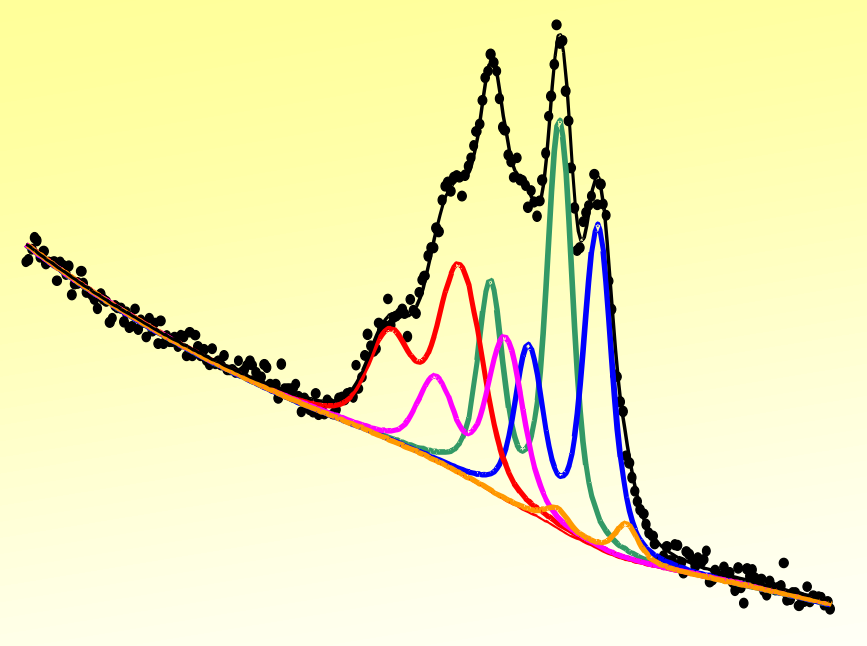




# UNIFIT 2025 – the Improved Spectrum Processing, Analysis and Presentation Software for XPS, AES, XAS and RAMAN Spectroscopy

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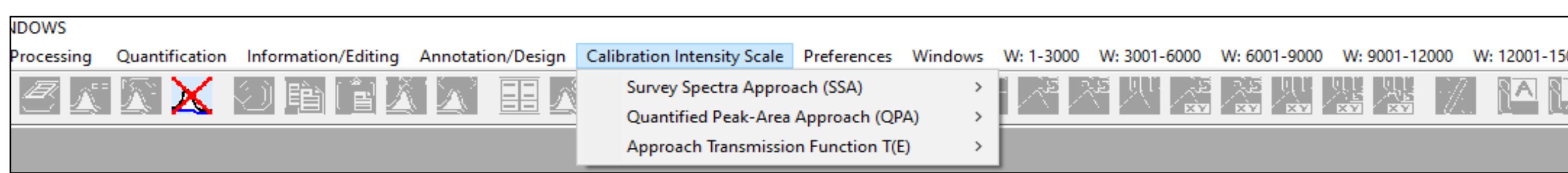


## Abstract

Main focus of the advancement of **UNIFIT 2025** was the optimization of the iteration procedure for the estimation of the transmission function  $T(E)$  (*IERF*). Now, the three methods of the  $T(E)$  estimation, **i)** Survey Spectra Approach (SSA), **ii)** Quantified Peak-Area Approach (QPA) and **iii)** Approach Transmission Function  $T(E)$ , are clearly separated. The dialogs of the sub-menu 'Calibration Intensity Scale' were reworked. The currently used method, the iteration error and calculation time are displayed. The disadvantage of the QPA method, the very long estimation time, was removed. In order to accelerate the iteration the **i)** existing programme code 'Step by Step' was completely reworked and **ii)** a new iteration method 'Randomize' was implemented. A comparison of both methods will be presented. Additionally, the dialogue 'Programme Parameters' was redesigned and expanded. The definition of the QPA-iteration method and design option were implemented. The options of the window-selection and quantification dialogue were expanded. The selected windows can be activated or deactivated optionally. The menus 'Plot Energy/Wavenumber Axis' and 'Plot Intensity Axis' have now two new defining options: **i)** Size of Increments and **ii)** -DS and +DS for the changing of the dialogue size. Regarding the dark-mode option of Windows a corresponding dark-mode option was implemented.

