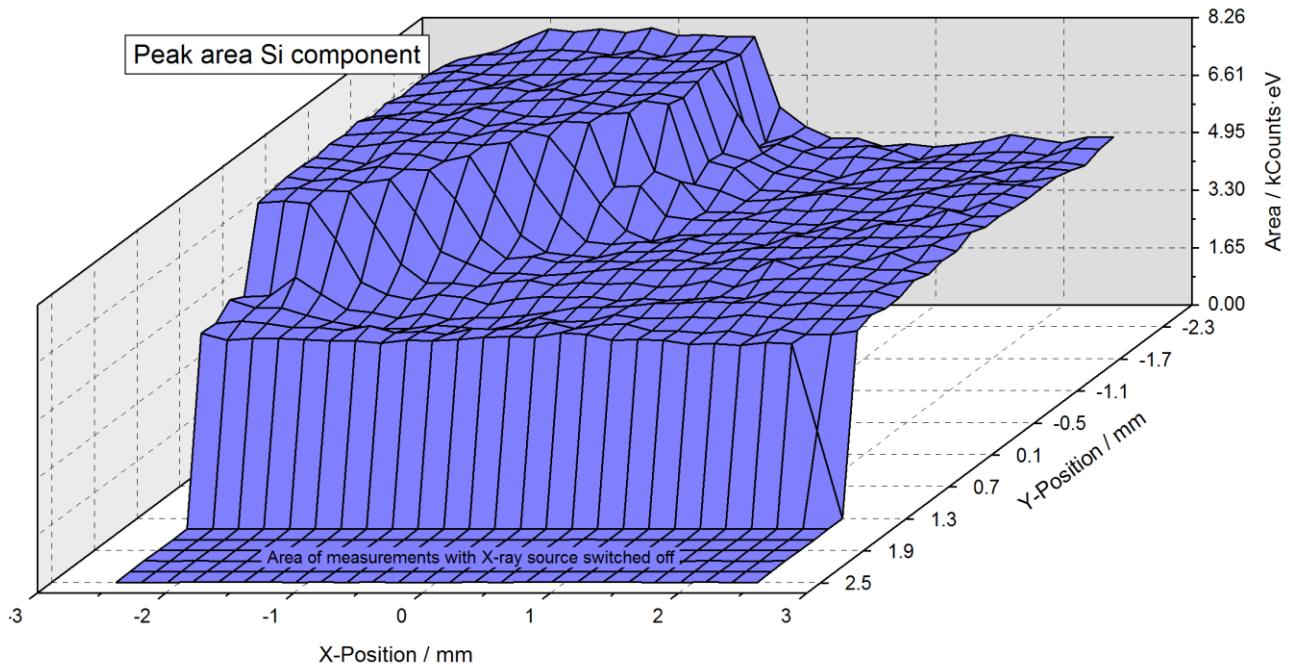


Fig. 69. 'XY 3D Plot 45°' of the fitted Si component of Si 2p (Si/SiO₂) using a reversed Y-axis, the removed oxide layer of the sputter crater results in higher intensities of the Si substrate signal (back on the left side), the zero intensities results from the measurement without X-ray excitation (in front).

