

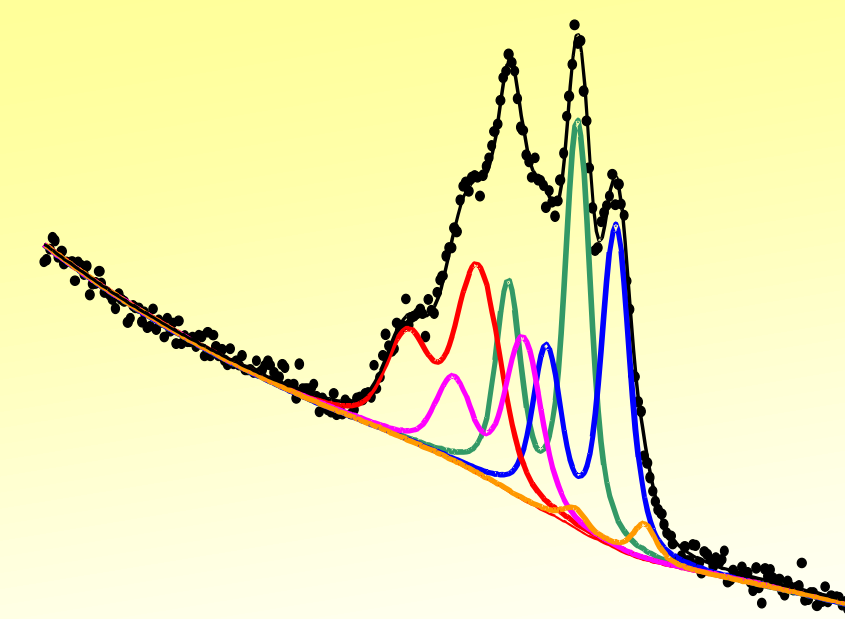
Improved Estimation of the Spectrometer-Transmission Function with UNIFIT 2022



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Abstract

The recent development of x-ray photoelectron spectroscopy using excitation sources different from the usual lab-source Mg K α and Al K α and spectrometers with more sophisticated lense systems (like ambient pressure setups) requires more flexible approaches for determining the transmission function than the well-established ones using reference spectra of noble metals. Therefore, the approach using quantified peak areas (QPA) was refined. A new algorithm allows a more precise estimation of the transmission function which could be shown by comparing the results obtained with the new version with former calculations. Furthermore, reference materials others than Cu, Ag and Au can be used. Ionic liquids can be used as reference for estimating the transmission function at beamlines with variable excitation energies. Comparison between the measured and stoichiometric composition shows that a transmission function was determined which allows a reasonable quantification.

Theoretical Basis

In order to expand the estimation of $T(E)$ using variable excitation energies, different kinetic energies E of the reference peaks or different reference compounds the quantified peak areas (QPA) method was improved. In an effort to clearly explain the method, the steps already used in the previous QPA approach are¹ also included here. With the known values of the inelastic mean free path $\lambda(E)$, the ionization cross section $\sigma(h\nu)$ and the background-free peak area A under the selected photoemission signals of the reference compound the corrected peak area A' is given by

$$A' = \frac{A}{\lambda(E)\sigma(h\nu)T(E)} \quad (1)$$

An approximate estimation of the atomic ratio X_1/X_2 of the element 1 and 2 is obtained neglecting the matrix effect originating from λ

$$\frac{A'_1}{A'_2} \cong \frac{X_1}{X_2} \quad (2)$$

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

$$\frac{X_2 \frac{A_1}{\sigma_1(h\nu)\lambda_1(E_1)}}{X_1 \frac{A_2}{\sigma_2(h\nu)\lambda_2(E_2)}} = \frac{T(E_1)}{T(E_2)} \quad (3)$$