## Improved Programme Menu 'Calibration Intensity Scale'

The software operations of the three methods of the  $T(E)$  estimation [1] were reworked and clearly separated:



### 1. Survey Spectra Approach (SSA):

**Estimation of  $T(E)$  using reference-survey spectra  $S(E)$  of Au, Cu and Ag using Al-Twin, Mg-Twin, Al-Mono or Mg-Mono excitation:** In order to find the unknown transmission function  $T(E)$  the SSA method uses the adaptation of a measured survey spectra  $M(E)$  on reference spectra by optimization of the free parameters of  $T(E)$ :  $M(E) = T(E) \cdot S(E)$ . The SSA method is applicable for measurements using laboratory spectrometers and large pass energies (>20 eV) and therefore spectra without strong internal scattering.

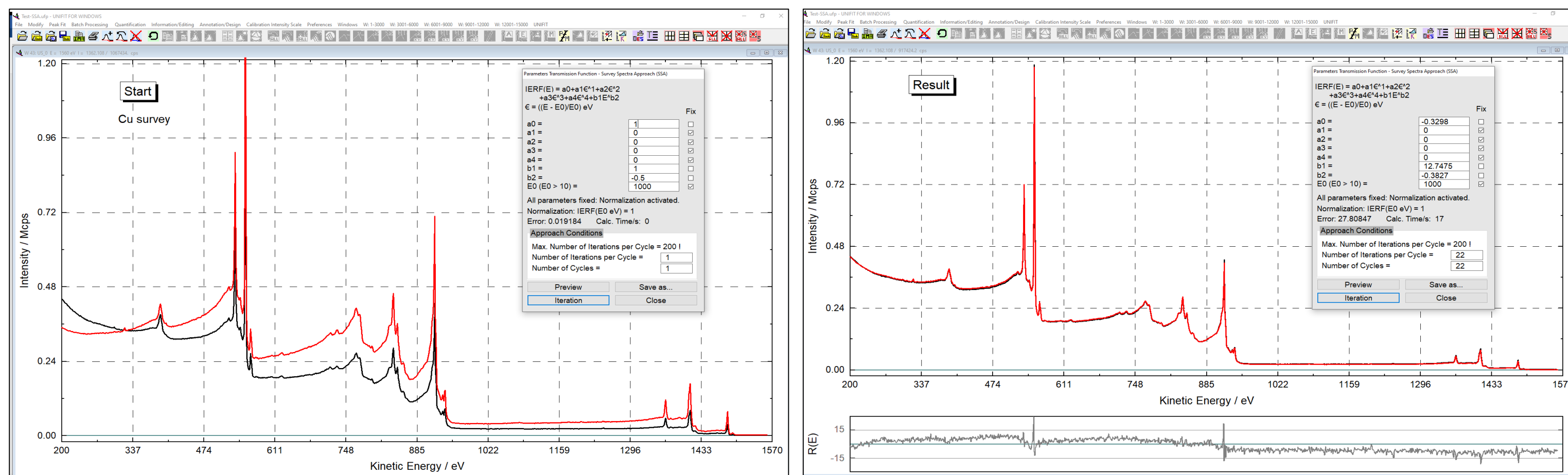


Fig. 1 Screen shots of an approach of a Cu survey excited with Al twin, left: start conditions, right: result after approach of  $T(E)$ ,  $T(E) \cdot S_{Cu}(E)$  (red),  $M_{Cu}(E)$  (black) and the  $T(E)$ -input dialogue

### 2. Quantified Peak-Area Approach (QPA):

**Estimation of  $T(E)$  using reference-peak areas  $I_N$  with  $T(E) = 1$ :  $I_N = I(\sigma \cdot \lambda \cdot 1)$ :** In order to find the unknown transmission function  $T(E)$  the QPA method uses the adaptation of the relative quantification of two photoelectron lines 1 and 2 (peak pair) of well known reference materials to the exact stoichiometric ratio [2]. The QPA is the most universal method for the calculation of  $T(E)$  and therefore also available for measurements on Synchrotrons or High-Energy XPS.