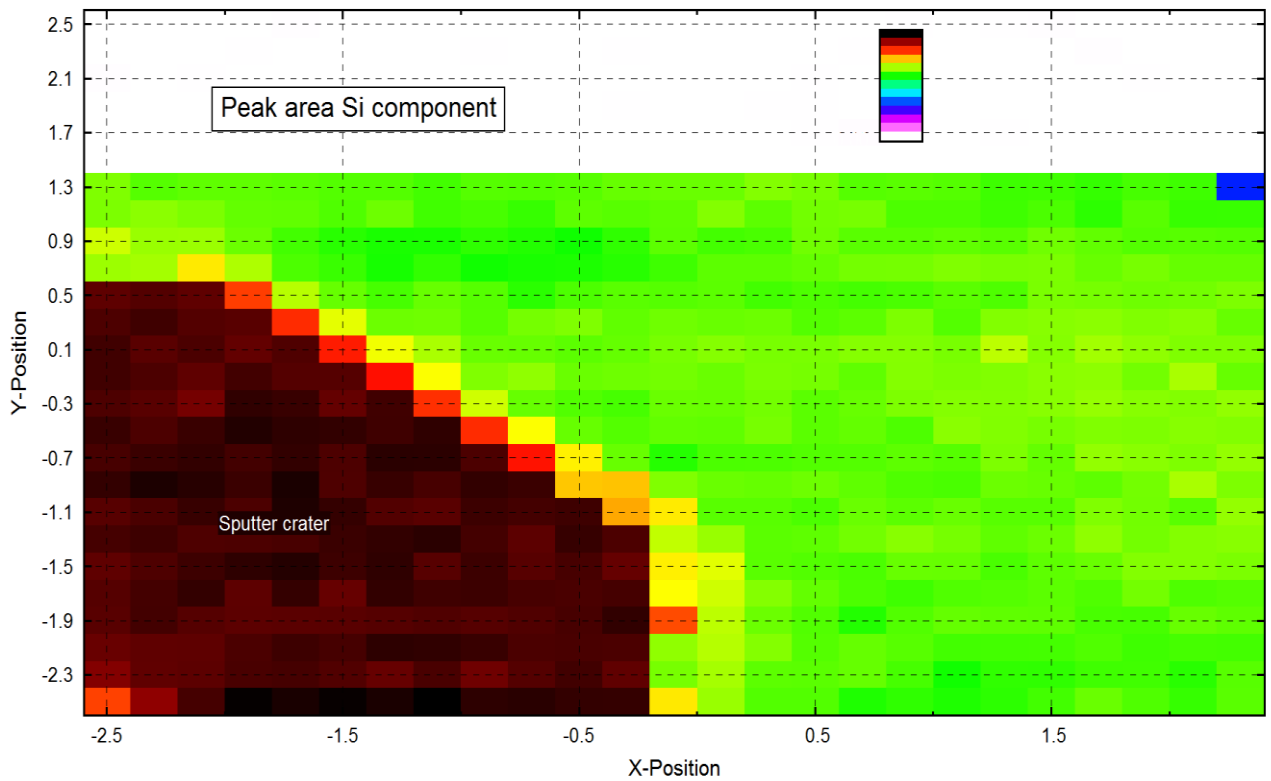


Fig 70.. 'XY 3D Colour Profile' of the fitted Si component of Si 2p (Si/SiO₂), the removed oxide layer of the sputter crater gives a dark colour of the Si substrate signal (on the left side)