Introducing the normalized reference value r_i of a photoelectron peak i :

$$r_i = \frac{A_i}{X_i \sigma_i(h\nu) \lambda_i(E_i)} \quad (4)$$

we can write for the photoelectron peak pair of peak 1 and 2 with the exact transmission function

$$\frac{T(E_2) \cdot r_1}{T(E_1) \cdot r_2} = 1 \quad (5)$$

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

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

$$T(E) = a_0 + a_1 \varepsilon + a_2 \varepsilon^2 + a_3 \varepsilon^3 + a_4 \varepsilon^4 + b_1 E^{b_2} \quad (6)$$

with the fit parameters $a_0, a_1, a_2, a_3, a_4, b_1, b_2, E_0$ and $\varepsilon = (E - E_0)/E_0$. After calculation of the reference values r_i (Eqn. 4) for the photoelectron peaks of the reference compound the transmission function $T(E)$ may be approximated by minimization of the sum of the squared deviations SSD varying the parameters of the chosen model function $T(E)$ from Eqn. (6):

$$SSD = \sum_{n=1}^k \left(\frac{T(E_{2n}) \cdot r_{1,2n-1}(E_{2n-1})}{T(E_{2n-1}) \cdot r_{2n}(E_{2n})} - 1 \right)^2 \quad (7)$$

with k = number of pairs of photoelectron lines (max. 10). The value “1” represents the situation with the transmission function according to Eqn. (5). Obviously, the SSD value represents the quality of the agreement between the model transmission function and the exact (but unknown) transmission function. The value of SSD depends also on the number of pairs k .

In order to find the minimum of SSD , all possible combinations of the free fit parameters of Eqn. (6) were optimized in maximal five sweeps (lowest accuracy: one sweep, highest accuracy: 5 sweeps) and maximal 99 cycles. Eleven optimization loops per sweep are carried out (x = start/fit parameter, n = number of cycle).

Sweep/cycle	$a_0, a_1, a_2, a_3, a_4, b_1$	b_2	E_0
1/n	$x-5$ to $x+5$	$x-1$ to $x+1$	$x-100$ to $x+100$
2/n	$x-0.5$ to $x+0.5$	$x-0.1$ to $x+0.1$	$x-60$ to $x+60$
...			
5/n	$x-0.0005$ - $x+0.0005$	$x-0.00002$ to $x+0.00002$	$x-5$ to $x+5$

Example

The transmission function $T(E)$ of the spectrometer ESCALB 220 iXL are estimated (**source:** Al/Mg Twin, **pass energy:** 10 eV, **lense mode:** LAXL (magnetic lense)). The reference peaks are Au 4d, Au 4p_{3/2}, Ag 3d, Ag 3p_{3/2}, Cu 3p, Cu 2p_{3/2}, Ge 3d and Ge 2p_{3/2} (Fig. 1). The calculation with UNIFIT 2022 was performed with five free parameters (a_0, a_1, a_2, b_1 and b_2 , table 1) and three sweeps and cycles were defined. The input data compared with the $T(E)$ function are displayed in figure 1 (start parameters) and figure 2 (estimated parameters). Figure 3 shows the calculated transmission functions $T(E)$ of different lense modes.

Parameters	Start	Result
a_0 , free	1.00	0.00
a_1 , free	0.00	0.00
a_2 , free	0.00	0.00
a_3 , fix	0.00	0.00
a_4 , fix	0.00	0.00
b_1 , free	1.00	2198
b_2 , free	-0.50	-1.11
E_0 /eV, fix	1000	1000
Error/SSD:		0.01046
Estimation Time/sec:		1953

