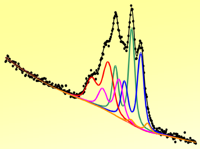
Unifit 2001 – The New 32-bit Program for XPS Peak Fitting under WINDOWS



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1. Motivation

An adequate modelling of experimental photoelectron spectra containing several different components has remained a challenge all the time, regardless of the achieved level for energy resolution and sensitivity of spectrometers. The higher the resolution, the more detailed information on binding energies and intensities of components with decreasing energetic distance can be gained. In order to obtain the desired information from core level spectra several computer codes have been developed in the past that base on the description of experimental data by synthesis of theoretical model functions.
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 program codes are very often tailor-made for single spectrometers and special applications. In many cases they have been written for use by insiders only.
In order to fill this gap, a program for peak shape analysis of core level photoelectron spectra has been developed, tested and used intensively by the author's group for years. The name is UNIFIT FOR WINDOWS, which involves appropriate description of the spectra by adequate models, excellent numerical performance for fast calculations, convenient data handling, and versatile opportunities for data transfer and representation [1].

Now, we present the second 32-bit version of the well approved XPS peak fitting program UNIFIT integrating a data bank of line positions and chemical shifts.

2. General Characteristics

UNIFIT FOR WINDOWS is an universal program for XPS core level peak shape analysis using Windows 95/98, Windows 2000 and Windows NT.

The peak fit is based on the non-linear least-squares curve fitting algorithm of Marquardt. The program allows to choose the theoretical model for peak shape as multiplied or convoluted Gaussian-Lorentzian functions. Additionally, it is possible to include the background parameters in the fit routine. All parameters may be determined on absolute scales or they may be related in different ways to those of another peak. A possibility for batch processing is included in the program which permits a fast and comfortable treatment of measurement series (depth profiles, angle resolved spectra etc.).

Further important features:

- User defined preferences for fit procedure, fit parameters, language, details of presentation (colours and symbols) on the desktop as well as for printing, etc.,
- Acceptance of VAMAS (Norm and SDP) and NPL format,
  Load routines created on users demand for several data formats provided e.g. by VG-ESCALAB,
- Simultaneous handling of up to 30 windows,
- Background simulation by five different methods or combinations of them,
- Including the background in peakfit,
- Several data treatment sub-routines like e.g. charge correction, satellite subtraction, spike correction, differentiation, integration, smoothing, spectrum manipulation and spectrum operation
- Description of the experimental curves by up to 15 single peaks or doublets,
- Different options in order to keep e.g. energy distances, peak widths or relative intensities of peaks constant during iteration,
- Peak parameters may be varied freely, varied within a chosen interval or fixed at certain values,
- All options for spectra modification and peak fit can be included in batch processing,
- Quantitative analysis using surveys, single spectra or fitted components with cross sections as given by Wagner or Scofield or defined individually by the user,
- Print of curve-fit results (parameter table and graphic) including acquisition parameters, and additional comments,
- Export for further treatment and presentation.
- Creation of different satellite functions,
- Improved handling
- Integrated data of peak positions and chemical shifts.

3. Fit of a Test Function

A test function was created by ORIGIN (Fig.1) consisting of two Voigt functions with different parameters given in Table 1.
After transfer of the sum curve data to UNIFIT, the „spectrum" was fitted. The iteration start parameters were selected consciously roughly (Fig. 2).
The parameters of the calculated curves correspond very well to those of the original test function. The fast convergence even with non-optimal start parameters is obvious.

Parameter	Peak 1		Peak 2	
	Fit	Test	Fit	Test
Intensity	49924	50000	9957	10000
G-width (eV)	1.71	1.70	0.30	0.30
Position (eV)	282.00	282.00	284.00	284.00
L-width (eV)	0.29	0.30	1.73	1.70
Backg. Fit	$B(E)=99+1.34\cdot E+0.25\cdot E^2$			
Backg. Test	$B(E)=105+1\cdot E+0.25\cdot E^2$			

Tab. 1. Comparison of fest function parameters and result of fit procedure

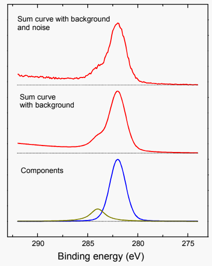

Fig. 1. Test function: generation

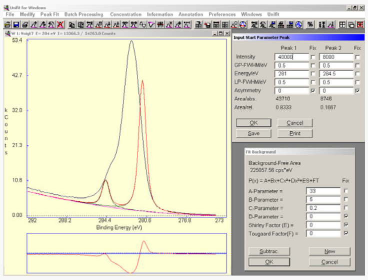

Fig. 2. Start iteration with rough parameter set

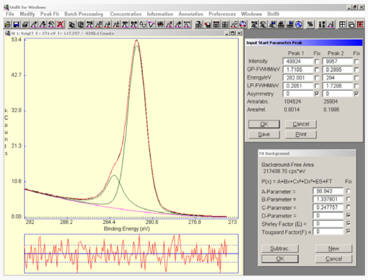

Fig. 3. Result of fit procedure (convolution) after 22 iteration steps with iterative background calculation

4. Batch Processing

The batch-processing sub-menu serves as fast and comfortable treatment of parameter-dependent experimental series e.g. depth profiles, angle resolved spectra etc..
The following possibilities are offered:

- Simultaneous loading of up to 80 parameter steps and 9 regions per step (i.e. 720 spectra),
- Acceptance of VAMAS format,
- Processing of 29 windows (30 minus the active one) in one step,
- Integration of all options for spectrum modification (e.g. background calculation, satellite subtraction...) and the peak fitting procedure,

Generation of data file for 3D-presentation and further treatment in commercial visualisation programs (e.g. ORIGIN, EXEL).