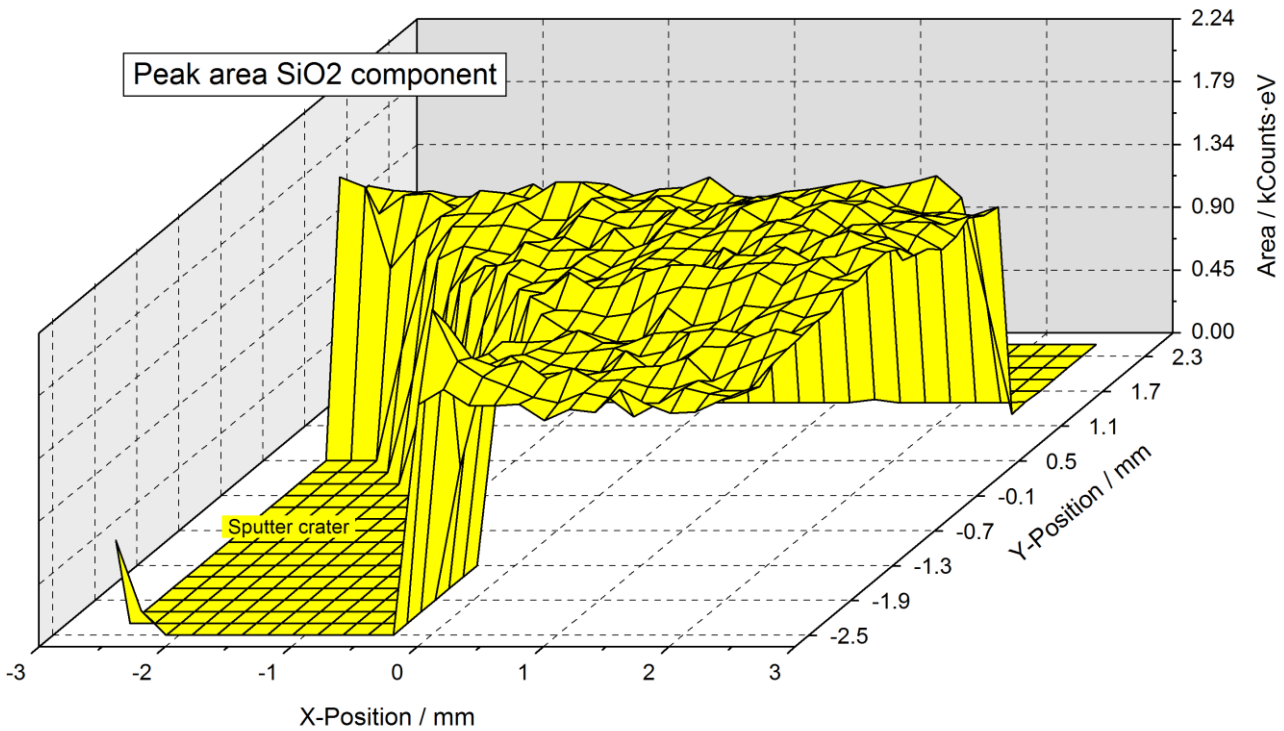


Fig. 71. 'XY 3D Plot 45°' of the fitted SiO₂ component of Si 2p (Si/SiO₂), the removed oxide layer of the sputter crater results in zero intensities of the SiO₂ signal (in front on the left side)

