



# Manual

WinXAS

Version 3.x

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The author welcomes bug reports, comments and suggestions. Please include in your e-mail: WinXAS license number, system details (OS, WinXAS path, etc.) **detailed** description of what you intended to do (if possible add ASCII attachment of spectrum, raw data,  $\chi(k)$  and content of **Result window**) and what the (unexpected) output was.



Please look out for this symbol throughout the manual. It indicates major differences between WinXAS 3.x and previous versions as well as details you will certainly appreciate. A first impression on how WinXAS can be used for XAS data analysis can be obtained from the **WinXAS Assistant!**.

New features in version 3.x are marked in **red** throughout the manual.

## 1. Introduction

WinXAS is a XAS data analysis program for PCs running MS-Windows<sup>®</sup> 95/98/2000/NT/XP. The most important feature of WinXAS is its graphical user interface where all functions and procedures can be selected using either a pointing device or single keyboard function keys. WinXAS allows up to four data files to be processed at a time and results can be superimposed and compared conveniently. Furthermore, WinXAS represents an excellent educational tool due to its immediate graphical response on changes in, for instance, XAS fit parameters, k weighting, number of nodes for cubic spline fits, etc. Thus, WinXAS can help to gain insight into the effect of atomic distances, disorder parameters, or number of shells on the XAFS function  $\chi(k)$ .

WinXAS contains all necessary numerical algorithms and procedures for standard XAS data analysis. Moreover, many additional analysis methods that exceed standard data reduction can be used, such as difference file technique, Principal Component Analysis, experimental XANES linear combination fits, XANES profile fitting, use of FEFF theoretical phases and amplitudes for XAS refinement. Nevertheless, WinXAS is meant to complement rather than substitute more advanced XAS data analysis programs and may not be adequate in all cases (for instance, full multiple scattering treatment using *ab-initio* theoretical phases and amplitudes requires additional XAS analysis codes).

Certainly an advantage of WinXAS is, that it can be employed at a very early stage of every XAS experiments. In many cases beamtime can be used much more efficiently if a preliminary data analysis is carried out on-line. Owing to its open and flexible data file structure, WinXAS can read a variety of different multiple column files without previous conversion. Besides its numerical and standard XAS features, WinXAS contains several routines for the analysis of energy dispersive XAS data. Furthermore, WinXAS macro can be employed in a serial treatment to a large number of consecutive spectra. These data may be obtained from time-resolved experiments at either energy dispersive or quick scanning XAS beamlines. Such experiment like standard XAS studies benefit from WinXAS in terms of speed, efficiency, and convenience.

This manual is organized in the following way: it starts with some introduction and describes afterwards the somehow more general features of WinXAS, such as its windows, buttons, etc. and what they are for and their capabilities. Thereafter, it just goes through the WinXAS menu left to right, top to bottom and explains each item and its function (for the XAS menu this coincides with the order of a conventional XAS data analysis).

## 2. WinXAS windows and buttons

### 2.1 Philosophy

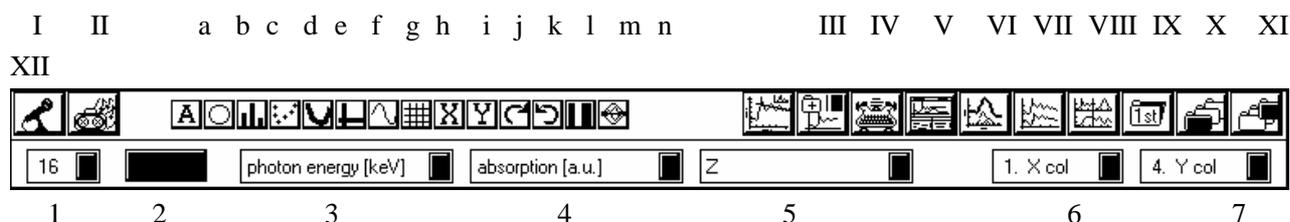
WinXAS consists of a menu, some buttons, and several different types of windows that can be arranged on its surface. It actually shares these features with a large number of other WINDOWS programs and you may already have encountered one or two. The most important type is the Graphic Window. It normally displays the content of a data file in a X,Y diagram (x,y-graph). The major part of the WinXAS menu items is related to the 'active' (last selected) x,y-graph of an open graphic window. (this means, that the attempt to calculated

the Fourier Transform of your Edit Window will be ignored). Up to four Graphic Windows can be open at the same time. Graphic Windows can be closed, which results in a loss of the related data arrays.

Additionally, WinXAS contains a Result Window and an Edit Window. The Result Window keeps track of all performed operations and contains the numerical results. The Edit Window displays the content of the 'active' Graphic Windows as plain numbers in two columns. Single values can be change or deleted or new values can be added. The Result Window and the Edit Window cannot be closed they only can be hidden away (made invisible). In the following, the windows and their particular features are described in more detail.

## 2.2 WinXAS buttons

The good news is all buttons are only short-cuts for functions you can reach via menus or dialog boxes, too. Therefore, you may as well use only the menus and your keyboard. The bad news is some functions may be buried in dialog boxes and difficult to get as quick as you would like to have them.



In the following the WinXAS buttons are shown as they appear on the desktop from left to right and their function is described.

- I) Start Macrorecorder (see **index**)
- II) Start Macro (see **index**)
- a) Open INSCRIBE AXIS dialog box (see **index**)
- b) Displays each data point as circle and connects data points with solid line
- c) Plots a bar at the position of each data point and connects the points
- d) Displays each data point as circle but doesn't connect points
- e) Increase/Decrease line width for Active X,Y-graph
- f) Increase/Decrease line width for axis
- g) Displays/hides the imaginary part of a complex data array
- h) Switches grid on or off
- i) Switches X inscription on or off
- j) Switches Y inscription on or off
- k) Decreases 3D view angle by 5 degrees and updates Active Graphic window.
- l) Increases 3D view angle by 5 degrees and updates Active Graphic window.
- m) Opens dialog box to change the color order. When a new session is launched, WinXAS defines the order in which consecutive graphs will be colored in a combination plot. In case you

- don't like the order, use this dialog box to change it. Just select one color on the left side, press the arrow bar, and the color will be appended to the right list.
- n) Opens the CHANGE PARAMETER dialog box (see **index**).
  - III) Quick-XAS button (see **index**)
  - IV) Loads and displays the next column from a multiple column file.
  - V) Prints the content of the Active Window (either Graphic Window or Result Window, see **index** for details).
  - VI) Arrange all open WinXAS windows on the desktop. (see **index**)
  - VII) Displays single profile functions in case the Active Function consists of more than one profile function.
  - VIII) Opens COMBINE dialog box (see **index**).
  - IX) Divides the visible area of the Active Graphic Window in four equal parts and displays all x,y-graph (see **index**, SHOW ALL).
  - X) Loads and displays the first column from the file of the Active Graphic Window (see **index**).
  - XI) moves to the previous x,y-graph of the Active Graphic Window/
  - XII) moves to the next x,y-graph of the Active Graphic Window.
- 1) Selects a new font size for all WinXAS Graphic Windows. This Font size is used for the axis and the inscription only.
  - 2) Selects a new font FAMILY from the standard Windows Font Select Box.
  - 3) Selects a new inscription for the X axis. In order to enter a new inscription press button (a) or go to INSCRIBE AXIS.
  - 4) Selects a new inscription for the Y axis.
  - 5) Selects a new inscription for the Z axis.
  - 6) Load and displays a new column as X-axis.
  - 7) Load and displays a new column as Y-axis.

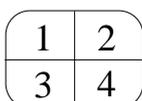
## 2.3 WinXAS Graphic Windows

With every new file you select from the menu OPEN, WinXAS opens a new Graphic Window. This window displays the content of the file in a X,Y graphical presentation (x,y-graph). The name of the corresponding file is shown in the window's title bar. Up to four Graphic Windows can be open at the same time.

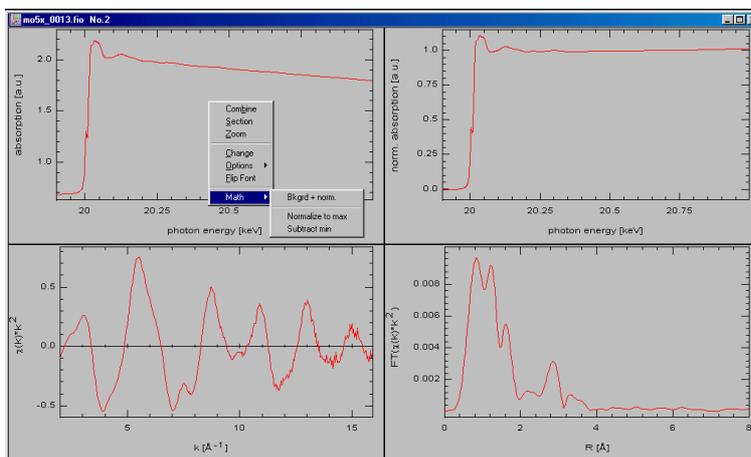
Each Graphic Window can hold up to four x,y data arrays. The arrays are assigned in a merry-go-round manner (1,2,3,4,1,... etc.). Each time you choose a numerical procedure from the menu, WinXAS will copy the current array to the next position and perform the operation on this array (note that there are some exceptions to this rule). For example, let's assume you select a two-column file. WinXAS will then open a new Graphic Window, load both columns and display them. In the next step you choose to calculate the second derivative. WinXAS will then copy the original columns to the next array and calculate the derivative. Thus, your Graphic Window holds two x,y-graphs now. You can go one step back and perform the calculation again with different parameters. In case all four arrays are used and you choose another procedure,

WinXAS will overwrite the first array and then carry out the calculation. And so on and so forth. Got the idea? That's the philosophy behind the Graphic Windows.

Basically, a Graphic Window offers two modes to display its x,y-graphs. First, the Active X,Y-graph (see below) fills the entire window. Second, all x,y-graphs are plotted in four equal quarters of the window (see **index**, SHOW ALL). The order is :



In order to change from one display mode to the other, just click with the left mouse button inside the Graphic Window. Moreover, you can select one out of the four plots by clicking the left mouse button inside its quarter.



Each time you press the left mouse button in one quarter of the SHOW ALL mode, a small gray rectangle appears, attached to the mouse cursor. This rectangle can be used to combine two or more x,y-graphs. In order to do so, press the left button in one quarter and keep it pressed. Move the rectangle to another quarter and release the mouse button. Both graphs will be displayed together in this quarter. In order to add another graph to the combination just do the same. The graphs don't have to be in the same Graphic Window.

In addition, you can choose whether you want to plot the next graph versus the left or right Y-axis by simply releasing the mouse button in the left or right side of the quarter, respectively.

As long as you add new graphs to an existing combination, the Graphic Window will remain in the SHOW ALL mode. In order to display the combined graphs on the entire Graphic Window, click with the left mouse button on the combined display. To switch off an existing combination you can use the combine option in the local menu.

**Local menu:** (activate with right mouse button inside the window, refer to menu items for details)  
 COMBINE, SECTION, ZOOM, CHANGE, GRAPHIC OPTIONS, DEFAULT FONT, ASSISTANT

**FLIP FONT:** Allows you to change font and several plot options of the Active Graphic window. The menu item flips between both WinXAS default fonts. The settings for these fonts can be changed in the dialog box DEFAULT FONTS. The start-up font is used as default font every time a new graphic window is opened.

**Maths:** Automatically searches for minimum and maximum in the Active X,Y-graph and permits to subtract the minimum, normalize to maximum, or do both at once.

Some terminology used in this manual:

- The '*Active Graphic Window*' refers to the currently selected Graphic Window, i.e. the window with the highlighted title bar. Almost all menu items refer to this window.

- The '*Active X,Y-graph*' refers to one out of the four data arrays of each Graphic Window. The Active X,Y-graph is the array that will be processed and changed by the next chosen action/menu item. If only one x,y diagram is displayed, well then this is the Active X,Y graph. If a Graphic Window is divided into four parts, the number of the Active X,Y-graph is shown in the window's title bar.

