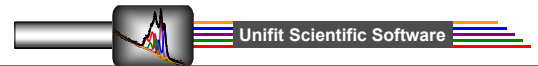


# Exercises

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## 1. Structure and concept of the program

### **Exercise 1.1: Program handling**

- Handling ‚Preferences‘ and pull-down menus
- Information in headline of the window
- First steps – getting to know the program

### **Demonstration 1.1: Program handling**

- Preferences (e.g. language, toolbar, setting up the toolbar, loading of saved presetting) without an opened spectrum window
- Preferences (e.g. dialog font/size, axis color, axis labeling, ...) with the project ‚**Example-01.ufp**‘
- Information in the headlines of the windows
- Overview over program parts (e.g. modify, batch processing, concentration, information)

# 1. Structure and concept of the program

## Task 1: Handling of the program

- Start the program
- Change the language from English to German and back
- Open and close the ,Toolbar‘
- Customize the toolbar with ,Preferences – Modify Toolbar...‘
- Open test project ,**Example-01**‘ with ,File – Open Project‘ from folder ,Documents\Unifit\_2014\_User\_Files\Exercises‘
- Customize the dialog font size of dialog ,Modify - Normalize‘
- Customize and test ,Preferences – Display - Graphs...‘ and ,Preferences – Display – Axis/Lines/Text/Display‘
- Test ,Preferences – X Axis‘ and ,Preferences – Y Axis‘
- Practice in ,Modify‘:
  1. Charge correction
  2. Differentiation
  3. Reduction (after setting boundaries) and expansion of the spectrum
  4. Activate spike correction and set up new data points by pushing the left mouse button, deactivate spike correction
  5. Spectra manipulation of the intensity and energy
  6. Normalization
- Recreate the original spectrum by ,File – Original...‘
- Load spectra information via sub menu of the menu ,Information‘ or by pushing the right mouse button

# 2. Background subtraction and peak fit

## Exercise 2:

- Fit of background before the fit or parallel to the peak fit
- Peak fit with different model functions
- Input of the starting parameters manually or by loading from the disc

## Demonstration 2a:

- Peak fit and background subtraction for test spectrum ,**Example-02**‘
  1. Shirley background calculation before the peak fit
  2. Shirley background calculation parallel to the peak fit
- Peak fit and subtraction of the background for test spectrum ,**Example-03**‘
- Peak fit with two different model functions and fittable background for test spectrum ,**Example-01**‘

**Example-01:** 1 Peak, Voigt profile, peak intensity: 1000 Counts, position: 190 eV  
Lorentzian width: 1 eV, Gaussian width: 1 eV

**Example-02:** 2 peaks, product, peak intensity ratio: 1:1, G/L, FWHM: 1 eV,  
peak distance: 1 eV, G/L-mixing: 0.25, Shirley background

**Example-03:** 1 Peak, Voigt profile, peak intensity: 1000 Counts, position: 190 eV  
Lorentzian width: 1.7 eV, Gaussian width: 0.3 eV

## 2. Background subtraction and peak fit

### Task 2.1 Shirley background subtraction, fittable background, input of starting parameters, peak fit

- Change fit procedure to ‚Product‘ and fit parameters to ‚Absolute‘
- Load test spectrum ‚Example-02‘, with ‚File – Open project...‘ from folder ‚Documents\Unifit\_2014\_User\_Files\Exercises‘
- Appropriately reduce spectral range
- Subtract Shirley background before the peak fit (a couple of iterations)
- Manually set up two components, peak fit
- Recreate original spectrum, appropriately reduce the spectral range
- Peak fit with fittable background and two peaks, compare the residual functions

### Task 2.2 Comparison of background subtraction before the fit and parallel to the fit

- Close all windows, change fit procedure to ‚Convolution‘ and ‚Absolute‘
- Open test spectrum ‚Example-03‘, with ‚File – Open Project...‘
- Subtract appropriate background with ‚Modify – Calculate Background‘
- Manually set up one component, peak fit
- Recreate original spectrum, appropriate reduction of the spectral range
- Peak fit with fittable background and one peak, compare residual functions