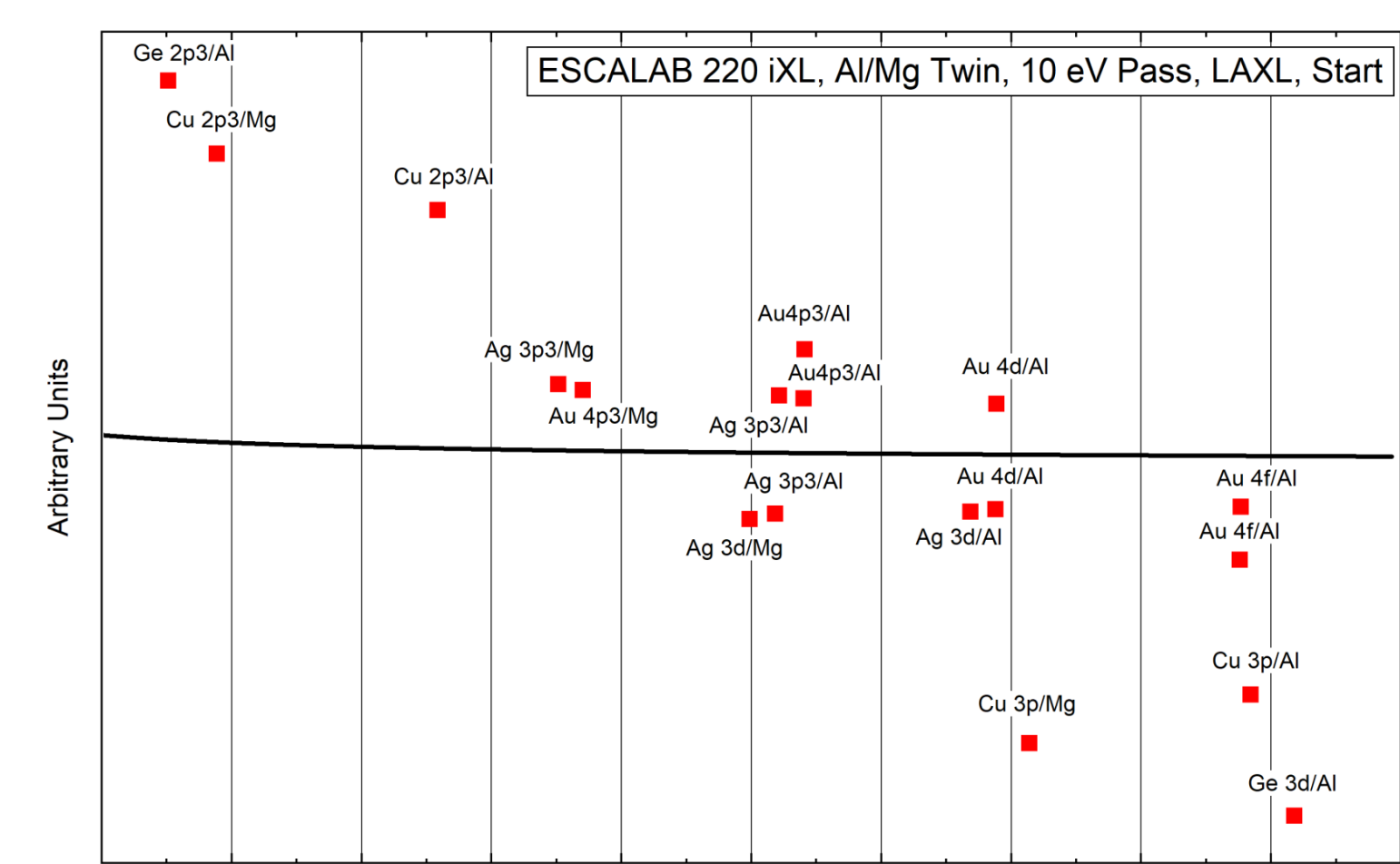


Fig. 1 Input values (squares) and $T(E)$ start function before the fit with the start parameters of table 1, (solid line),