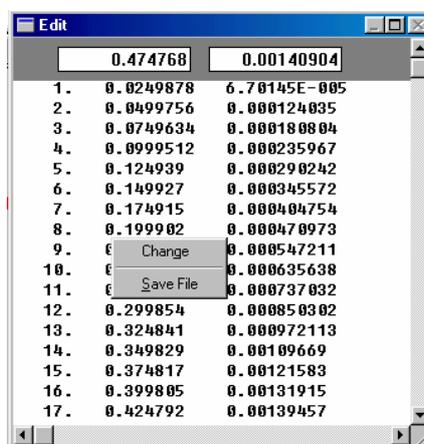
## 2.4 WinXAS Edit Window

The WinXAS Edit Window displays the content of the Active X,Y-graph as numbers in one X and one Y column. The Edit Window can be used in order to change single data values and to delete or add new lines.

In order to edit a single value, highlight the corresponding line in the edit window and change the X or Y value in one of the two edit boxes at the top of the EDIT window. Press [ENTER] and graphic window and Edit Window will be updated with the new value immediately.

In order to delete a whole line, press the [DEL] key. To create a new line, press the [ENTER] key and enter new X and Y values for the new line.

Furthermore, WinXAS allows you to select a particular position in the Edit Window by clicking on the corresponding position in the Graphic Window. Therefore, press the [SHIFT] key and click with the left mouse button on a data point in the Graphic Window. Immediately, the caret in the Edit Window will jump to the according position. Now you can change this data point and make the change visible with the [+] key on the number pad. This procedure, for instance, can be used to remove glitches from your spectrum. Just click on the glitch and change its Y value in the Edit Window.



In addition to change a value by hand in the Edit Window, you can also change it with the mouse directly in the graphic window. For that, press the [SHIFT] key and select the data point with the left mouse button (the caret in the Edit Window is at the according position now). Next, press the [CTRL] key and select a new ordinate value for the data point with the left mouse button. The Graphic Window will show your change immediately. In order to use this method, the Edit Window has to be open even though you might not need or use it. This procedure can also be used in the ZOOM mode of the Graphic Window! (to appreciate the convenience of this method, I would recommend to play around with it !).

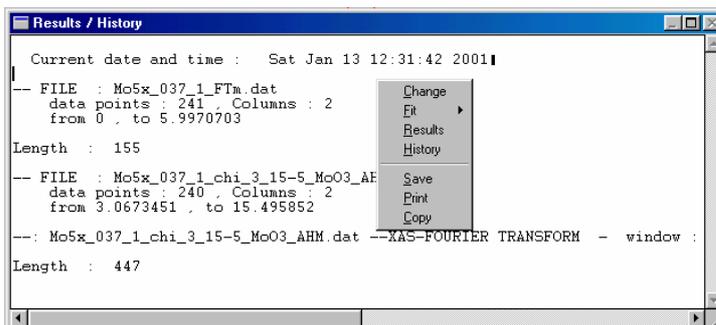
**Local menu:** (activate with right mouse button inside the window)

- CHANGE goes to the next WinXAS window
- SAVE FILE as WinXAS binary file (for ASCII format see **index**, SAVE)

## 2.5 WinXAS Result Window

The WinXAS Results Windows keeps track of all open files and performed procedures. Numerical results are saved in different 'regions' of the window. In order to change from one region to another you have to use the LOCAL MENU. Note that none of the normal WinXAS menu items apply to the Result Window.

Note also, that the editor which is used to display the content of the Result Window, doesn't change this content. That means, you can delete lines from the editor, without actually deleting them from the Result Window. The advantage is, that you can write in the editor, you can delete lines and copy parts of the editor into another type-setting program without changing the Results Window itself. In order to restore the original content just select *History* or *Results* from the local menu (this also works if the Result window does not show the most recent numerical results). **Re-selecting from the local menu also helps if moving the cursor or highlighting parts of the content do not seem to work anymore (XP).**



### Local menu :

**History:** The history region lists all procedures and files together with the entered parameters as well as all numerical results. Each entry in this region has the following format :

```
--: MGO.MES --GOLAY-SAVITZKY-SMOOTH
      - points : 10 - iterations : 2 degree of polynomial : 4 - (active : 2 )
```

The first part of the entry is the file name and the second part the 'name' of the chosen procedure. After the procedure, a number of parameters is listed as they were entered in the according dialog box. At the end of each entry the number of the Active X,Y-graph is added.

**Results:** The results region shows the numerical results of the last procedure, if there are any. For instance, if you had WinXAS searching for all roots in the Active X,Y-graph, you can find the result of this search listed in this region. Every time WinXAS comes up with numerical results, a copy is also stored in the History region for later comparison and such like. **Confidence limits and F test parameters are displayed and saved in the Result window.**

**Fit-Results and Fit-Difference:** Holds the numerical results as well as the fit difference of the last least-squares refinement. In addition to the History region more information such as the correlation matrix and a fit history are shown in this region.

**FEFF single scattering paths:** Displays single scattering FEFF paths from a XAFS refinement to an experimental  $\chi(k)$  or  $FT(\chi(k))$  using theoretical FEFF phases and amplitudes. Multiple scattering paths are not displayed. Furthermore, a table is generated which contains the fitting parameters CN, distance R, Debye-Waller factors,  $E_0$  shifts, and the relative weights of the scattering paths. In particular the latter can be used to conveniently transfer fitting results to a word-processing program.



**Note that the magnitude and imaginary part of the experimental and theoretical FT are saved together in a five-column file, while the experimental and theoretical  $\chi(k)$  are saved in a three-column file.**

The table above shows an example output of a least-squares refinement. Standard deviations are obtained from the diagonal elements of covariance matrix of least-square refinement (meaningful with suitable estimate of experimental error only). Residuals and  $\chi^2$  are calculated from:

Fit Parameters, Errors, and Residuals				Fit Correlation Matrix				
--LEAST-SQUARES FIT ( active : 1 )								
-- FILE : Assist_4.mes								
Iterations:	9			1	2	3	4	5
(CHI)'2:	0.022709075			1	0	0.273	0.762	0.241
Residual:	8.294249			2	0	0	0	0
Exp.Error:	5.855E-003			3	0.273	0	1	0.378
chi2 w/o error:	0.0068575031			4	0.762	0	0.378	1
data points:	321			5	0.241	0	0.971	0.331
-----								
parameter	initial			Correlation matrix is obtained from non-diagonal elements of covariance matrix of least-squares fit.				
feff-Fit				Values range between -1 and 1 with either indicating strong correlation (above: zero value indicates fixed parameter in fit).				
Coord.No.:	12.3425	+ - 1.0695487	12					
distance R:	2.74045	+ - 0.0034032	2.75					
sigma:	0.00361	+ - 0.0005272	0.005					

$$(\mathbf{CHI})^2 \text{ (minimized parameter in fit)} = \frac{1}{\sigma^2} \cdot \sum_{i=1}^N [y_{\text{exp}}(i) - y_{\text{theo}}(i)]^2$$

$$\mathbf{CHI2 w/o error} = \sum_{i=1}^N [y_{\text{exp}}(i) - y_{\text{theo}}(i)]^2$$

$$\mathbf{reduced CHI2} = \frac{1}{(N - np) \cdot \sigma^2} \cdot \sum_{i=1}^N [y_{\text{exp}}(i) - y_{\text{theo}}(i)]^2$$

$$\mathbf{Residual [\%]} = \frac{\sum_{i=1}^N |y_{\text{exp}}(i) - y_{\text{theo}}(i)|}{\sum_{i=1}^N |y_{\text{exp}}(i)|} \cdot 100$$

with  $N$  the number of data points,  $np$  the number of free parameters in the fit,  $\sigma$  an estimate for the experimental error, and  $y_{\text{exp}}$  and  $y_{\text{theo}}$  experimental and theoretical data points, respectively.

For XAS fits the Difference Window will not only show the difference between experimental and theoretical curve but also the Fourier transform of the experimental and theoretical  $\chi(k)$  as well as of the difference. Additionally, the difference together with the Fourier transforms is saved to a file '**RESID\_F.DAT**' in the WinXAS root directory for later processing.

**Save:** Saves the entire content of the region you just see in the Result Window to an ASCII file.

**Print:** Prints the entire content of the editor. In case you don't want to print all you see, don't hesitate to delete useless parts. As mentioned above, that doesn't change the content of the Result Window.

**Copy:** Copies the highlighted part of the Result Window to the Clipboard. Parts of the Result Window can be highlighted with either the mouse or the keyboard.

## 3. online help

### 3.1 WinXAS assistant

The WinXAS assistant contains a couple of guided tours meant to illustrate general operations as well as specialized data analysis steps. Just select a guided tour from the list box and follow the instructions given in the assistant's text window. Give it a try, some things may just be easier from „learning by doing“.

### 3.2 Status line

The status line is divided into two parts, showing information about the data array in the active graphic window (i.e. X and Y interval, number of data points)(right side) and either x,y coordinates of the mouse cursor in the active graphic window or help text for menu items (left side).

X = 1.79416 , Y = 0.074792	X: 0 to 7.9961   Y: -0.099501 to 0.099501   No: 321
----------------------------	---

## 4. WinXAS menus

### 4.1 FILE menu

#### 4.1.1 Open

Opens a new graphic window and displays the content of the selected file in a X,Y-diagram. I guess, you have seen the Windows "file select box" before. However, it offers some neat details that are worth emphasizing. It actually behaves like a mini-Explorer Window. You can rename and delete files, create sub-directories and copy/move files to them, and you can sort files in ascending or descending order with respect to date, size, or name. No more than four Graphic Windows can be open at the same time. WinXAS will tell you that no more windows are available in case you try to open a fifth window.

WinXAS does not require any particular file extension or data format. Also, no particular data format is expected. A large number of one, two, or multiple column ascii files can be read and processed. Hence, XAFS data from different beamlines, but also not XAFS related data from other experiments can be used. With any new file you attempt to open, WinXAS will seek to determine its file structure and see whether it can be read. In cases, where this operation comes out negative, WinXAS will tell you so.

A few words about the 'File-Open-Algorithm': WinXAS performs a sort of check on the selected file. First, it looks for the WinXAS binary format flag. If it finds the binary flag, the file is loaded according to the content of the file's header.

If the flag is not there, WinXAS will assume an ASCII file. This leads to the fact, that trying to open a binary non-WinXAS format file will most likely result in a crash of the program. Therefore, if WinXAS happens to crash while opening a file, it's recommended to have a closer look at the file structure with a simple editor.

In the next step WinXAS tries to determine some characteristics of the file, i.e. the number of text lines in the file's header, the number of data columns and how these columns are separated (space, comma, etc. ). Provided WinXAS can somehow recognize a readable format it reads the first two columns (X and Y) and displays them. Some information about the file is stored and can be accessed via the FILE-INFORMATION dialog box.

This 'recognize' algorithm works quite well for a large number of different ASCII formats (for instance, FEFF output files can be read without change). However, the automated file check procedure and the possibility to read and process a number of different formats has a price. There are some formats that can't be read instantaneously and WinXAS will issue a corresponding message. The formats in the following table, for instance, can not be read with WinXAS:

no text lines are allowed after the data columns	all data columns must have the same length	WinXAS requires at least one monotonous X column.
1      2.5 2      5.4 3      4.7 4      7.1 End, have a nice day	1      2.5 2      5.4 3      4.7 4      .	1      2.5 2      5.4 3      4.7 4      7.1 4      4.5

And there may as well be some more specialized file formats, for instance, that the 1st column of an ASCII file may be the Y- and the 2nd the X-column. But they exist, and by pure chance WinXAS is even capable of reading them.

### 4.1.2 Load

In contrast to OPEN, no new Graphic Window is opened, but the first two columns of the selected file are loaded and displayed as X,Y-diagram in the active Graphic Window. This function is useful for either combining more than four X,Y-graphs in a single graph or for a numerical combination of two spectra (i.e. in order to subtract one spectrum from another both have to be in the same Graphic Window (see **index MODIFY ORDINATE**)).

### 4.1.4 Save File

The X,Y-graph of the active Graphic Window is stored as a two column binary WinXAS file (see Appendix for WinXAS format).

### 4.1.5 Save ASCII File

 The X,Y-graph of the active Graphic Window is stored as a two column ASCII file (one text line, values separated by commas). **In addition, if the numerical function is displayed together with the experimental curve, the function is saved as third column in the ASCII file. Moreover, if a the numerical function consists of more than one individual function and all individual functions are displayed together with the**

experimental curve, all the individual functions are also saved in the multiple-column ASCII file. This way, fit results (e.g. FT XAFS fits, XANES fits, etc.) can be exported and displayed with some other plotting program.