### Task 2.3 Fit of a Voigt test spectrum with different model functions

- Open test spectrum ‚Example-01‘
- Perform peak fit in three windows with three different model functions (Preferences ‚Fit Procedures‘)
- Compare residual functions,  $\chi^2$ , *Abbe* criteria

## 3. Peak fit and calculation of the fit result errors

### Exercise 3: Calculation of fit parameter errors

- Calculation of the fit parameter errors
- Minimization of the fit parameter errors by elimination of redundant fit parameters

### Demonstration 3: Calculation of fit parameter errors

- Preferences fit procedure ‚Convolution‘, fit parameter ‚Absolute‘, error calculation ‚Matrix inversion‘
- Peak fit of ‚Example-04‘ with fittable background and two peaks
- Calculation of errors
- Reduction of the free fit parameters according to the error calculation (Fit parameter with an error >100% , set to zero and fix them)
- Repeat peak fit and error calculation

**Example-04:** 2 peaks, Voigt profile, background polynomial, statistic noise,  
 1. Peak: 10,000 counts, Lorentzian width 1.7 eV,  
 position: 192 eV, Gaussian width: 0.3 eV  
 2. Peak: 50,000 counts, Lorentzian width: 0.3 eV,  
 position: 190 eV, Gaussian width: 1.7 eV

### 3. Peak fit and calculation of the fit result errors

#### **Task 3: Peak fit with Fit-Background and two peaks, fit parameter error calculation**

- Close all windows
- Change fit routine to ‚Convolution‘ and ‚Absolute‘ and error calculation to ‚Matrix inversion‘
- Load project ‚**Example-04**‘
- Choose fittable background with Shirley and constant (a, e free, fix all other parameters to 0)
- Manuel input of two components, perform peak fit (iterate)
- Correct fittable background appropriately (additional polynomial, e.g.  $b = 1$  variable,  $c = 0,1$  variable)
- If fit was successful calculate the errors of the fit parameters
- Choose parameters having an error  $>100\%$ , set them to zero and fix them
- Repeat peak fit
- Repeat error calculation

### 4. Applying coupled fit parameters for the peak fit

#### **Exercise 4.1: Coupling of doublets**

- Use coupled **doublet lines** and coupled fit parameters
- Appropriate use of fixed parameters
- Fit with relative parameters

#### **Demonstration 4.1: Fit with coupled doublet parameters**

- Set up preferences fit procedure ‚Sum‘, fit parameter ‚Absolute‘,
- Use ‚**Example-06-Start**‘
- Satellite subtraction
- Perform peak fit with coupled fit parameters for S 2p
- Peak fit with and without relative fixing of fit parameters

#### **Task 4.1:**

- Close all windows, change preferences to ‚Sum‘ and ‚Absolute‘
- Load project ‚**Example-06-Start**‘
- Activate sulfur peak
- Satellite subtraction with ‚Modify – Satellite Subtraction‘
- Fit sulfur peak with Fit-Background and two doublets
- Couple doublet values appropriately, iterate, error calculation

**Example-06:** real spectra for the analysis of the chemical states of sulfur, oxygen, nitrogen and carbon

## 4. Applying relative fit parameters for the peak fit

### Exercise 4.2: Relative fit parameters

- Use of singulet lines and relative fit parameters
- Appropriately fixing of the parameters
- Fitting with relative parameters
- Estimation of an energy loss function

### Demonstration 4.2: Fitting with relative parameters

- Preferences fit procedure ,Sum‘, fit parameter ,Relative‘,
- Modify As 2p peaks of ,**Example-07-Start**‘
- Demonstration of the peak fit with relative fit parameters for As 2p
- Peak fit with and without relative fixing of fit parameters