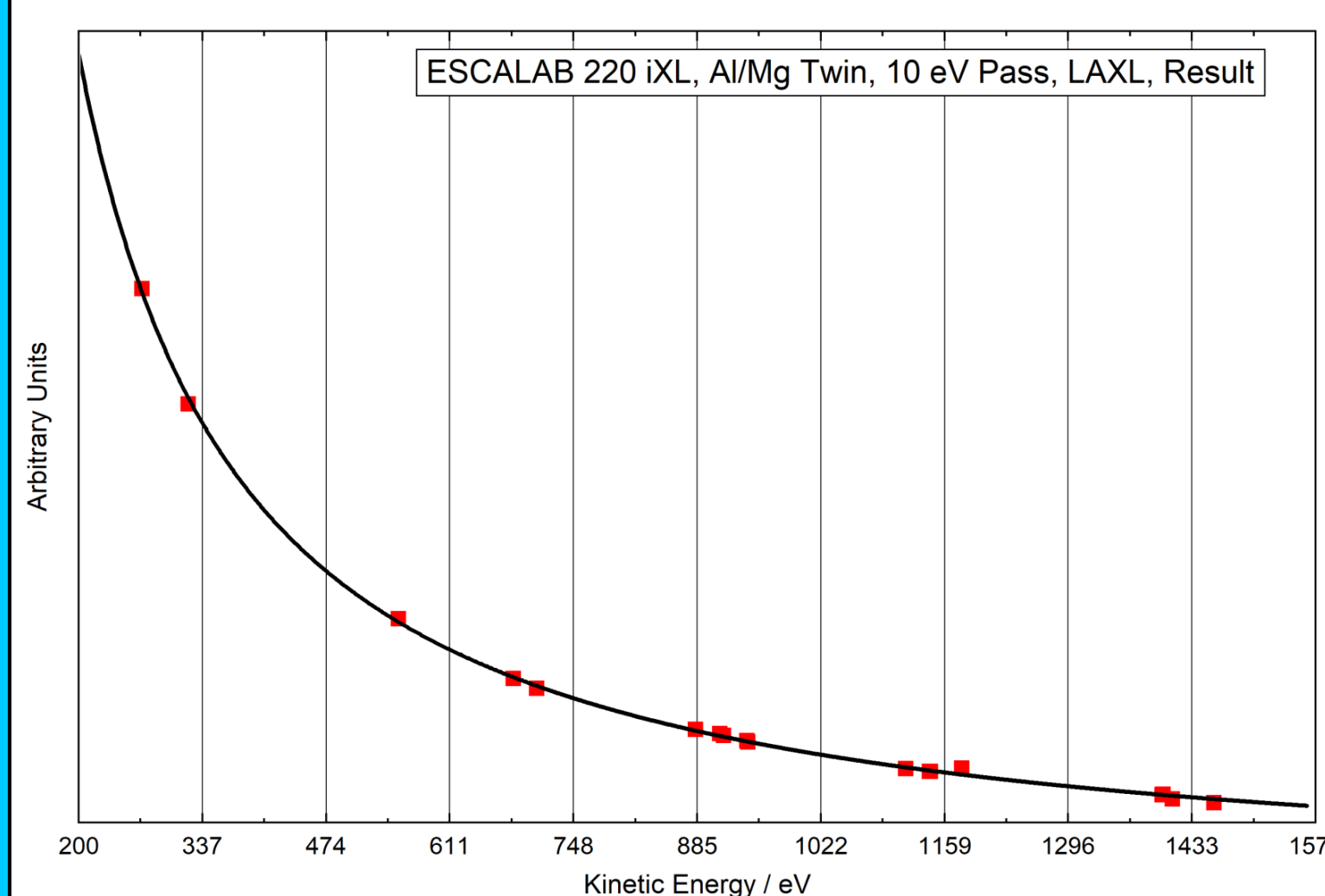


Fig. 2 Input values (squares) and $T(E)$ function (solid line) after the fit with the fit parameters of table 1