### 4.1.3 Average Spectra

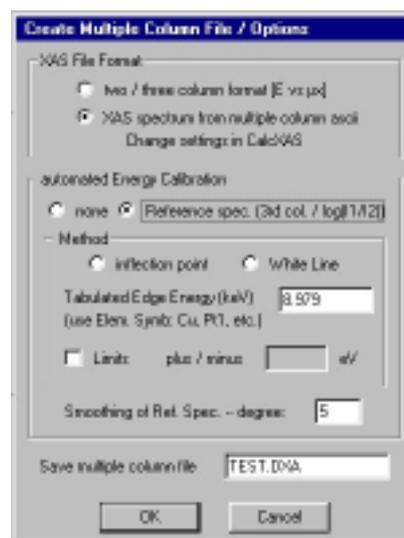
The Open-File dialog box allows a multiple selection of  $N$  files. All selected files are loaded, summed, and averaged. The resulting spectrum is displayed in the active Graphic Window and can be saved or further processed. The spectra from #2 through # $N$  are interpolated by cubic splines to the X-axis of the first spectrum.

Additional to mere averaging, XAS spectra can be calculated from multiple column ASCII files and an automated energy calibration can be carried out. For the former, 'your favorite format' from the CALCULATE XAS SPECTRUM dialog box is used. If you want to change this format, just OPEN one of the files you want to average and select columns that correspond to  $E$ ,  $I_0$ ,  $I_1$ , and  $I_2$ . In order to perform an energy calibration of each spectrum, a valid reference column has to be present (either  $I_2$  in multiple column ASCII files or  $I_{ref}$  in a three column file ( $E$ ,  $I_{sample}$ ,  $I_{ref}$ )). WinXAS can search for edge position (inflection point) or 'white line' position in the reference spectrum. The difference between the value found and the tabulated energy as input in the dialog box is calculated and the sample spectrum is corrected accordingly prior to averaging.

### 4.1.7 Create Multiple Column File

The open-file dialog box allows a multiple selection of  $N$  files. All selected files are stored in a binary multiple column file. The spectra from 2 through  $N$  are interpolated to the X-axis of the first spectrum. In addition, XAS spectra can be calculated from multiple column ASCII files and an automated energy calibration can be carried out (see AVERAGE SPECTRA). For the latter, inflection point (maximum in first derivative) or white line (maximum in second derivative) can be used. Instead of the tabulated edge energy an element symbol can be used (confirm with RETURN to substitute symbol with energy). Furthermore, a limit (in  $\pm$  eV) can be set to restrict the search range for the maximum determination to  $EDGE \pm LIMIT$ . For noisy reference spectra a smoothing algorithm (Fourier) can be applied prior to the maximum search.

A multiple column binary file is needed for a MULTICOLUMN-PLOT of more than 16 spectra or an automatic analysis using WinXAS macros. The latter is essential for a convenient analysis of data obtained from time-resolved experiments (either DXAS, QEXAFS, XRD, or any other technique).



### 4.1.8 Save Multi Column to ASCII

Saves a multiple column WinXAS binary file to a multiple column ascii file. The number of columns is restricted to 100 (Note that the multiple column ascii file can of course be read by WinXAS, however, no automated macro analysis or multiple column plotting can be performed.).

### 4.1.8 Extract MC Files

Saves the **N** individual columns of a multiple column file into **N** individual ascii or binary files (optional). The file names consist of the parent file name and the column number in the multiple column file.

### 4.1.8 Append to ASCII File

The X,Y-graph of the active Graphic Window is appended to an existing two column ASCII file. The continuity of the X-axis of the resulting file is not checked for and has to be verified by the user. For instance:

existing ASCII file		+ content of Graphic Window		leads to: (file cannot be opened anymore!)	
1	2.5	4	4.5	1	2.5
2	5.4	5	2.6	2	5.4
3	4.7	6	3.1	3	4.7
4	7.1			4	7.1
				4	4.5
				5	2.6
				6	3.1

### 4.1.6 Add to Multiple Column File

The X,Y-graph of the active Graphic Window can be appended to an existing binary WinXAS file. The spectrum is interpolated to the X-axis of the selected file (see **index**, Create Multiple Column File).

### 4.1.9 Print

Prints the content of the active window on the selected standard printer. If a Graphic Window is active, the X,Y-graph will be printed in a more or less WYSIWYG manner. The appearance of the graph can be changed in GRAPHIC OPTIONS (also see **index**, COPY TO CLIPBOARD). Size and orientation of the output can be changed in PRINT-OPTIONS. If the Result Window is active, its content will be printed.

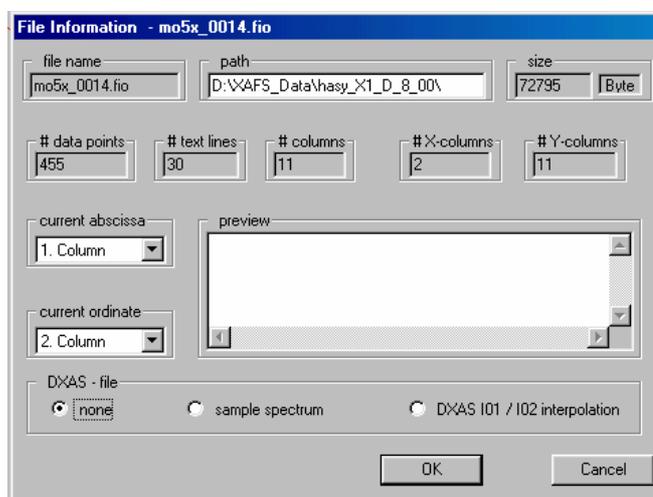
### 4.1.11 Edit

Opens the Edit Window and displays the content of the active Graphic Window in a two column format (see **index**, EDIT WINDOW for details).

### 4.1.12 File Information

Opens the File-Information dialog box. The box contains some general information obtained from the OPEN file check such as size, path, number of data points, text lines, and columns, etc.

In case the active Graphic Window is related to a multiple column file, these columns can be accessed by choosing one X- and one Y-column. Only appropriate X column can be selected. X- and Y-columns can also be loaded using the BUTTON window.



(The DXAS options are only for advanced users of the DXAS beam lines at the ESRF (ID24) or at HASYLAB, Hamburg.)

### 4.1.13 About

Contains WinXAS version, license number (needed for correspondence), and name and institution of licensee.

### 4.1.14 Convert data

Some particular data formats can be converted into more suitable, more compact, or simply readable formats. For expert users only.

### 4.1.15 Exit

Terminates WinXAS. If there are open Graphic Windows you will be prompted to confirm your choice.

## 4.2 EDIT menu

### 4.2.1 Function → x,y-graph

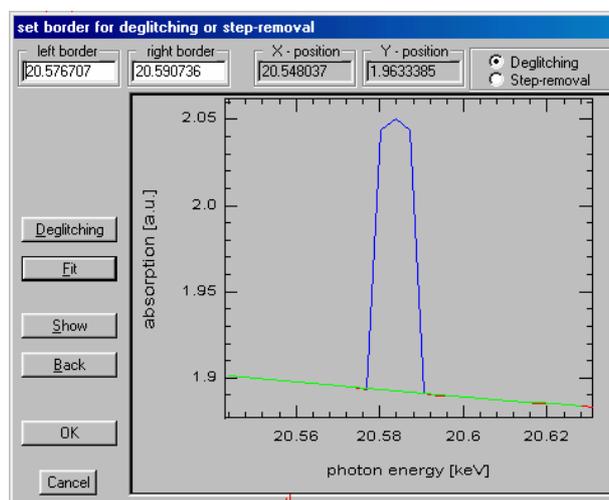
The function of the active Graphic Window (by default blue) is calculated into a data array. The number of data points can be chosen, except for XAS formulas, where the number of points for the original array and the function have to be equal.

This menu item allows one to save a function as a data array or to process the array in a way which is not available for functions (i.e. FFT, etc.). Furthermore, in case a function consist of several single functions, each single function can be extracted and calculated into an array. In this way, for example,  $\chi(k)$  or  $FT(\chi(k))$  for each contributing path in an EXAFS formula can be obtained.

### 4.2.2 Deglitching

So-called 'glitches' can be removed from a spectrum. If the glitches consist of only one or two data points, please refer to FILE OPTIONS. There, very narrow features can be optionally removed already while the spectrum is loaded.

In case the glitches consist of several data points, a more elaborate method is described in the following: The overall aim is, to refine a polynomial to a selected region around the glitch while disregarding the glitch.



Afterwards, the glitch is removed by taking the polynomial values in the region which was excluded from the fit.

1. choose a degree for a polynomial to represent the data in the neighborhood of the glitch (normally 3 or 4 is sufficient).
2. select a region of the spectrum which includes the glitch plus a smooth part of the spectrum to the left and the right of the glitch. Press the 'SHOW' button.
3. select the glitch (highlighted in blue) but don't 'SHOW'.
4. press the 'FIT' button. The polynomial is refined to the visible region, excluding the selected glitch.
5. press the 'DEGLITCHING' button, in the selected region the glitch is substituted by the polynomial.

The same procedure can be used to extract pre-edge features. After substituting the pre-edge peak by a smooth polynomial, just go one step back in the active graphic window and subtract the 'degitched' spectra from the original data (see **index** MODIFY ORDINATE).

### 4.2.3 Paste x,y-graph

The active X,Y-Graph (source) can be pasted into another x,y-graph (destination) of the same Graphic Window. The original content of the destination is overwritten in the source region, but the number of data points of the destination is maintained. This procedure requires, that the source border lie within the destination borders.

X,Y-graphs can only be pasted within one Graphic Window. In case, one file shall be pasted into another, use LOAD in order to get both files in one window.

### 4.2.4 Copy x,y-graph

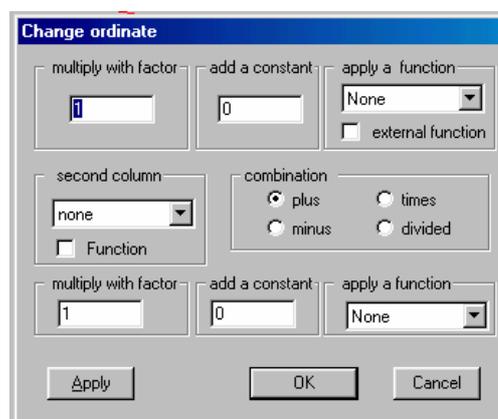
The Active X,Y-graph of the Active Graphic Window can be copied to any other x,y-graph of any other Graphic Window. The destination x,y-graph is overwritten.

### 4.2.5 Modify Ordinate

The ordinate values of the Active X,Y-graph can be changed (this procedure is applied to all values. If only single values shall be changed, refer to EDIT WINDOW).

The MODIFY ORDINATE dialog box offers the following options (changes can be displayed immediately by pressing APPLY):

- all ordinate values can be multiplied with a constant or a constant can be added. The values 1 and 0, respectively, will be ignored. The order of evaluation goes from left to right.
- one of the available functions can be applied to all ordinate values. In addition, the currently set window FUNCTION can be applied to the ordinate of the Active graph. This permits a maximum flexibility in modifying the ordinate value (e.g. conversion of ordinate values by applying a suitable polynomial)



Moreover, the ordinate value of the Active X,Y-graph can be combined with another x,y-graph of the same Graphic Window or with another data column of the basis file. The data array is interpolated to the abscissa values of the X,Y-graph. Additionally, this array can also be changed by multiplying or adding a constant prior to performing the procedure.

As an option, the function of the Active Graphic Window can be added, subtracted, etc. from the ordinate values. This procedure can for example be applied in order to obtain the residual  $\chi(k)$  after a XAS refinement (Difference File Technique, see EXAMPLES).