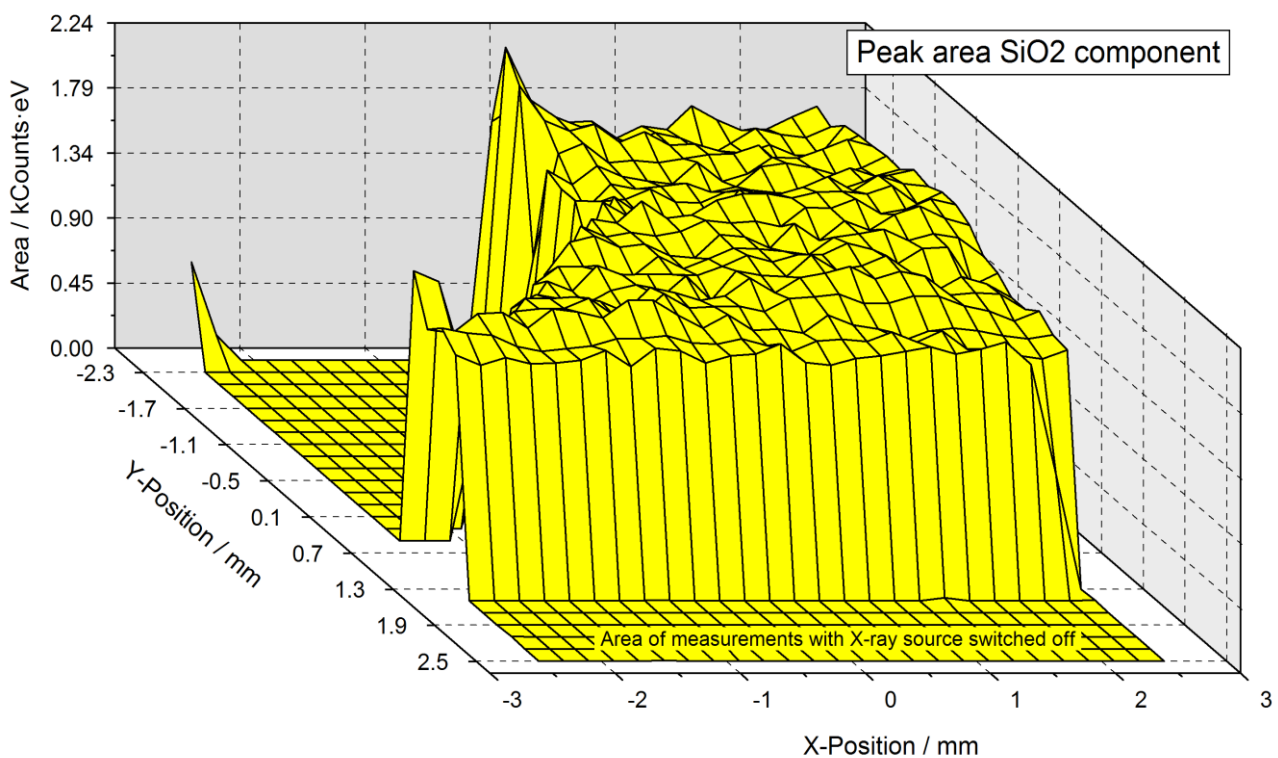


Fig. 72. 'XY 3D Plot -45°' of the peak area of the fitted SiO₂ component of Si 2p (Si/SiO₂), the removed oxide layer of the sputter crater results in zero intensities of the SiO₂ signal (back on the left side)