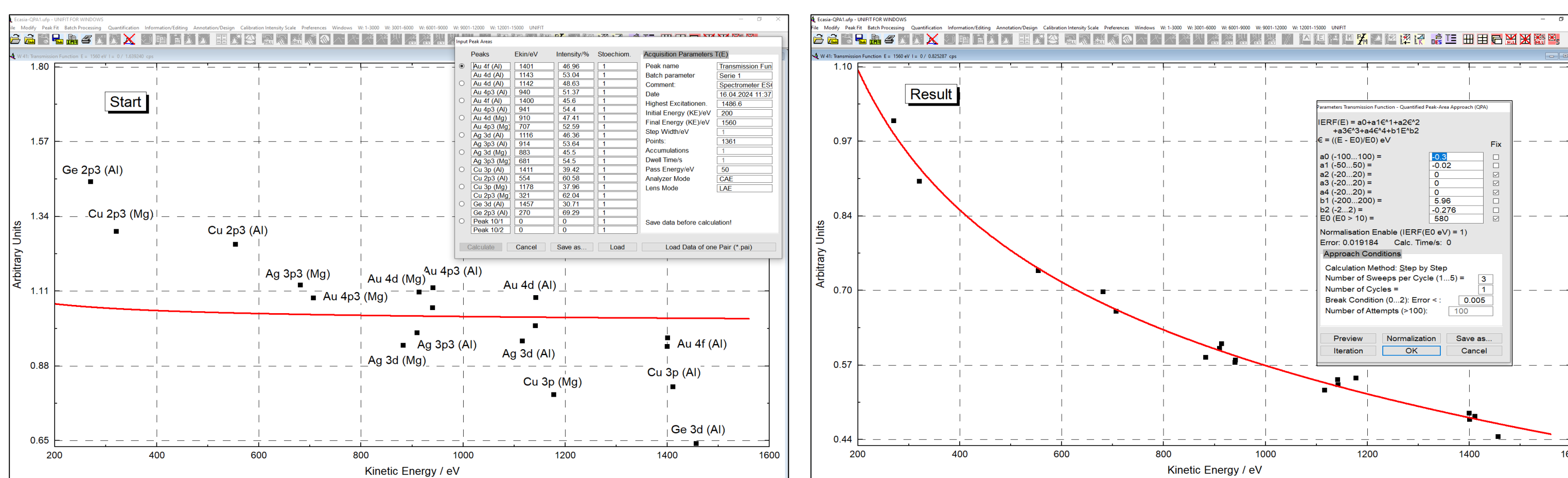


Fig. 2 Screen shots of an approach of reference peaks, left: start conditions with the table of the reference-peak intensities,  $T(E)$  (red), input data (black squares), right: result after approach of  $T(E)$ , estimated parameters of  $T(E)$ , error and estimation time using the displayed approach conditions ( $T(E)$ -input dialogue)

### 3. Approach Transmission Function $T(E)$ :

**Re-adaptation of the parameters of  $T_{New}(E)$  using an existing transmission function  $T(E)$ :** In order to find the optimized parameters of the new transmission function  $T_{New}(E)$  the adaptation of an existing  $T(E)$  function by optimization of the parameters of  $T_{New}(E)$  is used. The normalization of the  $T(E)$  functions ( $T(E) = 1$  at  $E_0$ ) facilitate the comparison of the different functions. If all parameters are fixed the normalization is activated.