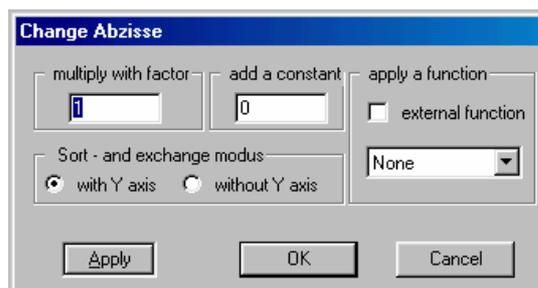
## 4.2.6 Modify Abscissa

The abscissa values of the Active X,Y-graph can be changed (this procedure is applied to all values. If only single values shall be changed, refer to EDIT WINDOW).

The MODIFY ABSCISSA dialog box offers the following options (changes can be displayed immediately by pressing APPLY):

- all abscissa values can be multiplied with a constant or a constant can be added. The values 1 and 0, respectively, will be ignored. The order of evaluation goes from left to right.
- one of the available functions can be applied to all basic values. In addition, the currently set window FUNCTION can be applied to the abscissa of the Active graph. This permits a maximum flexibility in modifying the abscissa value (e.g. conversion of abscissa values by applying a suitable polynomial)

Additionally, the function of the Active Graphic Window can be used on all abscissa values. This procedure for example can be applied in order to change from monochromator steps to photon energy if an appropriate formula can be expressed with the built-in WinXAS profile functions.



## 4.2.7 Noise Generator

Adds some random noise to the Active X,Y-graph. The input value represents approximately the 'root-mean-square deviation' for each data point.

## 4.2.8 Write FEFF - "Files.dat"



A new FEFF "files\_x.dat" file is generated based on the FEFF phases and amplitudes used for a XAFS simulation (perform FEFF simulation prior to attempting to generate a new "files\_x.dat" file). "feffxxxx.dat" (and the corresponding phases and amplitudes) are included in the "files\_x.dat" file according to their current relative weight (e.g. 5 %) in the simulation. The new "files\_x.dat" file can then be used for XAFS simulation or fits just as the original "files.dat" file (while containing only the significant FEFF paths and amplitudes). Moreover, the "paths" information of the phases used is copied from the "paths.dat" file into the new "files\_x.dat".

## 4.2.8 Change FEFF Angle

Permits to recalculate a FEFF simulation with a slightly changed angle of one particular scattering path. Is intended and works best for linear scattering paths where the effect of a deviation from 180° is most promi-

ment. The angle of a linear scattering paths is changed by displacing the central atom of this path in the FEFF input cluster. The remaining part of the structure is left unchanged. This certainly holds for minor deviations from 180° only.

In order to run this option you need to have a version of FEFF installed in a folder called "feff" in your WinXAS root directory. Ideally, this is not your normal FEFF working directory, because WinXAS will modify input files and run FEFF to create new "feff000x.dat" files. The newly created phases and amplitudes are used to perform a XAFS  $\chi(k)$  simulation.

### 4.2.8 Show FT Magnitude

The magnitude of the complex Active X,Y-graph is calculated and displayed. The procedure automatically switches off the SHOW IMAGINARY PART (see **index**, GRAPHIC OPTIONS) thus only the positive part can be seen. If the entire magnitude shall be plotted the imaginary part can be switched on again by pressing the corresponding button (see **index**, WINXAS BUTTONS).

This menu item must be chosen in order to obtain the 'FT[ $\chi(k)$ ]' which than can be used for a XAS refinement in R space (see **index**, XAS-FIT) or to be compared or plotted together with other FT[ $\chi(k)$ ]. For back transformation (see **index**, XAFS - FOURIER TRANSFORM) this menu item must not be chosen prior to the transformation.

### 4.2.9 Extract Imaginary Part

The imaginary part of a complex Active X,Y-graph can be extracted and displayed as a single real x,y-graph. This procedure is intended for graphical purposes only, i.e. if you want to display the FT magnitude together with only the imaginary part, or to compare magnitude and imaginary part from two different samples, you first have to extract the imaginary part from the complex FT.

### 4.2.10 Copy to Clipboard

The content of the active Window is copied to the Clipboard for later use with other programs (word processor, graphic, etc.). If the active window is a Graphic Window the Active X,Y-graph will be copied to the clipboard in a more or less WYSIWYG manner. For the format, you can choose between Windows metafiles or Bitmaps. The advantages of metafiles are their smaller size and that they can be re-scaled without loss of quality. Unfortunately, not all program do interpret the metafile format correctly. In these cases it may be preferable to save the graphic as a Bitmap in its final size. (please note that special characters in the axis inscription are displayed best in the same X to Y ratio as on the screen. The latest versions of common word-processors allow to change the graphic by double-clicking on the plot).

If the active window is the Result Window, the highlighted (selected) part of the content will be copied to the Clipboard. This means, in order to copy the content of the Result Window or parts of it to the Clipboard, this part first has to be selected using either the mouse or the keyboard (see **index**, RESULT WINDOW).

### 4.2.12 Open New Window

A new Graphic Window will be opened with the Active X,Y-graph. The file information is taken from the 'parent' Graphic Window. This procedure is convenient, if you want to process the Active X,Y-graph but don't want to overwrite other data arrays in the Active Graphic Window. For example, given that you have ex-

tracted the  $\chi(k)$  from your absorption spectrum. At this point, the Active Graphic Window probably still contains the spectrum versus energy. If you now proceed and calculate the Fourier Transform of your  $\chi(k)$  this spectrum will be overwritten. Therefore, it may be better to open a new window with the  $\chi(k)$ , calculate the FT and if you don't like it, you can just dismiss the new window, go back to the original Graphic Window and start over again with the old spectrum. If already four Graphic Windows are open this menu item will be disabled.

## 4.3 SHOW

### 4.3.1 Function

Switches the display of the function of the Active Graphic Window on or off.

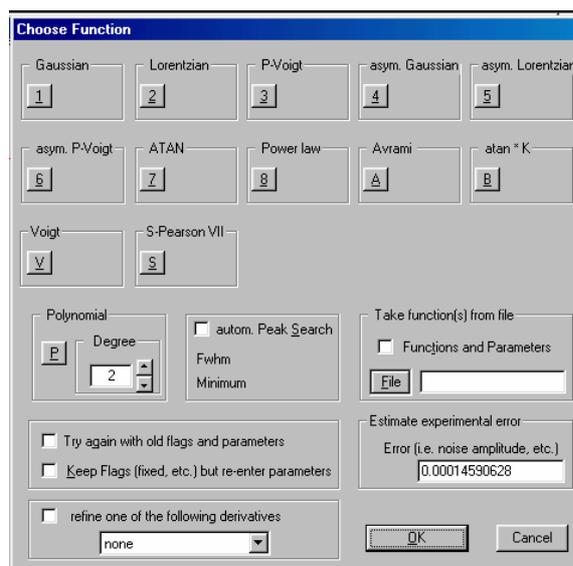
### 4.3.2 Data array

Switches the display of the Active X,Y-graph of the Active Graphic Window on or off.

### 4.3.3 Choose Function

Opens the CHOOSE FUNCTION dialog box. The function of the Active Graphic Window can be composed out of several built-in profile functions. In order to enable a profile function, press the corresponding button and thereafter change the number of functions by using the corresponding scroll bar. Any values smaller than one will be ignored. In order to disable a profile function press once again on its button.

Functions together with their parameters can also be chosen from an existing parameter file. For this, press the FILE button and select a file. Close the dialog box. Profile functions and parameters will be taken from the file and the resulting function can be displayed by pressing [F8] (see **index**, FUNCTION).



The following lists some formulas for built-in profile functions (where  $H$  is peak height,  $P$  is peak position, and  $W$  is Full Width at Half Maximum (FWHM))

$$\text{Gaussian : } f(x) = H \cdot e^{-\left(4 \cdot \ln(2) \cdot \frac{(x-P)^2}{W^2}\right)}$$

$$\text{Lorentzian : } f(x) = H \cdot \left[1 + 4 \cdot \frac{(x-P)^2}{W^2}\right]^{-\alpha} \quad (\alpha=1 \text{ for standard Lorentzian})$$

$$\text{Pseudo-Voigt : } f(x) = \alpha \cdot \text{Gaussian} + (1 - \alpha) \cdot \text{Lorentzian}$$

$$\text{Arctangent :} \quad f(x) = \frac{H}{\pi} \cdot \arctan\left(\frac{\pi}{W} \cdot (x - P)\right) + \frac{H}{2}$$

$$\text{atan*K :} \quad f(x) = \frac{H}{\pi} \cdot \arctan\left(\frac{\pi}{W} \cdot (x - P)\right) + \frac{H}{2} + (x - P) \cdot \text{slope}$$

Other options contained in the CHOOSE FUNCTION dialog box are not available when the box is called from the main menu and should be left alone. Those options apply during a LEAST-SQUARE REFINEMENT (see **index**) only.

### 4.3.4 Enter Parameter

Opens the ENTER PARAMETER dialog box. Parameters for each profile function are shown in four columns with the function's name at the top. If more than four profile functions are selected use the NEXT and BACK button to change between the functions. If the ENTER PARAMETER box is accessed from the WinXAS menu, all other options such as FLAGS or GRAPHIC are not available and should be left alone.

Those options become important only if the box is called during a least-squares refinement (see below). In this case, the following FLAGS can be set for each parameter :

**fixed:** Parameter will not be changed during the refinement.

**constrained:** Parameter will not exceed given limits during the refinement.

**correlated:** Parameter A can be correlated to parameter B in a least-squares fit. Correlation means that each time parameter A is changed during the refinement, parameter B will be modified according to a pre-set scheme. For instance, if the selected scheme says „B shall always be set to A + 0.5“ the refinement algorithm will only modify A and always set B equal to A + 0.5. Therefore, correlation reduces the number of free parameters during the fit and allows to introduce meaningful restrains (e.g. the number of atoms in an octahedral coordination should be 6. Therefore, in case you want to refine to different backscatters in the first coordination shell, the sum of both coordination numbers should be set to 6). The SET CORRELATION dialog box (pops up when the correlation flag is checked) enables you to set such correlation for parameters in a least-squares fit. In order to do so, follow this procedure:

- The ‘*selected parameter*’ is the one that will be refined in the fit.
- The first list box ‘*free parameters*’ contains all parameters that are not fixed or correlated yet and that can be correlated to the ‘*selected parameter*’ (‘2. #1, Gaussian, Position’ means 2. Parameter (position) of the 1. Function, which happens to be a Gaussian)
- Select one or more parameters out of the first list box.
- Choose a correlation scheme. Possible schemes are:

- Parameter(s) can be equal to the '*selected parameter*' or their sum can be equal to a given value.
- Parameter(s) can set to the '*selected parameter*' plus, minus, times, or over a given value.
- In addition to a fixed value, a third parameter can be used in the aforementioned schemes.
- After you have chosen a suitable correlation scheme press the *arrow* button between the two list boxes. The chosen parameter(s) will disappear from the first list box and appear in the second list box indicating the selected correlation scheme.
- If necessary, repeat the procedure to correlate other parameters to the '*selected parameter*' using a different correlation scheme. All desired correlations to the '*selected parameter*' have to be chosen during one step. Once the dialog box is closed this parameter will not be available for further correlation.
- Close dialog box with OK if you want to confirm the choices made. Otherwise cancel the box and start again.

(Note that once you have chosen a correlation scheme for a set of parameters, you can't un-correlate them again for this fit. You will have to cancel the ENTER PARAMETER box and start the refinement again).

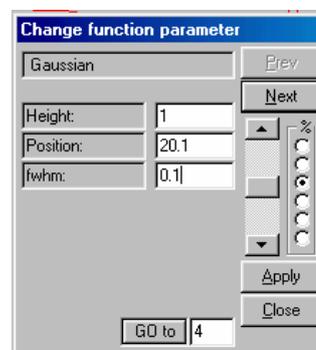
A correlation scheme together with all parameters can be saved and restored for later use. Select one out of three possible schemes and press the [SAVE] button. This procedure is intended to facilitate XAFS fits using higher shells or multiple scattering paths. Therefore, as an example, basic correlations and constrains can be saved in scheme #1. Afterwards, more correlations can be introduced to study their effect on the refinement. In case you need to start all over again or want to remove certain correlations, you can restore correlation scheme #1 and don't have to input all basic correlations and constrains again.

### 4.3.5 Change Parameter

Opens the CHANGE PARAMETER dialog box. This dialog box is one of WinXAS independent dialog boxes, which means it can be left open while other procedures are carried out. However, in order to avoid confusing WinXAS with unexpected input (and yourself with unexpected results) it's recommended to close the CHANGE PARAMETER box when its not needed anymore.