### Task 4.2:

- Close all windows, change preferences to ,Sum‘ and ,Relative‘
- Open project ,**Example-07-Start**‘
- Activate As 2p<sub>3/2</sub> peaks
- Fit As peaks with Fit-Background (a, b, c, e free) and five singulet lines (GaAs: 1323.1 eV, As: 1.2 eV, AsO: 2.6 eV, As<sub>2</sub>O<sub>3</sub>: 3.3 eV, As<sub>2</sub>O<sub>5</sub>: 4.3 eV)
- Fix rel. fit parameters of the peaks 2 - 5 appropriately, e.g. L-G Mixing = 1, fix; FWHM = 1, fix, 22 iterations
- Label lines of the five chemical shifts with ,Information – Identify Lines – As 2p<sub>3</sub> – Chemical Shifts)‘, display the fit parameter table

**Example-07:** real data for the analysis of the oxidation of GaAs by ozone

## 4. Applying relative fit parameters for the peak fit

### Demonstration 4.3:

- Fit Ga 2p peaks of an oxidized GaAs sample with four peaks
- Parallel calculation of the loss function integrated into the Tougaard background
- Load test spectra ,**Example-08-Start**‘, (survey spectrum)
- Correct survey spectrum with transmission function
- Reduce Ga 2p range appropriately (e.g. 1170 eV – 1095 eV)
- Manual alignment of *B*, *C*, *C*‘ and *D* (recommended values: *B* = 24, *C* = 99, *C*‘ = -0.3 *D* = 20)
- Peak fit with fittable background and four peaks
- Define fittable background, ,Peak Fit – Fit Background‘, load the saved loss function ,GaAs-Oxid-Hes.cro‘
- Set *e* = 0, fix (Shirley), *a*, *b*, *c* free, with ,Peak Fit – Manual Input of Start Parameters – Singulet Peaks‘, choose four lines via mouse
- Set and fix G/L-ratio of the 2., 3. and 4. peak to 1, use 22 iterations, subsequently release the parameters of the loss function
- Display the loss function
- Verify the intensity ratio of the p lines

**Example-08:** survey spectrum of oxidized GaAs

## 4. Applying relative fit parameters for the peak fit

### Task 4.3: Tougaard-Background, loss function, peak fit with relative parameters

- Close all windows
- Set fit procedure to ‚Sum‘ and fit parameters to ‚Relative‘
- Load test spectrum ‚Example-08-Start‘, with ‚File – Open Project...‘ from folder ‚Documents\Unifit 2014 User Files\Exercises‘
- Load transmission function ‚ESCALAB220 MONO LAXL\_50EP.trm, via ‚Preferences – Load/Define Transmission Function‘
- Correct survey spectrum with transmission function via ‚Modify – Correct with IERF: ESCALAB220 MONO ...‘
- Appropriately reduce As 2p range (e.g. 1375 – 1315 eV)
- Manually adjust the loss function of the Tougaard background by variation of the parameters  $B$ ,  $C$ ,  $C'$  and  $D$  (recommended values:  $B = 24$ ,  $C = 100$ ,  $C' = -0.3$   $D = 20$ ) via ‚Modify – Calculate Background – Tougaard‘
- Save the estimated loss function as ‚Test-GaAs.cro‘
- Peak fit with fittable background and four peaks
- Define fittable background via ‚Peak Fit – Fit Background‘, load the saved loss function ‚Test-GaAs.cro‘, set  $e = 0$ , fix (Shirley),  $a$ ,  $b$ ,  $c$  free, via ‚Peak Fit – Manual Input of Start Parameters – Singulet peaks‘
- Choose four lines appropriately with the mouse
- Set and fix L-G Mixing for 2. 3. und 4. peak to 1, 22 iterations, release parameters of the loss function one after the other
- Repeat iteration

## 5. Calculate the transmission function $T(E)$

### Exercise 5: Transmission function

- Calculation of the transmission function from the survey spectrum
- Verification of the accuracy of the saved  $T(E)$  functions
- Comparison with quantification via Wagner factors

### Demonstration 5: Calculation of $T(E)$ of a Cu survey spectrum

- Calculation of  $T(E)$  function of a Cu survey spectrum, ‚Example-09-Start‘
- Quantification of the Cu 2p and Cu 3p lines