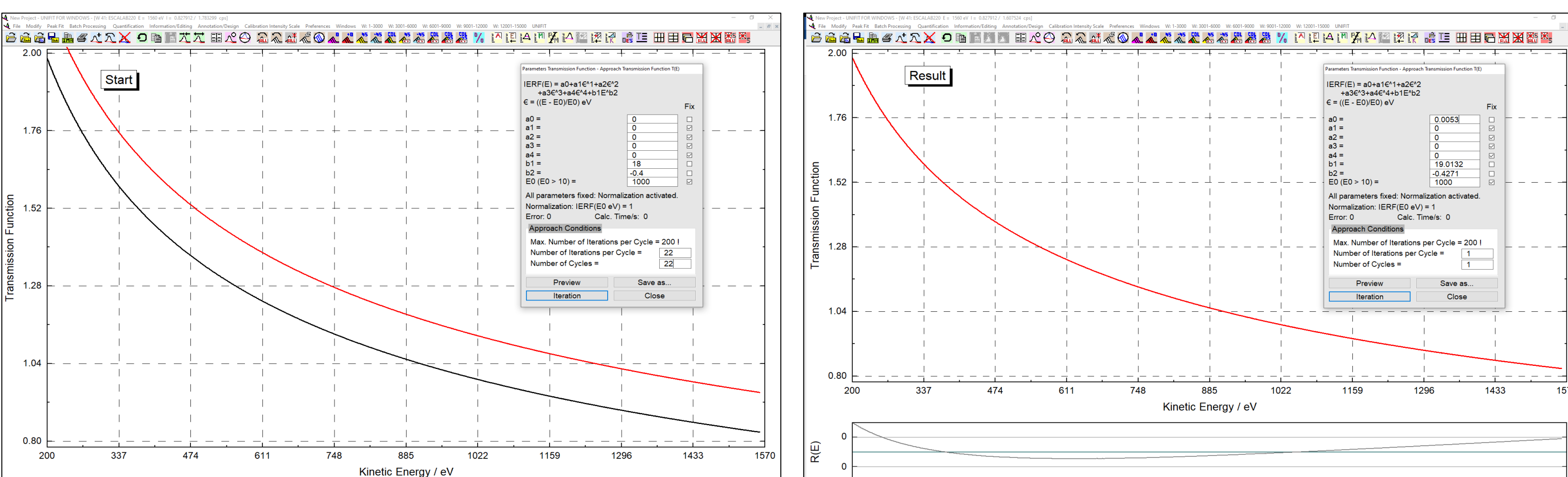


Fig. 3 Screen shots of an new approach of a existing  $T(E)$  function, left: start conditions, right: result after approach of  $T(E)$ ,  $T_{New}(E)$  (red),  $T(E)$  (black) and the  $T(E)$ -input dialogue

## Improved QPA Method

The disadvantage of the QPA method is the long iteration time (also a strong critic point of the referees of the last paper [3]). In order to accelerate the iteration:

- a) The existing programme code (**Step by Step**) was reworked completely.
- b) A new iteration method (**Randomize**) was implemented.

### 1. Generation of a synthetic test function $T(E)$

In order to test the reworked and new iteration method, a synthetic test function  $T(E)$  with the corresponding relative intensities of the peak pairs were generated:

$$T_{Test}(E) = 0.8 - 0.8 \cdot \varepsilon + 0.8 \cdot \varepsilon^2 + 0.8 \cdot \varepsilon^3 - 0.8 \cdot \varepsilon^4 + 80 \cdot E^{-1}, \quad \varepsilon = (E - E_0)/E_0, \quad E_0 = 400 \text{ eV}$$