The controls of the dialog box allow you to change the parameters of each profile function sort of interactively. The procedure is the following :

- select one of the parameters by clicking into its edit field.
- select a suitable 'sensitivity' on the %-scale (top=big change, bottom=slight change).
- use the scroll bar to change the selected parameter, the effect of each change will be shown immediately in the Graphic Window.



The "GO to" button permits to jump to a certain function by entering its number. Thus, you don't need to scroll through 50 scattering paths to modify scattering path #51. For FEFF XAFS simulations, the "AREA" button (not shown) allows to calculate the relative weights of all scattering paths. The numerical values (in %) together with the nature of the corresponding path will be displayed in the Results window.

Additionally, it is possible to enter a new value by hand in one of the parameter edit fields and see its effect on the function by pressing the APPLY button. In order to browse through the available profile functions use the PREV and NEXT buttons.

### 4.3.6 Change Border

The borders in which the function of the Active Graphic Window is displayed can be changed. This item is available only if the display of the data array is switched off (see **index**, DATA ARRAY). Otherwise the function is always plotted within the border of the Active X,Y-graph.

### 4.3.7 Save Parameter

Saves all functions, parameters and flags of the Active Graphic Window in an ASCII format file (extension \*.par). This file can be used for later least-squares refinements instead of re-entering all functions and parameters. Slight changes to this file can be made using a normal editor.

### 4.3.8 Load Parameter

Loads functions and parameters for the Active Graphic Window from a PAR-file (see **index**, SAVE PARAMETER).

### 4.3.9 Zoom

The ZOOM option allows to enlarge a part of the Active X,Y-graph. The zoom options represent a break with the general WinXAS philosophy in the sense that procedures chosen from the WinXAS menu still are applied on the entire Active X,Y-graph, not only on the visible part. Users have to bear in mind that something like searching for a maximum in the zoomed part of the Active X,Y-graph will most likely not result in the desired value, but in all maxima of the entire data array.

The zoom option is for graphical purposes only. However, if the COPY GRAPHIC TO CLIPBOARD option is chosen on a zoomed X,Y-graph indeed only the zoomed part will be copied to the Clipboard !

Operating the zoom cross is straightforward. First of all, don't leave the Active Window with the cross, unless you want to see it change back to a normal arrow immediately! Press the left mouse button in one corner of the to-be-zoomed rectangle. Keep the button pressed and drag the gray rectangle until it encloses the part of the spectrum you want to enlarge. Release the mouse button. The selected array will be enlarge to the entire Graphic Window. In order to remind you of the above-mentioned philosophy break, the word ZOOM will appear in the window's title bar. In case you try to leave the Graphic Window with the mouse cursor, the display will jump back to the entire Active X,Y-graph.

### 4.3.10 Section

Opens the dialog box CHOOSE SECTION where an appropriate section can be chosen from the Active X,Y-graph. The edit fields LEFT and RIGHT BORDER contain the current new border. Provided the mouse cursor is moved inside the x,y-plot and the input caret is either in the right or left border window, the edit fields X-POSITION and Y-POSITION will display its actual position inside the graph and a gray line will appear.

In order to choose a new border just click with the left mouse button inside the graph. The actual position of the mouse cursor will be taken as new selection and displayed in LEFT or RIGHT BORDER (de-

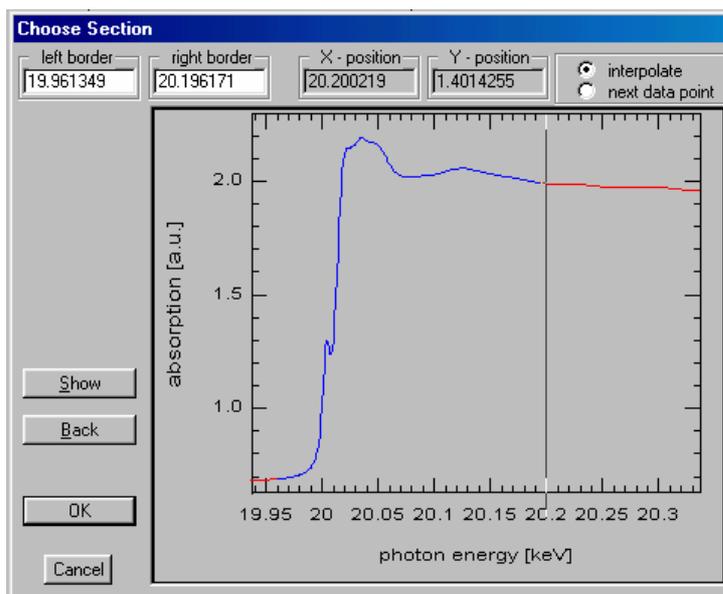
pending on in which edit field the caret was). In order to show the current selection press **SHOW**, to go back to the entire spectrum press **BACK**.

In order to change from the **LEFT** to the **RIGHT BORDER** window, press the right mouse button. This, for instance, enables you to repeat the input of the same border or to maintain one border and just change the opposite one.

Two options are available in order to determine how WinXAS cuts a section out of your data. **NEXT DATA POINT** takes the next nearest data point to the entered value. **INTERPOLATE** linearly interpolates between the two data points that present the interval in which the entered point is situated.

The difference in both ways is obvious : given an X-array [1,2,3,4,5], the selection of 2.1 and 4.7 will result in the array [2,3,4,5] for the **NEXT DATA POINT** style and in the array [2.1, 2, 3, 4, 4.7] for the **INTERPOLATE** style. Note that the later can result in non-equidistant data points! (Nevertheless, the **INTERPOLATE** style is set as default)

Even if no new borders are selected, this procedure will always copy the displayed (or highlighted) part of the spectrum to the next data array. Therefore, the procedure can be chosen in order to just copy the entire spectrum to the next data array. Doing so can be desirable if the next reduction steps will result in a non-reversible change of the spectrum (as it is the case with **MODIFY ORDINATE**) and the spectrum is to be conserved.



### 4.3.11 Original

The first X and Y column are loaded from the original file and displayed in the Active Graphic Window. This procedure is useful in case you have processed and changed your spectrum without obtaining satisfying results and want to start over again with the original as-measured spectrum (see **index**, **OPEN NEW WINDOW** for a clever alternative).

### 4.3.12 Show all x,y-graphs

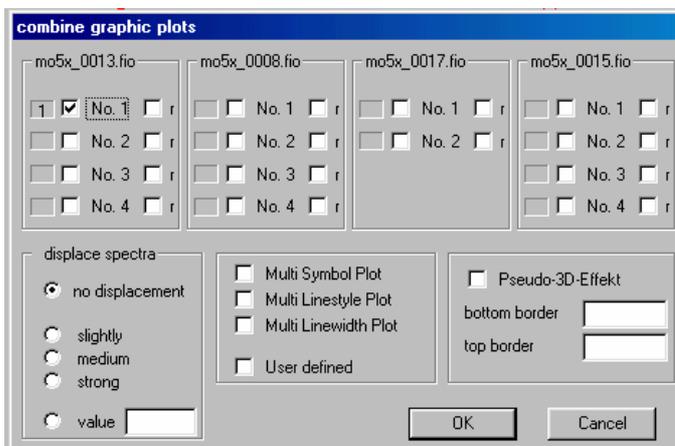
This menu item divides the Active Graphic Window into four parts and displays all data arrays side by side. See **WinXAS BUTTONS** and **WinXAS GRAPHIC WINDOWS** for details.

### 4.3.13 Combine x,y-graphs

Opens the **COMBINE** dialog box. Up to four Graphic Windows are represented in four columns with one select button for each x,y-graph. A combination of all available x,y-graphs can be composed by simply ticking the corresponding select button. The edit field on the left side of each button will display the 'order number'. (for 'easy combining' see **index**, **WinXAS GRAPHIC WINDOWS**).

Several options are available from the COMBINE dialog box :

- by default all selected x,y-graphs are combined on one (left) ordinate. If a x,y-graph shall be plotted versus a second (right) ordinate, select the corresponding 'r'- button.
- all selected x,y-graphs can be plotted with a variable displacement according to their 'order number' from bottom to top. Three default settings are available for the degree of displacement. Additionally a user defined value can be set.
- all selected x,y-graphs can be plotted in different styles (either increasing line width, different line styles or different symbols for each graph). Furthermore, the plot style for each graph can be defined separately,



Except for the USER DEFINED style, the selected graphs are displayed in different colors according to a default color setting. This setting can be changed with the CHANGE COLOR button (see **index**, WinXAS BUTTONS) or within the USER DEFINED dialog box.

- All selected x,y-graphs can be plotted versus a third (Z) axis (Pseudo 3D plot). For this plot equidistance between all spectra is assumed. Bottom and top border refer to the inscription of the Z-axis (bottom > top is allowed !).

#### 4.3.14 Previous

Causes the Active Graphic Window to go one step back in its x,y-graphs and to display the new Active X,Y-graph (full window mode) or to update its title bar (SHOW ALL mode).

#### 4.3.15 Next

Causes the Active Graphic Window to go one step forward in its x,y-graphs and to display the new Active X,Y-graph (full window mode) or to update its title bar (SHOW ALL mode).

#### 4.3.16 Start Macro

Applies an existing WinXAS Macro to the Active X,Y-graph (see **index**, START MACRO REORDER). If the chosen Macro contains invalid values with respect to the Active data array, the Macro processing will be terminated. (i.e. if you have defined a Macro for background subtraction, Energy calibration, E0 determination and  $\mu(0)$ -Fit for a Cu K edge spectrum you can't apply this Macro to a Ti K edge spectrum!).

#### 4.3.17 Start Macro recorder

Starts the WinXAS Macro recorder and saves consecutive data reduction steps in a chosen file. The handling of WinXAS Macros is quite easy, but doesn't offer many options. The procedure is the following :

- press the Macro Recorder button and input a file name. After closing the file select box, the Macro Recorder button will remain pressed until you release it to stop the recording process.
- while the Recorder button is pressed, all performed reduction steps together with the corresponding parameters and functions will be saved to the Macro file (if an action is canceled, it won't be saved).

What sort of operations can be stored in a Macro? Well, almost all! For certain, all numerical operations (i.e. roots, FT, differentiation,  $\mu(0)$ -fit, etc.) but also some graphic steps, such as PREV, NEXT, or PASTE and others like MODIFY ORDINATE or MODIFY ABCISSA. Pure display changes like ZOOM or COMBINE are not saved. Operations such as change to another Graphic Window or OPEN or LOAD another file will terminate the current recording process.

In case an unwanted operation is saved to the Macro file, there is no convenient way to delete it! The Macro recorder has to be stopped and the recording process has to be started again. In uncertain cases, just apply the Macro to the same spectrum it was created with and make sure that the results are consistent.

The Macro options was originally intended for an automatic and convenient treatment of a large number of spectra obtained from time-resolved studies (see **index**, AUTOMATIC ANALYSIS). But of course, that doesn't mean that macros can't be used at any occasion where a fast analysis is required and where the same reduction steps has to be repeated several times. Anyway, in some cases it may be recommended to break up one Macro into a couple of separate steps. That means, instead of making one step from the as-measured spectrum to the EXAFS refinement, have some steps in-between, like  $\chi(k)$ , FT etc.

### 4.3.18 Edit Macro

WinXAS macros are simple ASCII files and can be changed with any editor. In general, the first number of each line is the internal number of a WinXAS menu item. The following numbers represents the necessary parameters related to this item. The next two lines stand for the functions and their flags.

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## 4.4 NUMERIC

### 4.4.1 Least-Squares Fit

The function of the Active Graphic Window is refined to the Active X,Y-graph using a Levenberg-Marquardt least-squares algorithm (refer to *Numerical Recipes in C [1]* for details on algorithm as well as calculation of standard deviation and parameter correlation from covariance matrix). The overall function can consist of several profile functions. (see **index**, CHOOSE FUNCTION for details).

The entire least-squares fit procedure is divided into the following steps :

- I) choose profile functions
- II) enter initial parameters
- III) perform refinement

I)

(see **index**, CHOOSE FUNCTION for details). Functions can either be entered or loaded from a PAR file. Additionally to the refinement of the function itself, its 1st or 2nd derivative can be refined. The algorithm calculates only the derivative of the function. The Active X,Y-graph already has to contain the according derivative.