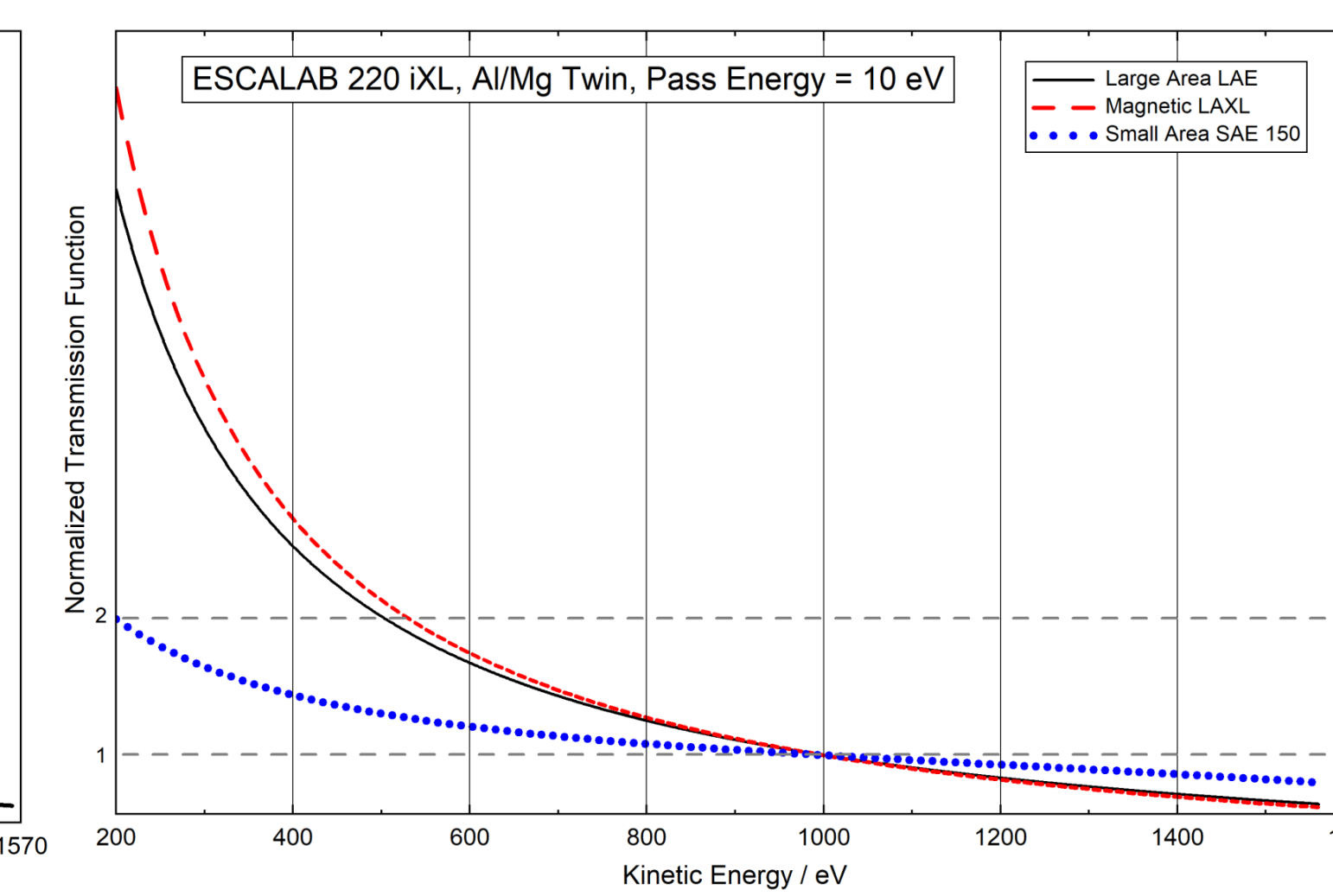


Fig. 3 Calculated $T(E)$ functions, ESCALAB 220 iXL, Pass energy: 10 eV, lense modes: LAE, LAX and SAE 150

Operating the Programme

The following operation steps illustrate a simple way to generate reference pairs:

1. Load a typical project for quantification
2. Open the quantification routine for two peaks of one pair
3. Set all $T(E) = 1$ and press ‘Calculate’ (Fig 4)
4. The reference values r_i (Eqn. 4) are shown in the last column (Fig 5)
5. With the key combination ‘Alt-’ the concentration results (name, energy (always in kinetic energy), quantification (in %, last column)) of exactly two elements can be saved. The file with the extension *.pai can be loaded using the command ‘Load Data of one Pair (*.pai)’ (Fig. 6).

After pressing ‘Calculate’ the input data and the model functions are plotted in one frame (Fig. 8, x axis in kinetic energy) and the menu for the input of the parameters for the model function $T(E)$ appears. Additionally, the number of cycles, number of sweeps and the break condition can be defined. At the displayed energy range $T(E) > 0$. Calculation time = Number of cycles · Number of sweeps · 11 Number of free fit parameters.

