UNIFIT - Spectrum Processing, Peak Fitting, Analysis and Presentation Software for XPS, AES, XAS and RAMAN Spectroscopy Based on WINDOWS

UNIFIT FOR WINDOWS is an universal processing, analysis and presentation software for photoelectron spectroscopy (XPS, SXPS and ARXPS), X-ray absorption spectroscopy (XAS [XANES, NEXAFS, and XMCD studies]), 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 may considerably reduce the loading and processing time of projects with a large number of spectra. The software can be ten times executed simultaneously.

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. The monitor setting has to be 'True Colour (32 Bit)' in case of using the high resolution image export routine.

The programme permits the simultaneous handling of up to 75600 windows with spectra or other presentations. 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 and 3D windows can be displayed only using windows with the numbers 1 - 100. 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. 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. Fourteen presentations are available:

1. **Standard:** presentation of spectra, saved transmission or loss functions,
2. **Wagner Plot:** presentation of Auger parameters.
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.
4. **3D Waterfall 0° Plus:** presentation of fitted spectra of parameter dependent measurements without x-shift in one window.
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.
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.
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.

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.
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.
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.
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.
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.
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 ...).
14. **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.

With the menu point **preferences** the operator can define, store and load (*.set) all setting parameters of the programme handling. In order to optimize the using of the main memory the dimension of the five general programme parameters and the number of the first standard window (1 - 101) may be aligned to the current analysis task. The toolbar can be modified and switched on or off. The size of the icons is variable. The size, form and colour of the menu text and table export (fit parameters, fit-parameter errors, quantification results, and XAS background parameters) may be modified independent of the spectra windows setting. The

programme language is German or English. 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. The layout of the printout can be equal to the monitor setting or defined separately. The user can activate an automatic restore function of the UNIFIT projects and define the cyclic saving time. The loading of projects with or without the showing of saved quantification and film thickness tables is offered. The decimal character and delimiter of the exported data can be defined. Four options for the VAMAS and one option for the ScientaSES input are available. The resolution of the exported images may be changed in six levels up to 1200 dpi. The number of average points for the smoothing, differentiation and background calculation is variable. The presentation of the XP spectra may be done in kinetic energy or binding energy, the intensities in counts or cps. 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. 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. 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. The transmission function *IERF* can be loaded and defined manually. UNIFIT offers different mathematical backgrounds of the model function (product, sum or convolution of Lorentzian and Gaussian functions) and fit parameters, XAS background parameters, and the XPS background parameters of inhomogeneous samples (absolute or relative) to realise the peak and background fit. 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). The option 'Batch Processing - Load Original Spectra' can be activated or deactivated. In case of a mamual spike correction before the batch processing this option should be deactivated (typical for RAMAN spectra). Additionally, the user can choose from two different methods for the calculation of the fit-parameter errors.

An extended **input routine** allows the direct reading of measurement data of different kinds (see book: Line Positions and Data Formats, saved on USB-memory card). All processing steps, the window sizes, positions and design elements of all opened windows, the quantification table as well as the film thickness estimation may be stored as one project. The original measurement data are saved in a separate directory. The automatically saved backups of the projects can be opened. Auger parameters can be easily plotted as Wagner plot. Images (all typical data formas: wmf, tif, jpg,...) can be loaded (e.g. corresponding SEM images of a SAM measurement). The integrated test spectra and the well chosen examples enable the user to test the different functions of the programme without measured data. A closing function for all windows or all standard windows is available. The presentation of the active window can be transferred to the clipboard via the copy–paste function or exported as image taking a commonly used format (jpg, bmp, gif, wmf, etc.). The resolution may be selected stepwise from the monitor resolution to 1200 dpi in six steps. The data achieved with the spectra analysis 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. The menus 'Select Spectra' and 'Select Blocks' allow the individual displaying of spectra from the loaded data file.

For the spectra **modification** menu there is an undo function, a copy and paste function, a correction with the IERF, options for charge correction of the active window, several procedures for the background calculation, satellite subtraction, reduction, expansion, smoothing, differentiation, integration, mirroring, and spike correction as well as the possibility for spectra manipulation and operation. Additionally, a normalization routine with four different methods is available.

The **peak fit** 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. 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 the first out of a group of peaks. 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 or Fermi levels. The curve-fit results can be printed including fit, acquisition parameters, and additional comments, or exported for further treatment and presentation.

The **batch-processing** 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, 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 and five presentations for multipoint measurements are available. A charge correction and a reload of the original measurement data for all or specific selected standard windows are available.

A **quantitative analysis** 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.

The **information** about the acquisition parameters or the processing steps may be displayed any time. The charge correction, the quantities of the peak fit and the correction of the magnetic field (important for XMCD measurements) can be displayed of maximal 100 windows. The minimum and maximum of the intensity of the activated standard window can be shown. The FWHM 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 is available. Identification and labelling of the peaks may be realized with the integrated data base of photoelectron lines. An additional data base of Auger parameters can be presented as chemical state plot (Wagner plot). A project comment can be used for the specification of the individual treatment of the sample. The data banks integrated in UNIFIT (sensitivity factors, line positions, Auger parameters, doublet data, AES target atom subshells) can be shown, edited and extended directly with special sub-programmes. The calculated inelastic electron cross-section can be plotted. A special tool for the caculation of AES sensitivity factors is available. Additionally, the main memory usable and currently used by UNIFIT can be displayed.

The subroutine **Annotation/Design** gives the user the manual control over the scaling and labelling of the energy/wave number, intensity, parameter axis as well as the x and y recording position. Grid lines can be plotted optionally. Additionally, the spectrum may be entitled and labelled with formatted or unformatted text. 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 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 (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 design setting, the spectrum title and the complete labelling of the active window can be stored (*.dsg). 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 can be displayed using different forms.

The menu **Calibrate Intensity Scale** 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** handling gives the following options:

- three different tile arrangements of the windows,
- direct selection and activation of the windows, particularly next or previous ones,
- hide standard windows,
- hide standard windows (manual),
- changing manually the window size and position,
- changing of the windows number,
- four closing functions for windows and standard windows,
- show windows video sequence.

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

The menu point **UNIFIT** 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.