Additional options are :

- start values for the parameters can be automatically determined using a peak-search algorithm (works reasonably well for gaussian-like, separated peaks)
- if a previous refinement shall be repeated, two options can be used :
  - 1.) the entire refinement can be repeated with the current parameter and flags.
  - 2.) the current flags are kept but parameters have to be re-entered.

II)

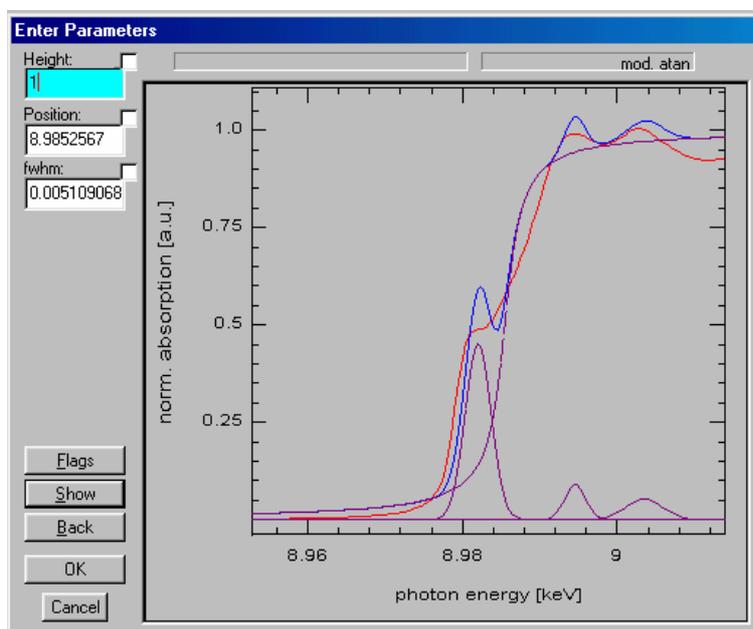
Setting the initial parameters can be performed in two different ways. As default the ENTER PARAMETER/GRAPHIC dialog box is displayed at this point. It allows to enter each parameter interactively from the function/x,y-graph. Alternatively, parameters can be entered by hand in the ENTER PARAMETER/FLAGS dialog box (see **index**, ENTER PARAMETER for details). You can easily switch between both dialog boxes by pressing the buttons GRAPHIC or FLAGS, respectively.

The ENTER PARAMETER/GRAPHIC box offers the following features :

Parameters can be entered by hand for each input field. By pressing the button SHOW the profile function is updated.

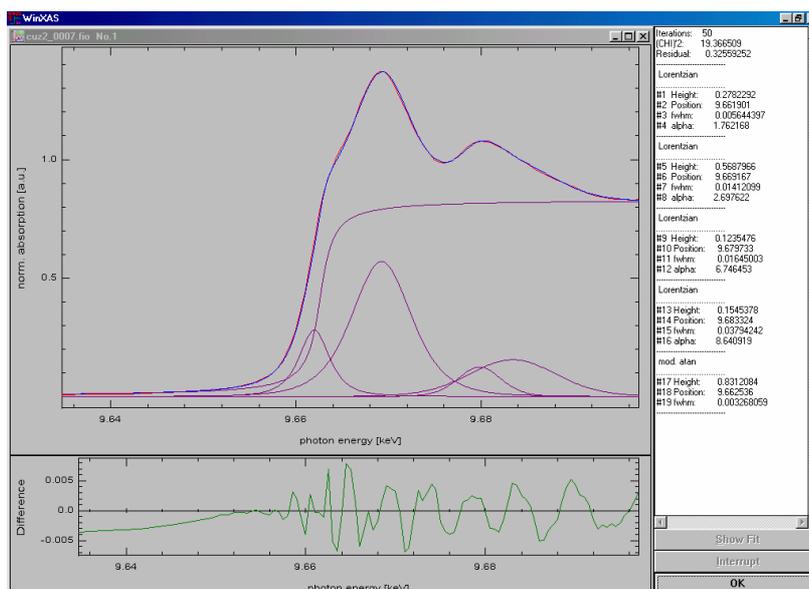
Furthermore, parameters can be entered directly by clicking with the left mouse button inside the x,y-graph. For that, the input caret (this blinking, vertical bar) has to be in the input field of the corresponding parameter. In order to enter an absolute value (such as positions) click once inside the graph at the position of the peak. The corresponding value is taken into the parameter input field, the caret is set to the next field and the profile function is updated. For all other parameters (such as height, full width at half maximum, etc.) click twice inside the graph (from - to, order makes no difference).

Again (see **index**, SECTION) the RIGHT mouse button can be used to just change the caret from one input field to the next without any changes.



The button BACK goes one step back to the previous function. As long as not all profile functions have been initialized the OK button reads NEXT for the next profile function. Once all functions are set the button changes to OK and by pressing it the least-squares refinement will begin !

Parameters can be fixed by ticking the little square at the top/right corner of each input field.



### III)

If the refinement is started, the WinXAS window will change dramatically and there is only one way to

restore all the little buttons and menus; press the OK button (or the CANCEL button during the fit). Although the graphic window is not disabled during or after the fit, fiddling around with it will accomplish nothing. But now from the beginning : during the refinement the WinXAS desktop is divided into three parts.

I) The Graphic Window which displays the data array together with the profile functions and the difference between data array and function. If more than one profile functions is selected, the top graph will display the array, the overall function and each single profile function (dotted lines).

II) An Edit window which shows the numerical values for each parameter during the refinement as well as the fit residual, number of iterations, etc.

III) The third part consist of three buttons :

- OK/CANCEL button : if the refinement is finished, this button will read OK and pressing it will return to the normal WinXAS surface. During the fit this button reads CANCEL and pressing it will terminate the fit and return to WinXAS.
- INTERRUPT button : during the refinement, this button opens the ENTER PARAMETER dialog box for changes of single parameters.
- SHOW FIT/CONTINUE button : depending on the chosen refinement style (see **index**, FIT OPTIONS) this button reads SHOW FIT for the CONTINUOUS style (no display of each iteration if not SHOW FIT was pressed) and CONTINUE for STOP ITERATION style (stops fit after each iteration and updates the graphic window). For the AUTOMATIC style the button is disabled.

**Important:** pressing one of the buttons will not immediately result in any action ! Only after the algorithm returns from the current iteration, user input is evaluated. Hence, just press a button once and then wait what happens! The results of a refinement are stored in the RESULT Window (see **index**).

### 4.4.2 Restore parameters



Restores the fitting parameters after a failed least-squares refinement. Convenient to use if a refinement goes completely wrong and you want to start over again. This item should be used before you reenter into the refinement or simulation dialog boxes. It is also available from the local menu of the active graphic window.

### 4.4.3 Confidence limits



Confidence limits can be calculated for each individual parameter. In the corresponding procedure, one parameter is successively varied by a certain percentage (e.g. 0.05 % for R and 5 % for  $\sigma^2$ ) and the refinement is restarted with this parameter kept invariant. The parameter is repeatedly increased or decreased until the fit residual exceeds the original fit residual by more than 5 %. Eventually, the confidence limit of the parameter is obtained from linear interpolation between the last and second last increment for an increase in fit residual of 5 %. This procedure is consecutively performed for each fitting parameter. (See examples section for application.)

### 4.4.4 Automatic F-Test



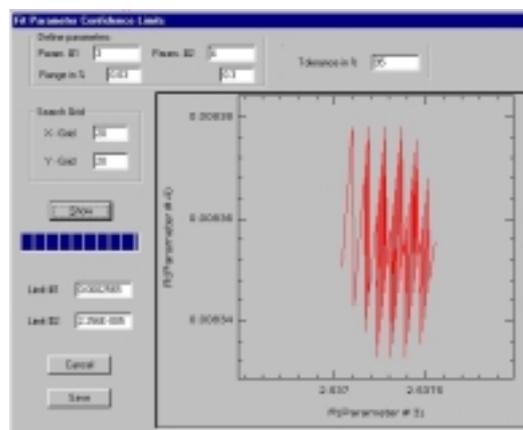
A so-called F test is performed to assess the significance of the effect of additional fitting parameters on the fit residual. The corresponding procedure was adopted from the well-known library “Numerical Recipes in C” where it is described in detail. In short, one parameter is again varied by a certain percentage (i.e. between 2 and 8 % for R and between 10 and 80 % for  $\sigma^2$ ) and the refinement is restarted with this varied parameter kept invariant. Subsequently, the difference between experimental and theoretical function (i.e. magnitude and imaginary part of  $FT(\chi(k)*k^3)$  for a refinement in R space) is calculated and compared to that of the original refinement (F test). The corresponding F parameter ranges between 0.0 and 1.0, where  $F = 1.0$  indicates an insignificant change in the fit residual, while  $F = 0.0$  indicates a highly significant change in fit residual. The iterative procedure is terminated when the corresponding F parameter was below 0.7. Fit parameters with  $F = 0.8$  or higher are most likely strongly correlated and may be statistically insignificant. These parameters should be kept invariant in the refinement. Eventually, this procedure was also consecutively performed for each fitting parameter. (See examples section for application.)

Rough estimate:	0	<	F	<	0.2	independent
	0.2	<	F	<	0.5	largely independent
	0.5	<	F	<	0.8	maybe dependent
	0.8	<	F	<	1.0	dependent

## 4.4.5 2D Confidence Limits



In addition to the standard deviation that is calculated as an error estimate for fitting parameters, confidence limits of pairs of parameters can be determined. A confidence limit is defined as a range in which a certain parameter can be varied without changing the residual  $R$  by more than a given *tolerance* (accurately "1 - tolerance" in dialog box). The procedure is to choose two parameters, give a range in which the parameters shall be varied (start 'large' (e.g. 10%) and decrease stepwise when not enough points are found) and set a search grid (the larger the numbers, the more time takes the calculation). Press show to start the calculation.



The graphical output indicates an area in which the residual remains within tolerance times the original value. A symmetric circle or ellipse indicates two non-correlated parameters. A tilted ellipse is obtained for two strongly correlated parameters. The confidence limits give half of the extent of the ellipse in either X or Y direction.

(Note that no refinement is performed with the changed parameter. Hence, confidence limits obtained may deviate somewhat from what one would obtain by this "ideal" procedure.)

When the dialog box is closed by pressing SAVE, a multiple column DXA file is generated (in current folder), that can be used to obtain a 3D contour plot of the residual versus the two parameters.

## 4.4.6 Smoothing

### 4.4.6.1 Fourier

Smooths the Active X,Y-graph by averaging a given interval in the Fourier transform (refer to *Numerical Recipes in C [1]* for details). The algorithm normally results in well smoothed spectra. As a drawback, one has to be aware of a significant amplitude reduction of sharp features (such as white lines, etc.) even for small intervals. In these cases the Goley-Savitzky algorithm may be more suitable.

### 4.4.6.2 Goley-Savitzky

Employs the Goley-Savitzky algorithm in order to smooth the Active X,Y-graph (refer to *Numerical Recipes in C [1]* for details). The procedure calculates a polynomial of a given degree in a given interval and substitutes the data points in this interval by the polynomial. The degree of smoothing increases with an increasing number of data points per interval and a decreasing polynomial order. The algorithm normally preserves very well amplitude and width of sharp features.

## 4.4.7 Integration

The area under the Active X,Y-graph is determined. The procedure employs the SIMPSON 3/8 algorithm (refer to *Numerical Recipes in C [1]* for details). The result is stored in the RESULTS WINDOW.

Provided the profile function of the Active Graphic Window is displayed, the area under the profile function can also be calculated.

## 4.4.9 Differentiation

### 4.4.9.1 Differenzenquotient

### 4.4.9.2 Splines

Both procedures calculate 1<sup>st</sup> and higher derivatives. 4.4.4.2 determines the 1<sup>st</sup>, 2<sup>nd</sup>, or 3<sup>rd</sup> derivative of the Active X,Y-graph from the coefficients of a cubic spline. Additionally, the number of data points can be reduced or increased and the data can be smoothed by varying the number in the INTERPOLATION MODUS input field (large value = interpolation, small value = smoothing) (refer to *Numerical Recipes in C [1]* for details).