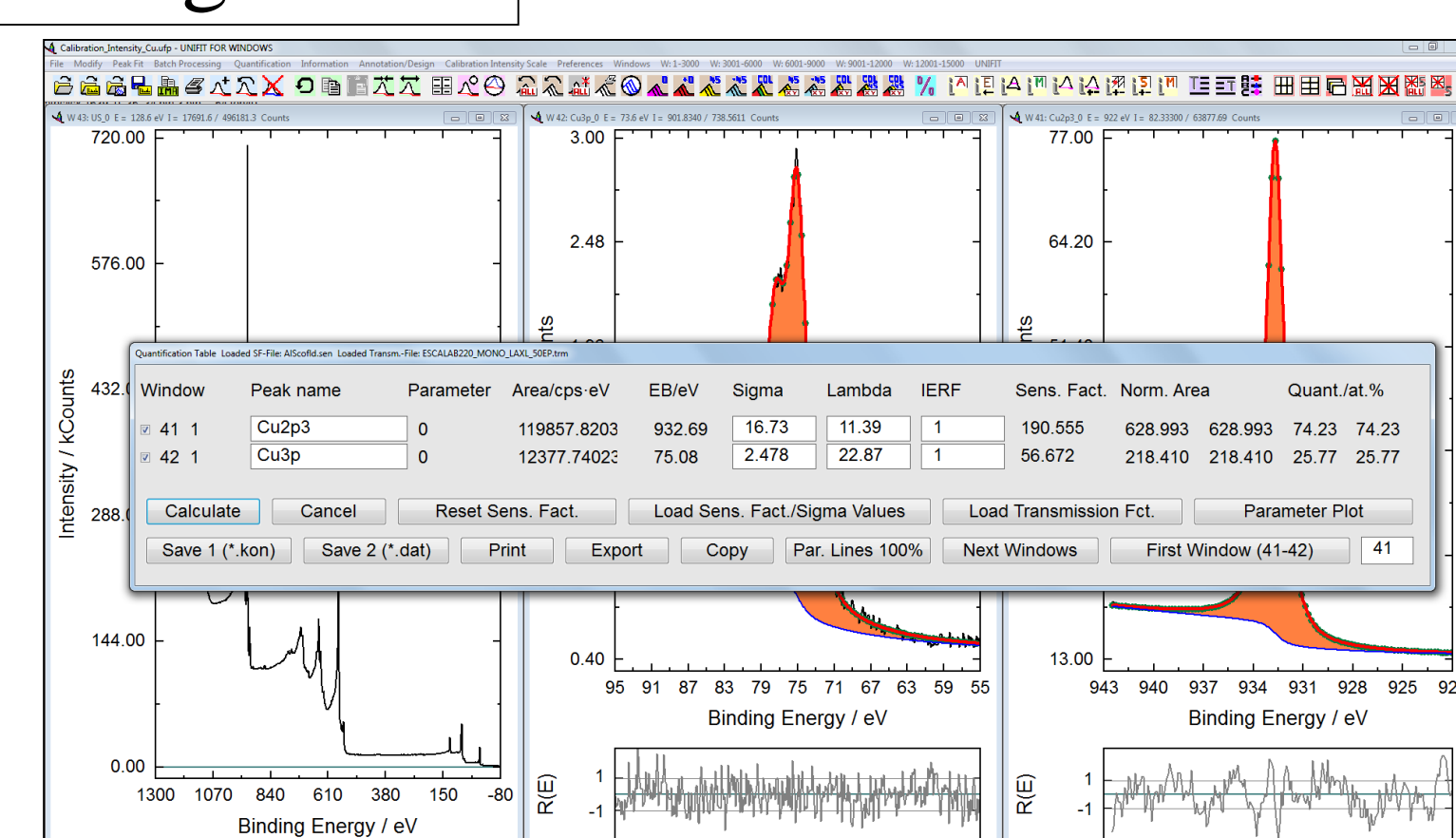


Fig. 4 Dialog of the quantification with $T(E) = 1$

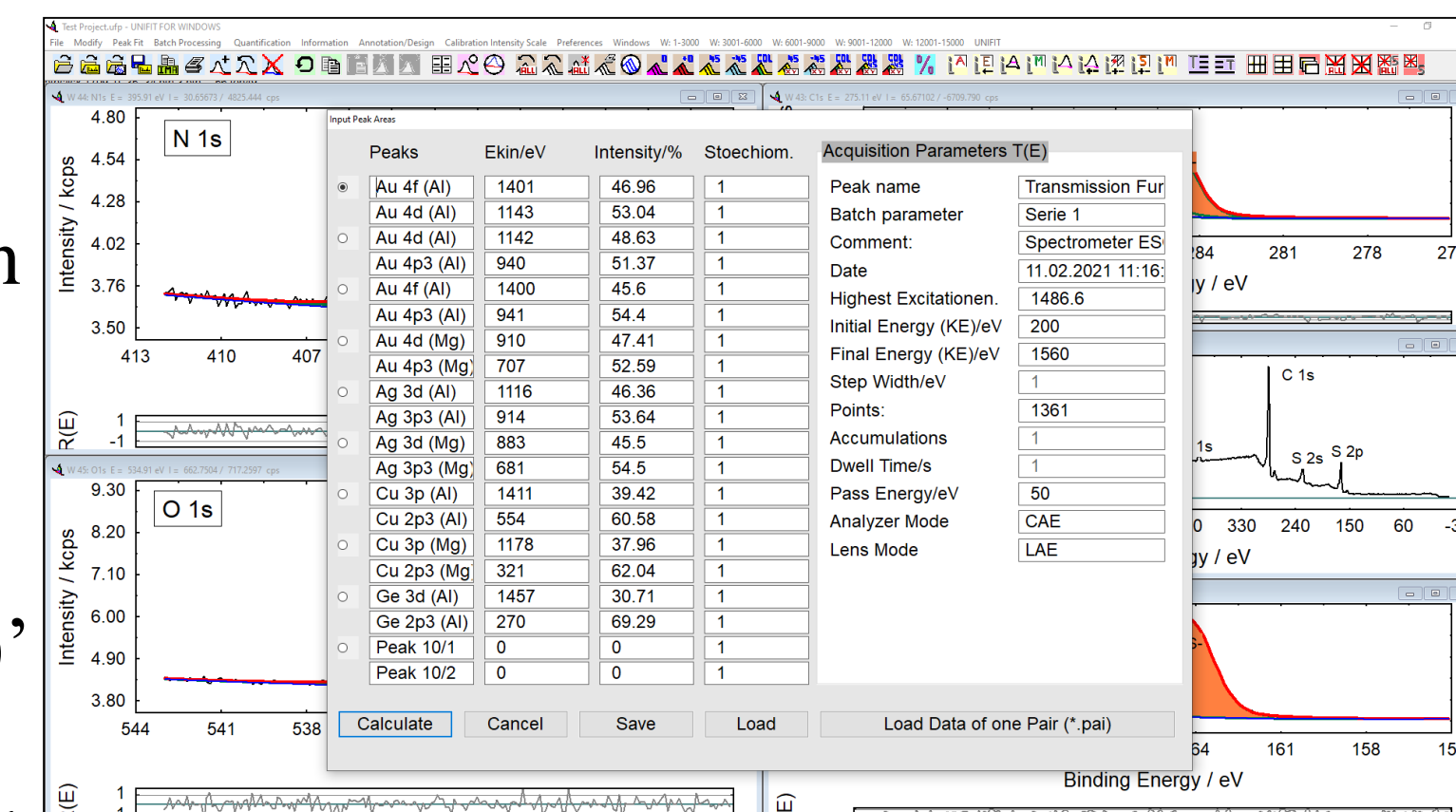


Fig. 5 Input dialog for the normalised intensities