### Task 5: Calculation of $T(E)$ with Cu survey spectrum

- Load ‚Example-09-Start‘, maximize survey spectrum window
- Calculation of the transmission function from the survey spectrum via ‚Calibration Intensity Scale – Load Reference Spectrum – Cu-twin‘
- Calculation of the fit parameters via iteration of  $a_0$ ,  $b_1$  and  $b_2$ , save calculated  $T(E)$  via ‚Documents\Unifit 2014 User Files\Temp‘ and display with ‚Calibrate Intensity Scale - Plot Transmission function‘
- Quantification of Cu 2p and Cu 3p lines, 50 eV pass energy, with:
  - a) Wagner factors and b) Sigma, lambda and the corresponding  $T(E)$
- Quantification of Cu 2p<sub>3/2</sub> and Cu 3p lines, 10 eV pass energy, with:
  - a) Wagner factors and b) Sigma, lambda and the corresponding  $T(E)$

**Example-09:** real data of Cu for the analysis of the  $T(E)$  function, anode: Al-Twin, lense: LAX, pass energy: 50 eV and 10 eV

## 6. Qualitative and quantitative analysis of XPS-standard measurements

### Exercise 6: Quantitative analysis

- Identification of lines
- Identification of chemical states
- Labelling of spectra

### Demonstration 6: Analysis of XPS-standard measurements:

- Identification of the lines of the survey spectrum .**Example-05-Start**'
- Four options for the identification
- Fit of the C 1s peaks via ,Sum ' and ,Relative'
- Charge correction, labelling of the chemical states

### Task 6: Analysis of XPS-standard measurements

- Close all windows, preferences: ,Sum' and ,Relative'
- Load ,**Example-05-Start**'
- Identification and labeling of all peaks of the survey spectrum
- C 1s active, with ,Information – Min/Max' all peaks to  $\text{CH}_2 = 285 \text{ eV}$  via ,Batch Processing – Charge Correction all Windows'
- Satellite subtraction of all spectra
- Fit of the C 1s spectrum (3 Peaks), O 1s (2 Peaks), N 1s (2 Peaks), Lorentz. width the same for all lines, Fit Background: constant, linear, Shirley
- Fit of S 2p width doublets, 2p intensity ratio 2:1 fix Lorentz. width same for all peaks, Fit-Background: constant a, Linear b, Shirley e
- Label all peaks appropriately and calculate concentration

## 7. Layer thickness estimation

### Exercise 7: Layer thickness estimation with two methods (ERXPS and ARXPS)

- Quantification
- Estimation of the layer thickness

### Demonstration 7: Layer thickness estimation of a Fe covered Cu sample with method ERXPS:

- Concentration and layer thickness estimation of an uncovered sample ,**Example-10A-Start**' and one covered sample ,**Example-10B-Start**' via method ERXPS

### Task 7: Comparative layer thickness estimation with ERXPS and ARXPS

- Close all windows and load file ,**Example-10A-Start**'
- Table of concentration pops up, close with ,Cancel'
- Choose ,Quantitative Analysis – Layer Thickness Estimation 1 (ERXPS)'
- Choose  $\text{Cu}2p_{3/2}$  and Cu 3p peak (thickness should be 0)
- Close all windows and open ,**Example-10B-Start**'
- Table of concentration pops up, close with ,Cancel'
- Choose ,Quantitative Analysis – Layer Thickness Estimation 1 (ERXPS)'
- Choose peaks  $\text{Cu}2p_{3/2}$  and Cu 3p (calculated thickness: 10 Å)
- Calculation of the thickness with method ARXPS and  $\text{Cu}2p_{3/2}$  and Cu 3p lines and compare the calculated values

## 8. Batch Processing

### Exercise 8: Batch processing

- Batch processing of data series (spectra depending on one parameter, e.g. angle, sputter time, time of deposition)
- 3D and parameter plot of the series

### Demonstration 8: Batch processing of a synthetic series

- Preferences: ‚Convolution‘ and ‚Absolute‘, load ‚Example-11-Start‘
- Fit of C 1s with one peak, quantification, parameter plot
- Fit of O 1s with two peaks, quantification, add to parameter plot