## 4.4.10 Roots

The roots of either the Active X,Y-graph or the profile function can be determined in the entire spectrum or a chosen section. Additionally, you can search for all or just the first root in the spectrum (1st root is the first one from left!). The results are stored in the RESULT WINDOW together with the information whether the required accuracy could be reached. The procedure employs the BRENT algorithm (refer to '*Numerical Recipes in C*' for details)

## 4.4.11 Interpolation

### 4.4.11.1 Cubic Spline

The number of data points of the Active X,Y-graph can be reduced or increased. The new equidistant data points are interpolated to the Active X,Y-graph using cubic splines (refer to *Numerical Recipes in C [1]* for details).

### 4.4.11.2 Level-out Spline

Additionally to a new number of data points, the Active X,Y-graph can be smoothed and up to the 3rd derivative can be calculated (refer to *Numerical Recipes in C [1]* for details).

## 4.4.12 Fourier Transformation

See **index**, XAFS Fourier transformation for details, FFT algorithm taken from *Numerical Recipes in C [1]*.

## 4.4.13 Convolution

The Active X,Y-graph can be convoluted with the profile function of the Active Graphic window. The convolution is obtained from a multiplication of the corresponding Fourier transforms. The procedure is described in the following: (refer to *Numerical Recipes in C [1]* for details) After selecting the menu item convolution from the NUMERIC menu, WinXAS asks you to choose one or more profile function from the CHOOSE FUNCTION dialog box. Let's assume, for instance, you want to convolute your spectrum with a Lorentzian shaped instrument function. Therefore, choose one Lorentzian and enter its parameters in the ENTER PARAMETER dialog box. Note that the position of the Lorentzian has to be set to ZERO! Click OK and WinXAS will calculate the convoluted spectrum.

## 4.4.14 Level-out Polynomials

### 4.4.15 Linear Regression

Calculates a linear regression from the Active X,Y-graph (refer to *Numerical Recipes in C [1]* for details). The 1<sup>st</sup> order polynomial coefficients together with the standard deviation and the correlation R factor are displayed in the Result window. The R factor ranges between 1 and -1, with 1 and -1 indicating 'complete positive or negative correlation', respectively, and 0 uncorrelated X and Y variables. Additionally, the Profile Function of the Active Graphic window is set to a 1<sup>st</sup> order polynomial with the linear regression coefficients.

### 4.4.16 Search Min-Max



Minima and maxima can be determined in the Active X,Y-graph. The algorithm computes the first derivative and searches for roots. Options are to store only minima or maxima and to save the corresponding ordinate value. Additionally, only the largest values found (min or max) can be saved. Data can be smoothed prior to the maxima search. The results of the search are stored in the RESULT Window.

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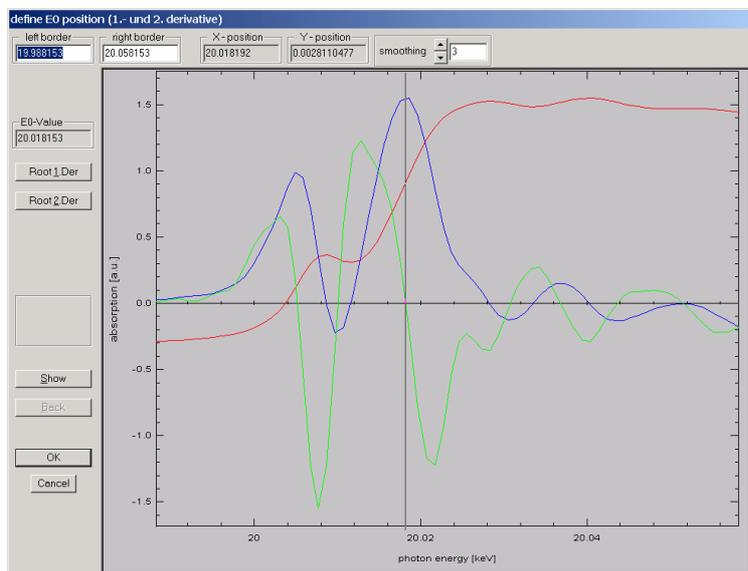
## 4.5 XAFS

### 4.5.1 Energy calibration (c) ← a series of new single button short-cuts in version 3.x

WinXAS offers three options for a reference XAS spectrum to be used for energy calibration. First and most convenient, the reference spectrum is assumed to be stored either as third column in a three column file or as  $I_2$  signal in a multiple column ASCII file. Second, a separate file containing the reference spectrum can be opened. This file can be either a two column file or a multiple column file where the reference spectrum is stored as  $\lg(I_0/I_1)$ . Third, a distinct feature in the sample spectrum can be used for calibration.

#### 4.5.1.2 1.-2. Derivative

 The threshold energy of a reference spectrum (3rd column) can be determined from its 1st or 2nd derivative. This procedure uses a modified version of the SECTION dialog box. Only the 'special' options, relevant for the E0 determination are described in the following. For general features of the SECTION dialog box see **index**. Initially, the graphic display of the dialog box shows the reference spectrum (red), the 1s derivative (blue) and the 2nd derivative (green). For energy calibration and sample  $E_0$  determination (see below) suitable starting parameters for the fitting range and the  $E_0$  parameter are determined automatically and displayed when the dialog box is opened. If this procedure fails, click on (show and) back to display the whole spectrum and perform the  $E_0$  search by hand. The following options are available:



- ROOT 1ST DER.: determines the root of the 1st derivative in the current section (blue part in the graphic display). In order to avoid ambiguity, only one root should be inside the chosen interval. The root is taken as  $E_0$  value into the  $E_0$  VALUE box.
- ROOT 2nd DER.: determines the root of the 2nd derivative in the current section (blue part in the graphic display). In order to avoid ambiguity, only one root should be inside the chosen interval. The root is taken as  $E_0$  value into the  $E_0$  VALUE box.
- SHOW: displays the current section of all three graphs.
- BACK: goes back to the initial display of spectrum, 1st and 2nd deriv.
- SMOOTHING: applies a smoothing algorithm to the spectrum before the derivatives are calculated.

The procedure to determine  $E_0$  is the following:

- select a near edge region of the spectrum and press SHOW
- make sure, that the selected region contains only one root of either the 1st or 2nd derivative
- press either ROOT\_1st\_DER or ROOT\_2nd\_DER
- if you are suspicious you may check the root with the mouse cursor and compare the values in E0 VALUE and X-POSITION.
- Close the dialog box with OK and enter the tabulated reference edge energy. The sample spectrum will be loaded and corrected accordingly.



Instead of entering the numerical value for the edge energy, you may use the element symbol. This option is available in several dialog boxes and usually indicated (usage: *Cu* or *cu* for copper K-edge, *Pt1* for platinum L<sub>I</sub>-edge, *Pt2* for platinum L<sub>II</sub>-edge, etc. Press OK after entering the symbol. WinXAS will substitute the symbol with the corresponding photon energy in keV)

#### 4.5.1.1 XANES Fit

The threshold energy of a reference spectrum (3rd column) can be determined from its 1st or 2nd derivative or from a XANES refinement.

Basically the same procedures are used for ENERGY CALIBRATION and SET E0. The main difference is that the energy calibration is carried out with a reference spectrum (3rd column) whereas Set E0 refers to the energy threshold of the sample spectrum (2nd column). For the sample spectrum E0 is stored for later use, whereas for the energy calibration a difference is calculated between E0 and a tabulated value. Afterwards the sample spectrum is corrected accordingly.

In the first step of the XANES FIT procedure a SECTION (see **index**) of the XAS spectrum has to be defined in which the XANES fit shall be carried out. The next step follows the descriptions already given for the LEAST-SQUARES-FIT procedure (see **index** for details). The underlying algorithm consist of i) choosing profile functions for the refinement (e.g. one modified arcustangens, one Lorentzian, two Gaussian ) - ii) enter suitable start parameter for the fit - iii) perform the refinement -

After the refinement is done, WinXAS will show you a dialog box with all profile functions. Select one profile function from the list box and the according position will appear in the OLD E0 VALUE box. In order to finish the calibration, enter the tabulated energy threshold in the edit field and press OK. WinXAS will calculate the difference between experiment and theory and correct the sample spectrum accordingly.

#### 4.5.1.3 Set Reference E<sub>0</sub>

WinXAS asks for the edge position of a reference spectrum and the corresponding tabulated value. Afterwards the difference between both values is calculated and the sample spectrum is corrected accordingly. This procedure is meant for those cases where none of the above-mentioned methods is applicable and the edge position of a reference spectrum had to be determined otherwise.

#### 4.5.1.3 Separate File

In those cases where no reference spectrum was measured in saved into the same file as the experimental XAFS spectrum, WinXAS offers to open a separate file with a reference spectrum.

#### 4.5.1.3 Third Column

It is assumed that a reference spectrum is contained in the experimental XAFS spectrum which is currently being processed. This spectrum is read and displayed for absorption edge determination.

### 4.5.1.3 Same Spectrum

For some reason it may be desirable to use a particular feature in the experimental XAFS spectrum for energy calibration. When this option is set, no reference spectrum is displayed but the XAFS spectrum in the active window is used.

## 4.5.3 Background Correction (b)

### 4.5.3.1 Victoreen Fit

### 4.5.3.2 Polynomial Fit

### 4.5.3.3 Two Polynomial Fit (b)

The background-correction procedures implemented in WinXAS again use the well-known SECTION dialog box. Either a single polynomial or the Victoreen function can be employed in order to remove the absorption contribution of other elements in the pre-edge region of the Active X,Y-graph (works best for XAS spectra, although this function also can be used to remove a linear trend from any x,y-graph prior to FT, for instance). The necessary steps are :

- Select a range in the pre-edge region of the spectra.
- Press the FIT button. The refinement will be carried out and the graphic box will show the whole spectrum plus the refined polynomial/Victoreen.
- For a Two-Polynomial fit repeat this procedure by selecting a range in the post-edge region and press FIT again. Prior to opening the Section Box, WinXAS searches for an absorption edge in the sample spectrum. Thus it can distinguish from a selected range in the post- or pre-edge region and can choose the right polynomial order. If both polynomials are set, *valid* will appear in the corresponding edit fields. (In case this procedure doesn't live up to your expectations, this is often related to a failure of the automated  $E_0$  search. Check your spectrum for additional edges, large glitches, etc.)
- If the fit looks fine to you, close the dialog box and the polynomial will be subtracted from the whole spectrum. If the fit looks weird, press the PARAMETER button and enter a lower polynomial degree (or Victoreen coefficients).

## 4.5.4 Normalization

The edge jump of a background corrected XAS spectrum (Active X,Y-graph) can be normalized to be equal to one. For that purpose a zero order polynomial is refined to a chosen section after the absorption edge. Afterwards the spectrum is normalized to the ordinate value of this polynomial (as already mentioned, this works best for XAS spectra, but of course can be used for any x,y-graph to be normalized to one in a given range). The section, in which the polynomial is refined can be selected in the well-known SELECTION dialog box (see **index** for details). Once a section is selected, you can press the FIT button in order to see the resulting zero order polynomial. Leave the box with OK to carry out the refinement (if not done previously) and to normalize the spectrum.

## 4.5.2 Set-E0 (e)

### 4.5.2.2 1.-2. Derivative

Opens a modified version of the SECTION dialog box in order to determine the energy threshold of the absorption spectrum from the roots in the 1st or 2nd derivative. The procedure is the same as described

above (see **index**, ENERGY CALIBRATION). After the E0 value is found, it is stored internally for later use (see **index**, CONVERSION).

#### 4.5.2.1 XANES Fit

Employs a refinement of a number of profile functions to the XANES region of the absorption spectrum. The procedure is the same as described above (see **index**, ENERGY CALIBRATION). After choosing an E0 value from the parameters of the refined profile functions, this value is stored internally for later use (see **index**, CONVERSION).

#### 4.5.2.3 Set E0

Prompts the user to enter a known E0 value. This value will be stored as mentioned above and can be used to convert the spectrum into k space.

