UNIFIT 2008 - Spectrum Processing, Analysis and Presentation Software for Photoelectron Spectra

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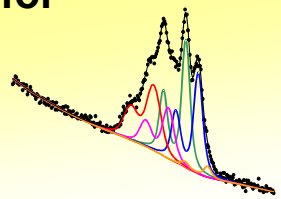

Motivation

The aim of the development of the program UNIFIT is to combine appropriate description of the spectra by adequate models, convenient data handling, excellent numerical performance for fast calculation with versatile opportunities for data transfer, comfortable handling, extensive graphical design options and fast export of high resolution graphics. The advantage of the presented software is the complete treatment of the data from the measurement up to the presentation.

Peak fit

1. Model functions for fitting photoelectron lines

The program offers all three commonly applied models for fitting photoelectron spectra: **product**, **sum,** and **convolution** of Gaussian and Lorentzian functions [1]. In order to illustrate the differences of the models a Cu 3p spectrum was fitted with two independent single lines and an adjustable background consisting of a 3rd degree polynomial and a Shirley background. The theoretically expected intensity ratio of $\mathbf{3p_{3/2}/3p_{1/2}}$ of **2:1** is well reproduced applying the sum or (correct) convolution model but not with the product function. (G', G'', L', L'' Gaussian and Lorentzian functions modified by the mixing ratio)

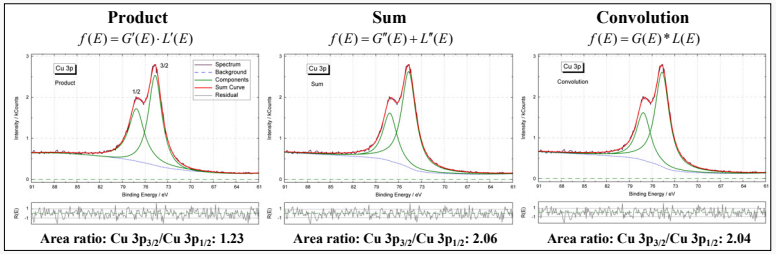

Fig. 1. Comparative study of the three commonly used model functions: product, sum, convolution, graphics created using UNIFIT

2. Estimation of the valence-band edge and Fermi level using curve fit

The study of the band structure of solids demands the knowledge of valence-band edge and Fermi level. We recommend improved methods for determination of these values.

In contrast to the traditional procedure defining the **valence-band edge** by a linear approximation of the decreasing intensity, a more realistic approach by convoluting square root $W(E)$ and Gaussian functions $G(E)$ is used: $f(E) = W(E)*G(E)$. A synthetic test spectrum $f(E)$ was generated with the following parameters:

- Valence-band edge (zero point of $W(E)$): E_{VB} = **1.50 eV**,
- FWHM Gaussian peak: **2.5 eV,**
- normally distributed statistical noise.

The presented example shows the approach with the traditional method (linear function, Fig. 2, green curve, E_{VB} = **0.5 eV**) and the more realistic approach (convolution function, Fig. 2, red curve, E_{VB} = **1.47 eV**).

In UNIFIT 2008 the **Fermi level** is approximated using the convolution of Theta function $\Theta(E)$ and Gaussian function $G(E)$ [$f(E) = \Theta(E)*G(E)$]. A synthetic test spectrum was generated with the following parameters:

- Fermi level (jumping point of $\Theta(E)$): E_F = **3.275 eV,**
- *FWHM* Gaussian peak: **2.6 eV,**
- normally distributed statistical noise.

The example shows the approach with the new implemented method (Fig. 3, red curve, E_F = **3.27 eV**) compared with a linear approximation (Fig. 3 green curve, E_F = **3.35 eV**).

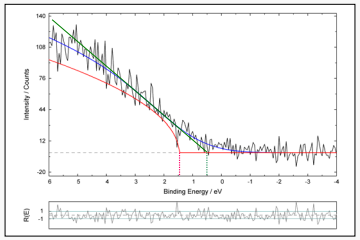

Fig. 2. Estimated valence-band edge
green: linear function E_{VB} = **0.5 eV**
red: square-root function E_{VB} = **1.47 eV**, *FWHM* = 2.72 eV
blue: convolution function

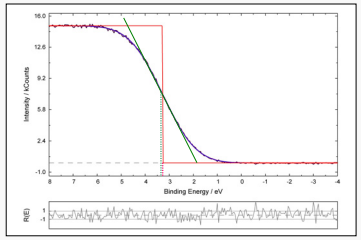

Fig. 3. Estimated Fermi level
green: linear function E_F = **3.35 eV**
red: Theta function E_F = **3.27 eV**, *FWHM* = 2,59 eV
blue: convolution function

Quantification

1. Quantification

UNIFIT allows the quantitative analysis of experimental data. The background-free areas of the peaks weighted with sensitivity factors SF are used for determination of element percentages. The components of a fitted peak are included in the quantification table (Fig. 4) for determination of the percentages of the chemical compounds. The following options are available:

- using of theoretical or experimental SF's,
- annotation of the chemical species,
- export of the quantification data,
- export of the quantification table as JPG image (Fig. 5),
- presentation of the quantification data as parameter plot.

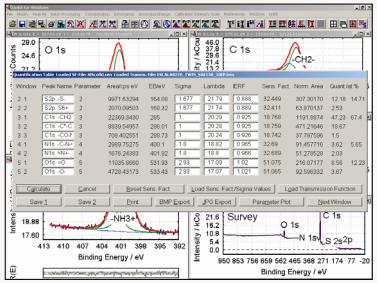

Fig. 4. Dialog of quantification of sulphur, carbon, oxygen and nitrogen using the sensitivity factors defined by the product of σ, λ and the predetermined transmission function IERF.