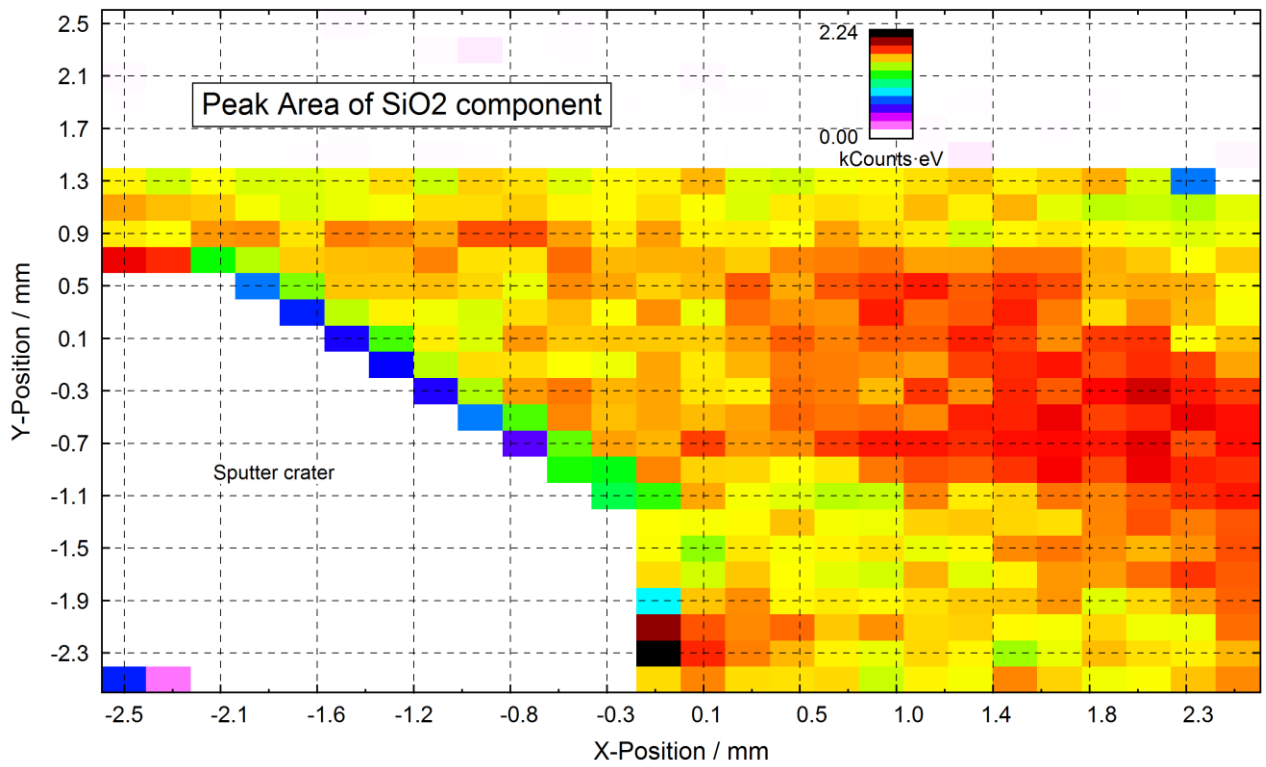


Fig. 73. 'XY 3D Colour Profile' of the fitted SiO₂ component of Si 2p (Si/SiO₂), the removed oxide layer of the sputter crater gives a white colour of the SiO₂ signal (on the left side)

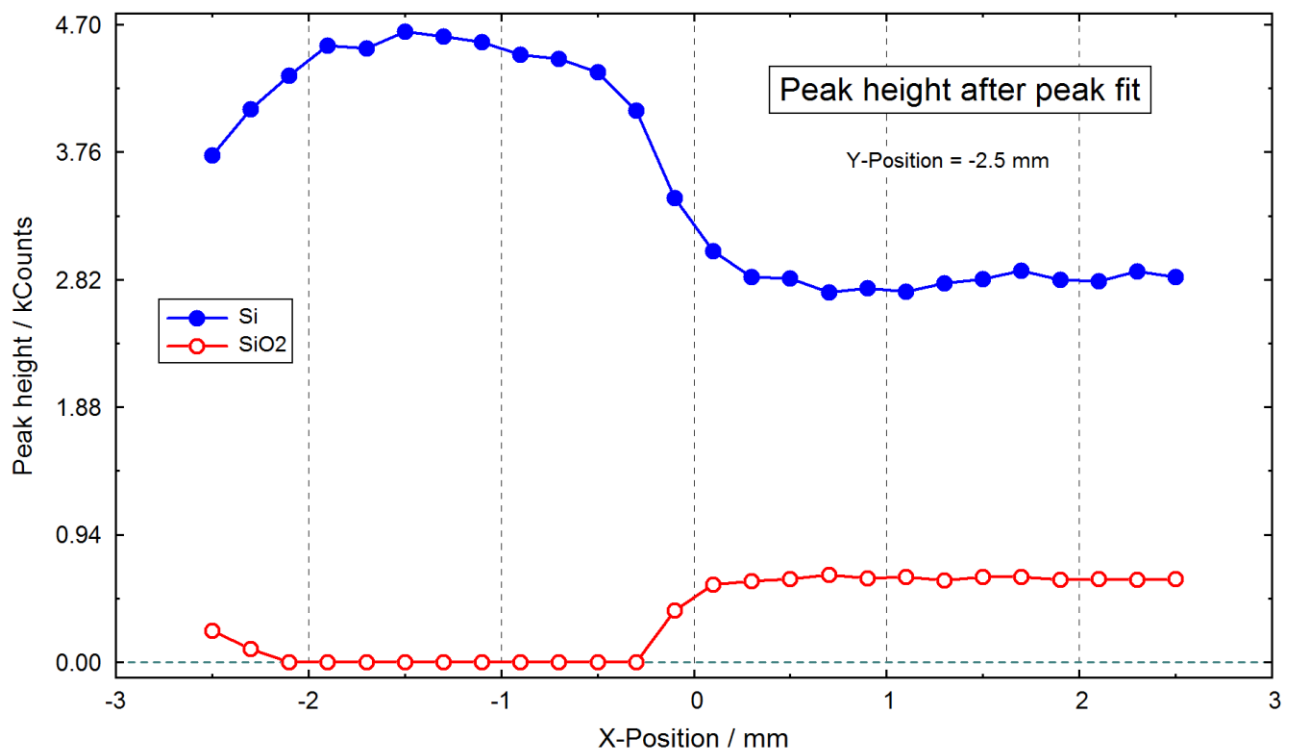


Fig. 74. Parameter plot of the peak height of the two components Si and SiO₂ of Si 2p with respect to the X position of the sample, Y position = -2.5 mm