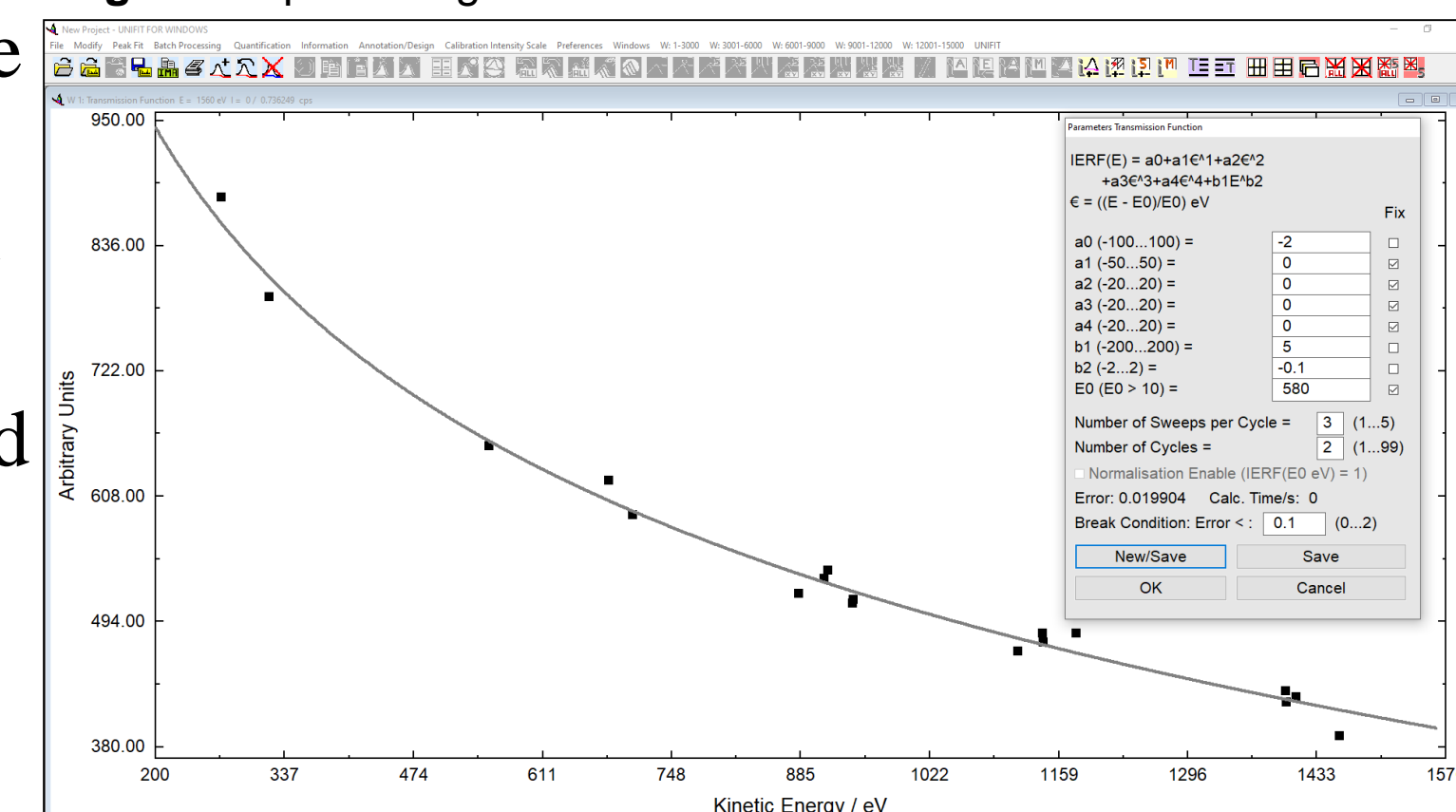


Fig. 6 Dialog to create the model function

Lit: [1] Hesse, R, Streubel P, Szargan R, Improved accuracy of quantitative XPS analysis using predetermined spectrometer transmission functions with UNIFIT 2004. *Surf. Interface Anal.*, 37: 2005: 589-607. doi:[10.1002/sia.2056](https://doi.org/10.1002/sia.2056).