In order to demonstrate the efficiency of the batch processing routine an 11 step test-series consisting of spectra simulated by three Voigt functions with different intensity behaviour was defined and fitted with UNIFIT:

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

Lorentzian and Gaussian widths are fixed to 1eV each, the signals being symmetrical.

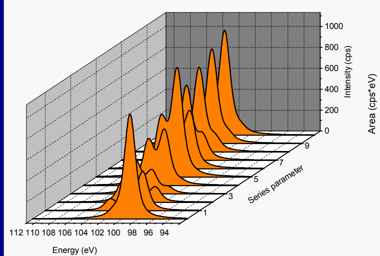

Fig. 4. Test profile: 3D-presentation

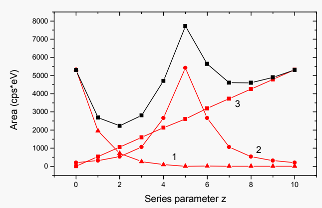

Fig. 5. Calculated areas in dependence on series parameter z: Black curve: total area after background subtraction only, Red curves (1-3): single peak areas 1-3 after batch processing with UNIFIT 2001

5. Integration of a data set of line positions and chemical shifts

In the new version of the well known program UNIFIT a data set of line positions and chemical shifts was integrated.
With this special feature it is possible to identify and annotate comfortably particular peaks (Fig. 6.). After peak fitting in a single region the components can be annotated with a suitable chemical name.
With a editing tool involved in the program the user can provide his own data set of chemical shifts.

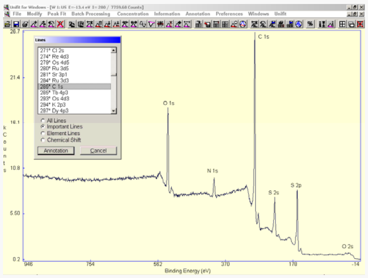

Fig.6. Example of peak identification and annotation of a survey

6. Adaptation of a typical synchrotron test function

The typical features of a synchrotron spectrum are:

- the intensity ratios my deviate from the multiplet rule,
- the intensity ratios of corresponding doublets in one peak are nearly the same.

For a test a doublet function (Tab. 2, Fig. 7) was generated with the software ORIGIN. A peak fit with the program UNIFIT 2001 and a special option was used to find the best adaptation for this complicated problem. The chosen start parameters were very rough (Fig. 8.). The results are presented in Table 2. and Figure 9.

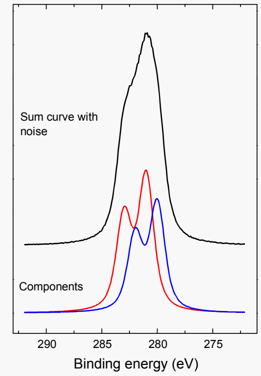

Fig. 7. Test doublet function: generation

Parameter	Peak11		Peak12		Peak21		Peak22	
	Fit	Test	Fit	Test	Fit	Test.	Fit	Test
Intensity	1070	1000	753	700	752	800	530	560
G-width	1.07	1.00	1,03	1.00	0,87	1.00	0,84	1.00
Position/eV	281,0	281.0	283,0	283.0	279,9	280.0	281,9	282.0
L-width	0,92	1.00	0,99	1.00	1,03	1.00	1,10	1.00

Tab. 2. Comparison of test doublet parameters and result of fit procedure

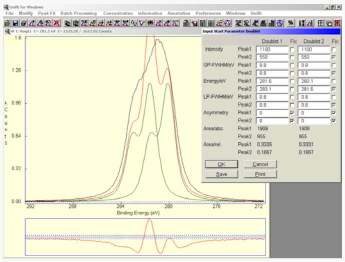

Fig. 8. Start iteration with rough parameter set and special options, black: generated peak, green: components, red: sum curve

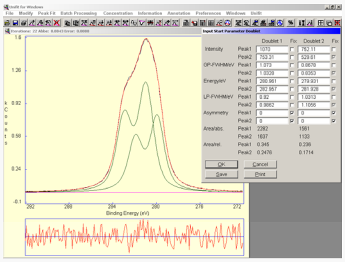

Fig.9. Result of fit procedure (convolution, special options) after 60 iteration steps

References :

[1] R.Hesse, T.Chassé, R.Szargan, Fresenius J. Anal. Chem., 365 (1999) 48

Website: www.uni-leipzig.de/~unifit

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