These presentations were designed and exported with UNIFIT and then inserted in this text document. Three results were received:

1. The sputter crater is shifted about 1.5 mm in both directions with respect to the normal recording position.
2. Because the sputter crater was not complete recorded, the size could not correctly estimated. The size is about $2 \times 2 \text{ mm}^2$.
3. The zero intensities of the area from the positions $y = 1.5 \text{ mm}$ to $y = 2.5 \text{ mm}$ represent the measurements without X-ray excitation.

4.5 Problem: Estimation of the recording size of a specific spectrometer setting

The recording size of a special setting of the spectrometer ESCALAB 220 iXL shall be estimated. A line scan measurement over the edge of a SiO_2 sample (73 recording points) was carried out (see Fig. 75). The spectrometer setting was the same as example 4.4. The project name is 'Unifit_2023_User_Files\examples\XPS\Si2p_LineScan_RecordingSizeEstimation.ufp'. The step size of the X-axis was 0.050 mm.

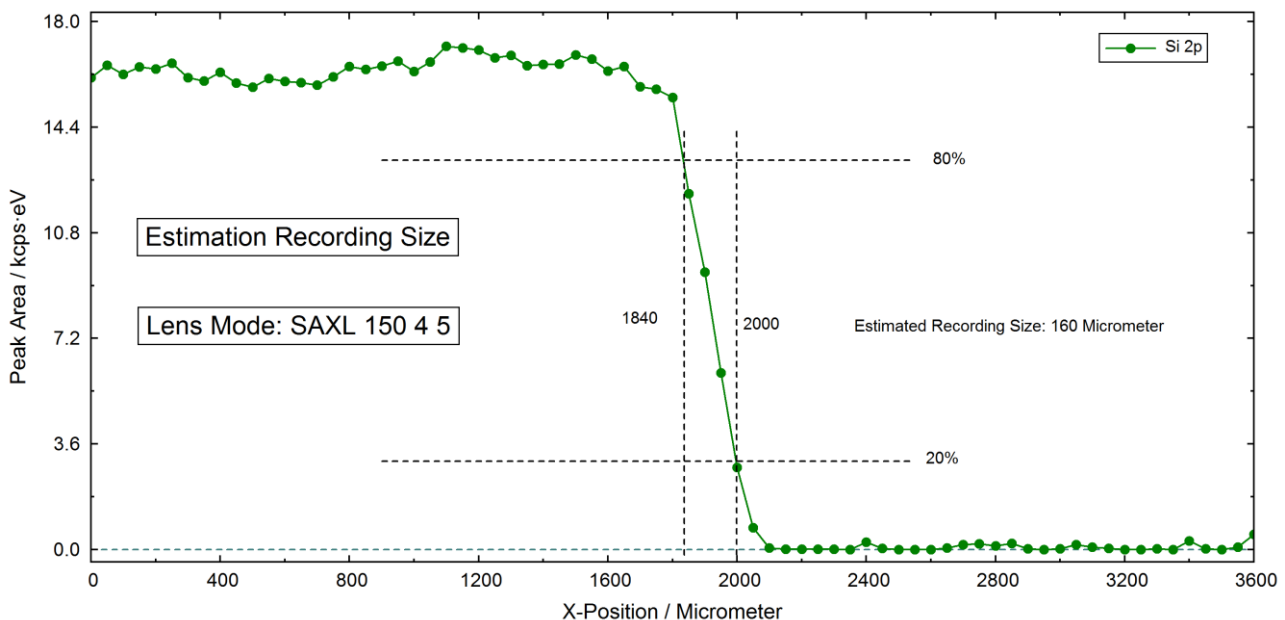


Fig. 75. Parameter plot of a line scan over the edge of a SiO_2 sample

5 Installation

A wafer USB card is supplied, which contains the installation programme setup-unifit2023.exe. Starting this, all software necessary for running UNIFIT will be copied to a user defined hard disk location:

1. Start Windows®.
2. Start Windows Explorer (Windows XP, Windows Vista, Windows 7, Windows 8, Windows 10).
3. Connect the wafer USB memory card on your computer, select USB disk.
4. Run setup-unifit2023.exe.
5. When the software has been copied, complete the installation process by arranging the UNIFIT 2023 icon on your desktop.
6. Change the setting of your monitor colour to 'True Colour (32 Bit) (important for image export and image copy).
7. Execute the programme using administrator mode and insert the activation key for activating the software.
8. Change the setting of the used anti-virus software. The programme Unifit2023.exe should be defined as 'Exclusion Process'. The setting steps of the Windows defender (Win 10) are:
 - a. Open 'Windows Defender'.
 - b. Open 'Virus & Threat Protection'.
 - c. Open 'Virus & Threat Protection Settings'.
 - d. Open 'Exclusions'.
 - e. Activate 'Add or Remove Exclusions'.
 - f. Activate 'Add an Exclusion' and 'Process'.
 - g. Add 'Unifit2023.exe'.

The first run of the software creates the directory 'Unifit_2023_User_Files' in the folder 'My documents'. This folder includes all editable user files, e.g. the preferences of UNIFIT, integrated data banks, examples, test spectra, folder for temporary files and the folder 'My Unifit Projects' for saving the received results.

| Folder | Comment |
|--|---|
| auger parameters | data for the Wagner plot |
| Lines | information about the line positions of the photoelectron lines, the chemical shifts and the energies of the Auger lines, energies of the AES target atom subshells |
| My Unifit Projects | this folder should be used for saving one's UNIFIT projects |
| presetting | preferences of UNIFIT |
| sensitivity factors | sensitivity factors for quantification |
| Settings | doublet data, default values for the peak fit, satellite data |
| Temp | for temporary saving |
| Temp1 - Temp60 | for temporary saving |
| XPS-transfct | calculated transmission functions |
| film | Reference data of film thickness estimation |
| Project Restore | includes backup files: Project Backup_1.ufp, ... , Backup_5.ufp |
| design | includes saved design files |
| inelastic electron scattering cross-sections | includes inelastic electron scattering cross-sections of different materials |

| | |
|---|---|
| examples | includes example projects for the demonstration of the software functions |
| Exercises | includes example projects for the UNIFIT workshop |
| ReadTaskList.bat | Reads the task list using tasklist.exe (important for multitasking) |
| TaskList.txt | Includes the current activated tasks |
| test spectra | includes special test projects for the testing of programme routines (e.g. background correction, generation of model functions, ...) |
| VamasConverterJeolJamp9500F/ VamasConverterJeolJamp9500F.EXE | Converts incorrectly exported *.npl files of the spectrometer JoelJamp9500F to VAMAS files with a correct data structure, the *.npl files and the converter programme must be in the same directory |
| VamasConverterJeolJamp9500F/ VamasPacker.EXE | Generates one VAMAS file (..._all.vms) using of other different VAMAS files (..._01.vms, ..., ..._10.vms) , the VAMAS files and the packer programme must be in the same directory |
| logo | Includes the Unifit logo.wmf |
| RRUFF RAMAN spectra | For saving of RRUFF RAMAN reference spectra |
| My Unifit Project Processing Steps | Default folder for *.ppd files, ppd files save processing steps and design features |
| AnimatedGIFs | Default folder for exported image files, includes also the converter software gifanimator.exe for the generation of animated gif files |

In case one loses the data included in *\Documents\Unifit_2023_User_Files a copy of the default settings is available in *\Unifit2023\Unifit_2023_User_Files. The data will be copied automatically.

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Λ

λ *see* inelastic mean free path (IMFP)

Σ

σ *see* sigma values, Scofield values, *see*
 sigma values, Scofield values

X

χ^2 *see* Chi-square
 χ^{2*} *see* Chi-square star