### Task 8.1: Batch processing of a synthetic series

- Close all windows, preferences: ‚Convolution‘ and ‚Absolute‘
- Load ‚Example-11-Start‘, all 11 C 1s peaks are shown
- Fit of C 1s in window 1, one peak, Fit-Background (constant, Shirley)
- ‚Batch Processing – Batch Processing‘ fit the remaining 10 peaks
- Concentration calculation for all 11 windows
- Parameter plot: x axis: Batch parameter, y axis: cor. peak areas
- Close all C 1s windows (except for the parameter window) via ‚Windows – Close all Standard Windows‘
- Load all O 1s spectra via ‚File – Select Blocks‘

## 8. Batch processing

### To task 8.1:

- Fit O 1s spectrum in window 6 with ‚Fit-Background‘ (constant, Shirley) and two peaks
- Batch processing for the 10 O 1s windows
- Calculation of the concentration for 11 O 1s windows
- Add results to C 1s parameter plot (Choose option in the parameter plot dialog: ‚Add to plot‘), close table, close all O 1s standard windows
- Plot all 11 Si 2p peaks with ‚File – Select Blocks‘
- Fit Si 2p spectrum in window 3 with Fit-Background (constant, Shirley) and three peaks
- Batch processing of remaining 10 Si 2p spectra
- Calculate concentration
- Add results to the plot
- Design parameter plot via ‚Preferences – Display – Parameter Plot‘
- Present Si 2p spectra with different 3D options

- Example-11:**
- Synthetic data series with three peaks (C1s, O 1s, Si 2p), without statistical noise
  - C 1s: one comp.: varies between two intensities
  - O 1s: two comp.: 1<sup>st</sup> linearly increas. 2<sup>nd</sup> linearly decreas.
  - Si 2p: three comp.: 1<sup>st</sup> lorentzian shape, 2<sup>nd</sup> linearly increas., 3<sup>rd</sup> exp. decay



## 8. Batch processing

### **Task 8.2: Batch processing of an angle dependent measurement of naturally oxidized Si (Si 2p, C 1s, O 1s)**

- Close all windows, preferences, 'Product' and 'Absolute'
- Open 'Example-12-Start' (all Si peaks plotted)
- Satellite subtraction and peak fit with two doublets and Fit-Background (a, e free, all others zero and fixed) in one window
- Batch processing of all Si peaks
- Calculate concentration and perform parameter plot (x: Batch parameter, y: corr. peak areas)
- Close concentration table and all standard windows (Parameter plot still open)
- Open O 1s peaks via 'File – Select Blocks'
- Appropriately subtract background
- Calculate concentration, add results to parameter plot of Si
- Close table and all standard windows (Parameter plot still open)
- Open all C 1s peaks via block selection, subtract background
- Calculate concentration and add to parameter plot
- Design parameter plot with options 'Annotation/Design' and design menus in 'Preferences'

## 9. Combined XPS and XAS analysis

### **Exercise 9: Peak fit of Ti 2p and Ti L edge**

- Both, the Ti XP spectrum and the Ti L edge XA spectrum were fitted
- XPS peak fit parameters (height, Lorentzian-Gaussian mixing (sum), peak position, FWHM) are introduced into the fit parameters of the spectral background of the XAS fit

### **Demonstration 9: Peak fit of the Ti L edge**

- Preferences: 'Sum' and 'Relative', load 'Example-13-Start'
- Display corresponding Ti 2p XPS peak and Ti L edge XAS peak
- Using of the XAS fittable background, Fit of the XAS spectrum using 9 peaks

### **Task 9.1: Peak fit of the Ti 2p XPS spectrum with one doublet**

- Close all windows, preferences: 'Sum' and 'Relative'
- Set the X-Axis to 'Binding Energy/neg. Photon Energy'
- Load 'Example-13-Start'
- Activate the Ti 2p window, reduce the energy range from 470 – 450 eV
- Satellite subtraction with 'Modify – Subtract Satellite'
- Generate a fittable background with: a – free, b = 0, free; c = 0, free; d = 0, fix; e = 0, fix; B = 0, fix
- Select 'Peak fit – Manual Input of Start Parameters – Doublet Peaks'
- Number of doublets: 1, Min/Max dialog - ok, Start parameter dialog is open
- Set the first maximum at 457.8 eV by mouse click
- Intensity/Peak 2: 0.38, fix; L-G Mixing/Peak 2: 1, fix; Asymmetry/Peak 1: -0.1, fix, Asymmetry/Peak 2: 1, fix, all other parameters free
- Iteration with 22 cycles, note the estimated fit parameters