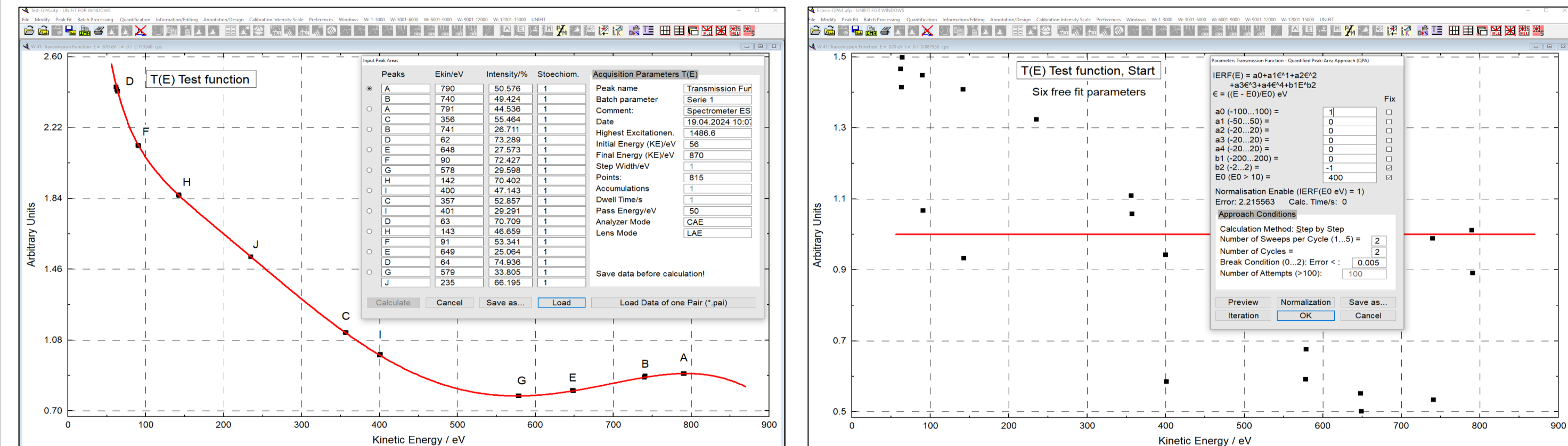


Fig. 4 Screen shots of QPA of the test function, left: test function data, right: QPA-start parameters

### 2. Comparison of the calculation time of the former (UNIFIT 2024), reworked QPA iteration 'Step by Step' method (UNIFIT 2025) and the 'Randomize' iteration method

- The fit results of the **Step by Step** method using both (Unifit 2024 and Unifit 2025) versions are identical.
- The reworked **Step by Step** method is about **20 times faster** with respect to UNIFIT 2024.
- In case of a large number of free fit parameters the method **Randomize** should be used. The estimation time is much faster (about 1000 times). Note, new calculations give new results (Win-32 random. proc.) (see also **Supporting Information**).

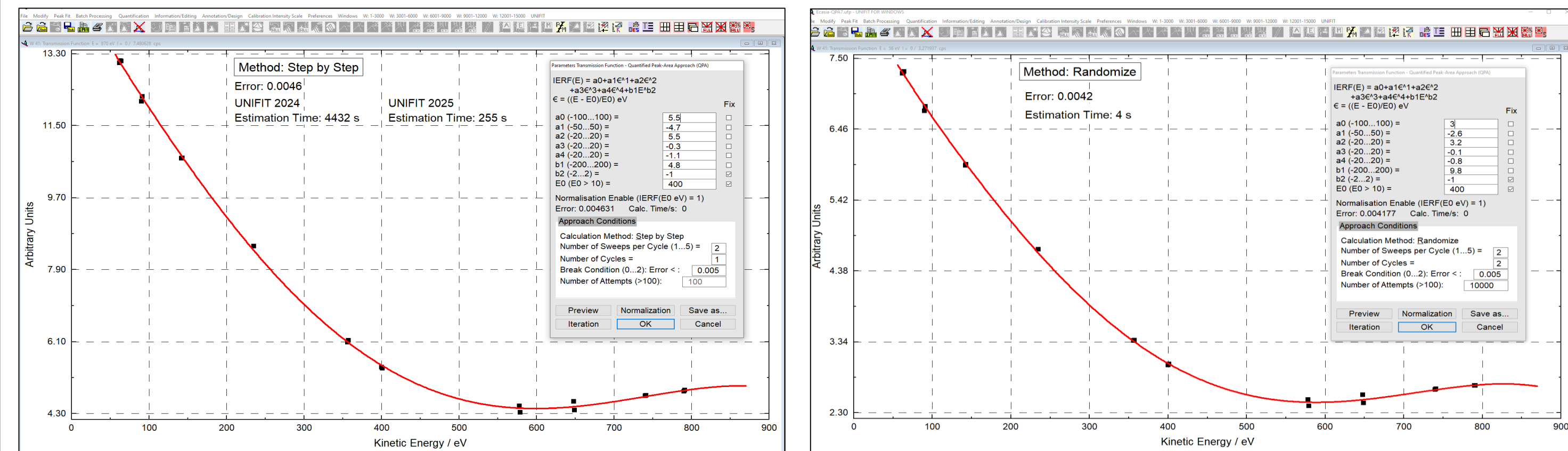


Fig. 5 Screen shots: left: result 'Step by Step' UNIFIT 2024 and 2025, right: result 'Randomize'

## Implementation of Dark Mode

Regarding the dark-mode option in Windows the dark-mode option in Unifit was implemented. Because the control of Windows regarding the control elements is not clearly defined, the Unifit dark-mode design is limited. The dark-mode in Windows is not complete realized (UWP (Universal Windows Platform) Apps only. Classical Windows Win 32 APIs are not supported).