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. 5. Exported and in this Power Point paper inserted quantification table

2. Calibration of the intensity scale

The presented software enables the user to determine the transmission function IERF (Intensity/Energy Response Function) of the used spectrometer in two different ways:

1. survey spectra approach on reference spectra,
2. quantification of standard peaks from Au, Ag and Cu.

The resulting functions IERF can be saved, printed out, and can be applied in the concentration analysis routine. Fig. 6 shows the calculated transmission functions of our spectrometer ESCALAB 220 iXL [2].

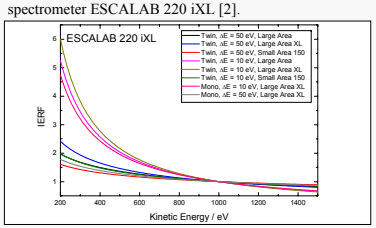

Fig. 6. IERF's of the spectrometer ESCALAB 220 iXL

Presentation

The software UNIFIT offers nine different presentations:

1. measured and fitted spectrum (Fig. 1),
2. transmission function (Fig. 6),
3. Wagner plot (Fig 7),
4. 3D-waterfall 0°,
5. 3D-waterfall 45°,
6. 3D-waterfall -45° (Fig. 10),
7. 3D-colour profile (Fig. 8),
8. 3D-presentation of fitted spectra,
9. parameter plot (Fig. 9).

Extensive graphical design tools permit the individual creation of the presentations. The graphics may be exported as BMP or JPG images with a resolution of 600 dpi. The saved pictures may be easily inserted in each Power Point presentation or Word document. The time for creating a presentable graphic may be reduced significantly using UNIFIT in comparison to Excel or Origin without loss of quality.

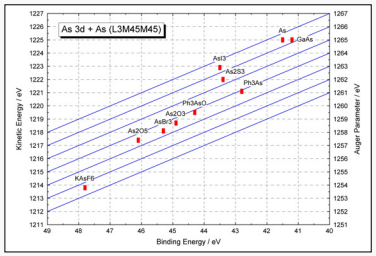

Fig. 7. Wagner plot As 3d + AS (L3M45M45)

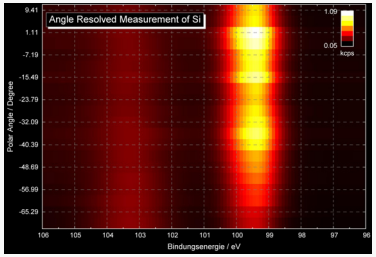

Fig. 8. Color plot of a angle resolved measurement of Si

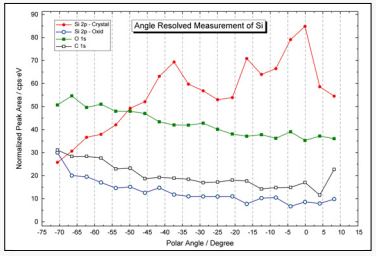

Fig. 9. Parameter Plot of a Angle Resolved Measurement of Si

Specials

1. Batch processing

The batch-processing submenu serves as a fast and comfortable treatment of parameter-dependent experimental series, e.g., depth profiles, angle resolved spectra etc. Special features are:

- Simultaneous loading of up to 80 parameter steps and 9 regions per step (i.e. 720 spectra),
- Processing of 99 windows (100 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 3D-presentation (Fig. 10) or parameter plot (Fig. 11) directly with UNIFIT or data export for further treatment (e.g. ORIGIN).

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: $I_3(z) = 100 \cdot z$

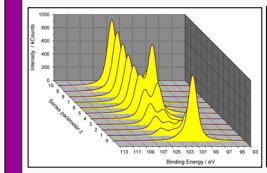

Fig. 10. Test series, 3D presentation -45°, graphic created using UNIFIT 2008

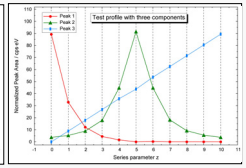

Fig. 11. Test series, parameter plot after quantification, graphic created using UNIFIT 2008

2. Calculation of fit-parameter errors

UNIFIT permits the calculation of fit-parameter errors after peak fitting (see Fig. 12). According to the chosen option the user can calculate the errors with two different methods: **matrix inversion** or **iterative calculation**. The uncertainties can be shown as absolute values or relative to the fit parameters. The parameter errors can be exported and printed out [3].

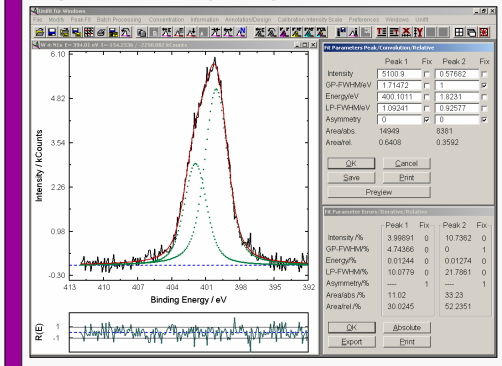

Fig. 12. Screen shot from UNIFIT 2008, peak fit of N 1s with two components, fit-parameter table and table of the calculated relative errors

References:

[1] R. Hesse, P. Streubel, R. Szargan, Surf. Interface Anal. (2007) Vol. 39, 381
[2] R. Hesse, P. Streubel, R. Szargan, Surf. Interface Anal. (2005) Vol. 37, 589
[3] R. Hesse, T. Chassé, P. Streubel, R. Szargan, Surf. Interface Anal. (2004) Vol. 36, 1373

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