## 9. Combined XPS and XAS analysis

### Task 9.2: Peak fit of the Ti L edge XAS spectrum with nine singulets

- Set the X-Axis to ‚Kinetic Energy/Photon Energy‘
- Activate the Ti L edge window
- Generate a fittable XAS background with two steps
- Use the noted XPS peak fit parameters for the generation of the XAS background
- e.g. Height: Step 1: 0.002, free, Step 2: 0.38, fix  
     E-A Mix: Step 1: 0.7, fix; Step 2: 1, fix  
     Position: Step 1: 457.8 eV, fix; Step 2: 5.84 eV, fix  
     FWHM: Step 1: 1.43 eV, fix, Step 2: 1.40 eV, fix
- Leave the dialog with OK
- Select ‚Peak fit – Manual Input of Start Parameters – Singulet Peaks‘
- Number of peaks: 9, Min/Max dialog – OK
- Start parameter dialog is displayed
- Mouse click of the nine possible intensities/energies to write in the values in the parameter table
- L-G Mixing: Peak2 – Peak9: 1, fix
- Iteration with 22 cycles

## 10. Export data and presentation of results

### Exercise 10.1: Export of images and tables

- Export of fitted spectra via ‚Copy Image‘ and ‚Paste‘
- Export of fitted spectra as \*.emf (400 dpi)
- Export of concentration table via ‚Copy – Paste‘
- Export of fit parameter table via ‚Copy – Paste‘
- Paste into a MS Word document

### Demonstration 10.1: Exports of images and tables

- Open ‚Presetting\_Image\_Export.set‘
- Load ‚**Example-06-Result**‘
- Export modified S 2p peaks
- Start MS Word, paste image, demonstrate resolution
- Export concentration table and paste in MS Word

### Task 10.1: Export of contents and concentration table as an image

- Close all windows, load ‚Presetting\_Image\_Export.set‘
- Open ‚**Example-06-Result**‘
- Change resolution ‚Preferences – Resolution Image Export/Copy‘ to 400 dpi
- **Copy and paste images:**
- Save image in clipboard via ‚File – Copy Image‘
- Start a new MS Word document, import image via ‚Modify – Copy‘

## 10. Export data and presentation of results

### to task 10.1:

- **Export as image file (\*.jpg, \*.tif, \*.emf, ...)**
- Activate window to be exported
- Choose resolution via ,Preferences'
- Save image via ,File – Export Image' in an appropriate file ,Documents\Unifit\_2014\_User\_Files\Temp'
- Paste in MS Word via ,Paste – Image – From file'
- **Export concentration table**
- Open concentration table via ,Copy' save to clipboard and include via ,Modify – Paste' into the MS Word document
- **Export fit parameter table**
- Start MS Word, open new document
- Open fit parameter table and copy into clipboard and include via ,Modify – Paste' into the document

## 10. Export data and presentation of results

### Exercise 10.2: To export of data

- Export of spectrum, background, components, sum curve
- Input into ,Origin'

### Demonstration 10.2: Export of data

- Introduce ,Preferences – Export – Delimitation' and ,Preferences – Export – Decimal Character'
- Load ,**Example-06-Result**'
- Subtract background in N 1s spectrum
- Export curves of fitted N 1s peaks
- Design image with ,Origin'

### Task 10.2: Export of data of the peak fit

- Open ,**Example-06-Result**'
- Activate window with data to be exported
- Choose and save curves to be exported via ,File – Export'
- Paste into ,Origin' and create an image

### Task 10.3: Design and label spectra windows

- Load ,**Example-12-Result**'
- Paste a text in a standard window
- Write a formula in MS Word and add to a spectra window of UNIFIT
- Design 3D curves differently