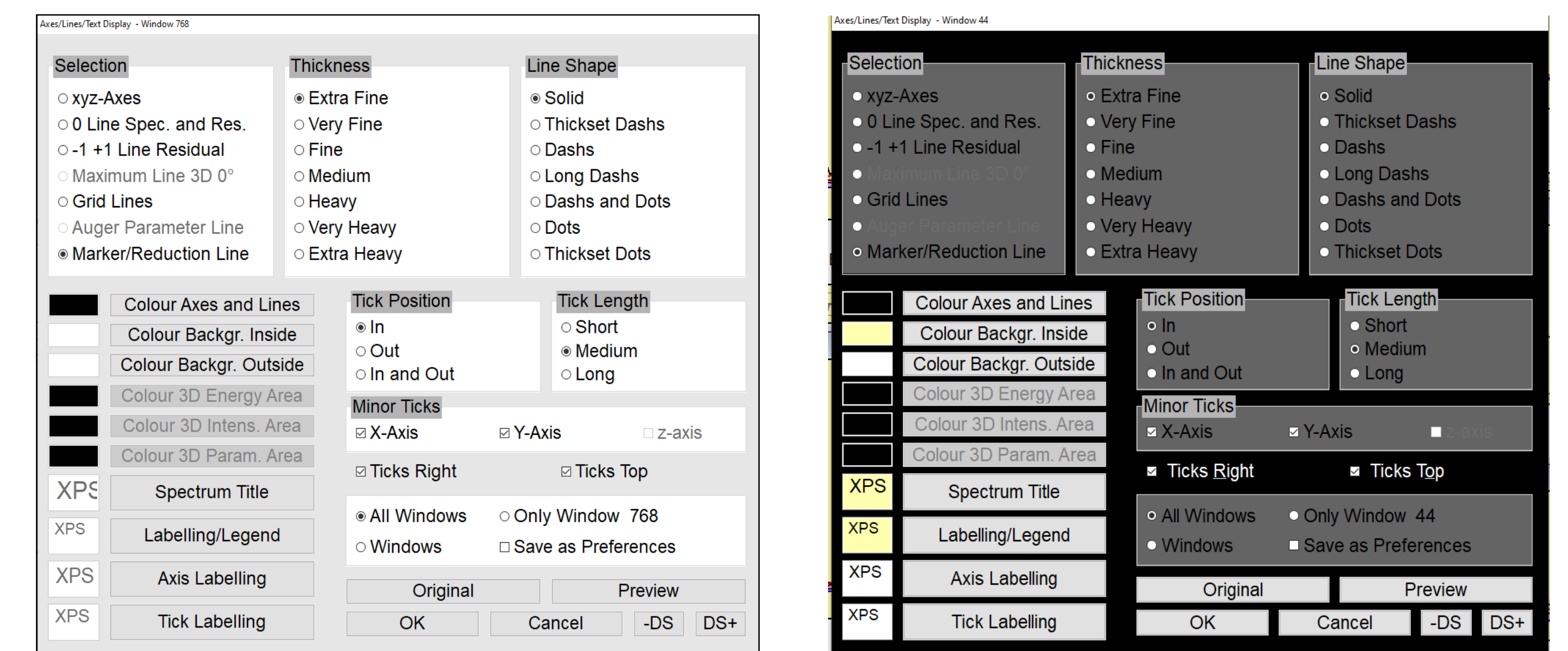


Fig. 6 Screen shots of the dialogue 'Axes/Lines/Text', left: 'Light Mode', right: 'Dark Mode' design

## References:

1. R. Hesse, T. Chassé, P. Streubel, R. Szargan, Surf. Interface Anal. 37 (2005) 589
2. M. Holzweber, A. Lippitz, R. Hesse, R. Denecke, W. Werner, W. Unger, J. Electron Spectrosc. Relat. Phenom. 233 (2019), 51
3. R. Hesse, R. Denecke, J. Radnik, Surf. Interface Anal., Short Communic., 7131 (2022) 1