### 4.5.5 Conversion

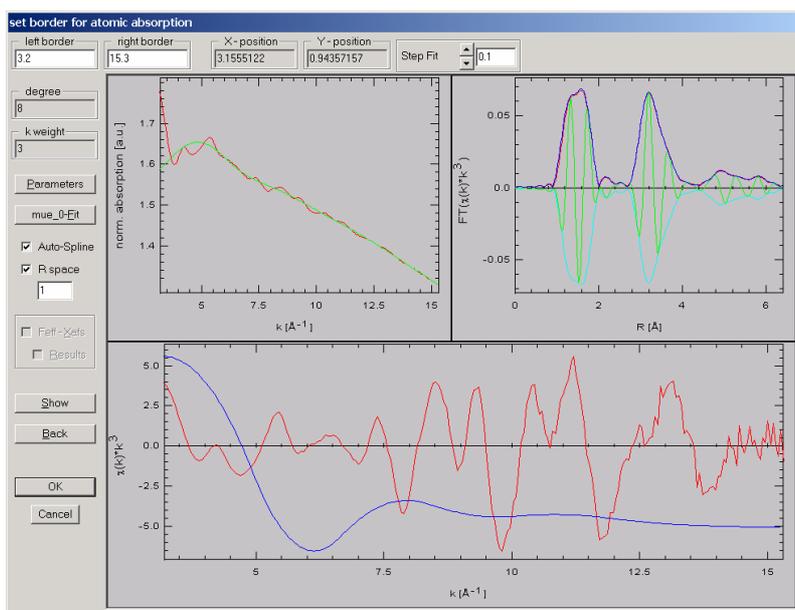
Converts the absorption spectrum from k space into R space. For this, WinXAS uses the E0 value obtained from a previous threshold determination (SET E0). This E0 value is shown again in a message box for verification. If the value appears to be incorrect, you will have to determine E0 again (see above). The absorption spectrum as well as the E0 value has to be in keV !!

### 4.5.6 $\mu(0)$ Fit (m)

#### 4.5.6.1 Cubic Spline Fit

WinXAS offers three different ways to determine the atomic absorption in the EXAFS region of the Active X,Y-graph. Because all three procedure basically employ the same dialog boxes, an entire road map for the  $\mu(0)$  fit will only be given here. For the next two menu items only the differences will be listed.

- The first dialog box asks you to enter the number of knots for the cubic spline and the k-weighting. These parameters can be changed later on. Applying a weighting scheme with  $k \neq 0$  for the refinement means, that not all data points of the  $\chi(k)$  are weighted equally but that the data array is multiplied with a weighting function. Hence, with a large k value, the algorithm will put more emphasis on the higher k region and vice-versa.



- In the next step WinXAS opens another slightly modified version of the SECTION dialog box (for details see **index**). Select a range of

your spectrum in which the spline fit shall be carried out and press the button  $\mu(0)$ -FIT. WinXAS will refine a cubic spline to the data and present the result in the SECTION dialog box. Thereafter, the graphic display of the dialog box is divided into three parts. The top/left part shows the spectrum (red) and the refined cubic spline (green), the bottom part shows the resulting  $\chi(k)$  (red) and the first derivative of the cubic spline (blue) and the right/top part shows the Fourier transform of the resulting  $\chi(k)$  (magnitude and imaginary part) (the red trace corresponds to the current  $\chi(k)$  while the blue trace belongs to the previous  $\chi(k)$ ). Hence, the effect of changing any of the parameter (e.g. left or right border or the number of splines) can be seen easily). By checking the 1st derivative of the spline, you can easily determine whether the  $\mu(0)$ -fit has already removed significant EXAFS frequencies from your  $\chi(k)$ .

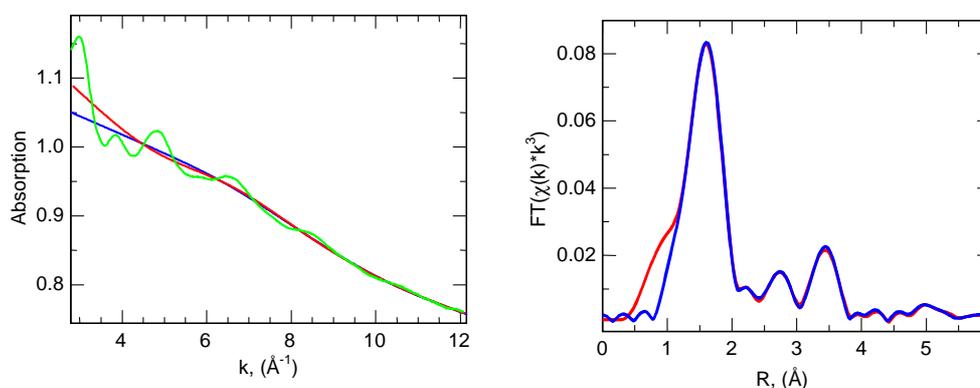


For the  $\mu(0)$  refinement, the “auto spline” option offers a way to calculate a suitable number of spline knots according to

$$N(\text{spline}) = 2/\pi * \Delta k * \Delta R + 1 \quad \text{Eq. } (\mu 1)$$

with  $\Delta k$  the selected range in  $k$  space and  $\Delta R$ . During the refinement procedure, the number of spline is readjusted according to the chosen range in  $k$  space ( $\Delta k$ ) and the “fitting” range in  $R$  space ( $\Delta R$ ). The starting parameters displayed upon opening the  $\mu(0)$  dialog box are also calculated based on Eq. ( $\mu 1$ ).

Furthermore, the  $\mu(0)$  refinement can also be performed in  $R$  space to minimize the amplitude in the FT( $\chi(k)$ ) at  $R < \Delta R$ . This results in a much improved and more stable  $\mu(0)$  refinement (Figures), while providing a maximum of transparency and control of the underlying procedures. The improvement is visible in the following figures with the red traces corresponding to the conventional procedure and the blue traces corresponding to the  $R$ -space refinement. For a combined XAS and  $\mu(0)$  refinement, the  $R$  space option needs to be switched off.



In addition to fitting a cubic spline function to the experimental spectrum, a sum of a cubic spline and a theoretical XAFS function can be refined. This procedure is particularly useful in those cases, where a single spline function appears to be unsuitable for a stable and reliable  $\mu(0)$  refinement. As an example, for metal oxides with very short metal oxygen bonds (e.g.  $\sim 1.6 \text{\AA}$ ) it may be very difficult to obtain a reasonable  $\mu(0)$  function in the low  $k$  region without subtracting any signal from the first shell neighbors. Here, it may be beneficial to add a theoretical XAFS calculation for the metal oxide to the  $\mu(0)$  fit.

With the recent implementation of the  $\mu(0)$ -fit algorithm, the refinement should be carried out in  $k$  space. Of course, you may feel free to perform a  $\mu(0)$ -fit in  $E$  space as well. Unfortunately, the weighting scheme for the

refinement is in  $k$  and will not work properly in  $E$  space. If a refinement in  $E$  space is necessary, you might overcome this drawback by doing an  $E0$ -normalisation (see **index**) prior to the  $\mu(0)$ -fit. Don't forget to add  $E0$  again afterwards before you convert the spectrum into  $k$  space !

#### 4.5.6.2 Advanced Spline Fit

The fit procedure is exactly the same as for the CUBIC SPLINE FIT (see above). Instead of using one spline with equal-distant knots and one overall weighting scheme, the  $k$  range can be divided in up to 5 sections. Each section has its own number of knots and its own weighting scheme. This way, a customized spline function can be generated in order to deal with bumps or slopes in the spectrum that could not be removed with a regular cubic spline. Different weighting schemes seems to work less well, but there may be purposes where such a procedure is required. The overall  $k$  weight in the dialog box concerns only the presentation of the resulting  $\chi(k)$  in the  $\mu(0)$ -fit dialog box.

#### 4.5.6.3 Single Polynomial

A single polynomial is used to represent the atomic absorption. The fit procedure is exactly the same as for the CUBIC SPLINE FIT (see above).

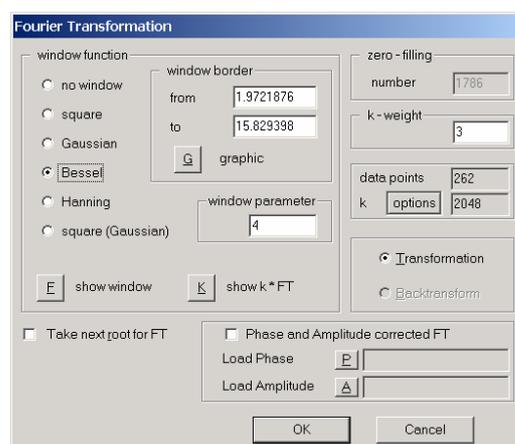
### 4.5.7 k-Weighting

Opens a dialog box and let you change the  $k$  weighting of the Active X,Y-graph. Input of zero removes any weighting. Normally the weighting should be indicated in the Y axis inscription. Because the  $k$ -weighting is not saved with the data array, it's recommended to remove any weighting prior to save.

### 4.5.8 Fourier Transformation (f)

The Fourier transform or the back transform of the Active X,Y-graph ( $\chi(k)$  or  $FT(\chi(k))$ ) can be calculated. The XAS relevant options of the FOURIER TRANSFORM dialog box are described in the following. For more general info about the underlying algorithm refer to Fourier Transform in the NUMERIC menu. **In many dialog boxes the parameters are saved and displayed next time (for instance, window function, parameter, and  $k$  weight in the Fourier transform dialog box)**

The procedure recognizes if you want to transform a real or a complex data array. In the latter it will assume that you want to calculate the back transform and select the BACK TRANSFORM button automatically.



- Select a window (for details see NUMERIC menu above) : each window has its own parameter which can be used in order to adjust the appearance of the window. If you change from one window to another the corresponding default value will be set to the PARAMETER box. For visualization of the window and its effect on the data press SHOW WINDOW. The up-coming dialog box allows you to change the window parameter and see how this alters the data.

- After you've selected a window, you may want to change the border in which the  $\chi(k)$  shall be transformed. This can be done by either setting the border by hand to the according box or by pressing the G(graphic) button and selecting the borders in the SECTION dialog box.
- In order to get the next root on each side as border for the transformation you really should not search for it in the SECTION box. This is what the TAKE NEXT ROOT FOR FT button is for. Give it a try, it probably won't change much.
- In the next step you have to set the k-weighting for the Fourier transform. Because a different weighting scheme can considerably change the appearance of the FT, you may want to compare what the FT looks like at different weightings. Well, this can be done at no extra charge. Just press the button K (show k\*FT). The up-coming dialog box, contains three FT that resulted from three different k weightings (default is 1, 2, 3). In order to examine other k values enter them into the edit boxes and press SHOW. In order to leave the box click inside one out of the three FT plots. The dialog box will be closed and the according k value will be set to the k weighting input field.
- For a normal FT that's all you have to do. However, in case you want to change more parameters, press the OPTIONS button (see **index**, EXAFS OPTIONS for details). Changing the zero filling parameter is not an option for the XAS FT.

Additionally, WinXAS offers the possibility to calculate a phase and amplitude corrected Fourier transform. Roughly that means, instead of transforming the  $\chi(k)$  as it is, the following formula is used :

$$\text{corr. FT}(\tilde{R}) = \frac{1}{\sqrt{2\pi}} \int_{k_{\min}}^{k_{\max}} w(k) \cdot \chi(k) \frac{\exp(-i\delta_j(k))}{F_j(k)} \cdot k^n \cdot \exp(i2k\tilde{R}) d(2k)$$

In a phase corrected FT the peaks have their maximum more or less at the real distances (removal of phase shift in FT). Moreover, if you have a coordination shell in your sample of the same backscatterer as for the used phase and amplitude, the imaginary part of the FT will be symmetrical for the corresponding peak and its maximum will coincide with the FT peak maximum. A non-symmetric imaginary parts normally points to a contribution of other shells to the FT peak.

In order to calculate the phase corrected FT, select button PHASE AND AMPLITUDE CORRECTED FT and enter file names for phase and amplitude in the according input fields.

Calculating a back transform is quite straightforward, because it doesn't give you much of a choice in the different parameters. As already mentioned above, WinXAS will recognize a complex data array and pre-select the Back Transform button. All that's left for you to do, is to determine the back transformation window by going into GRAPHIC and select the FT range (one or more distinct shell(s) you want to back transform). WinXAS automatically removes the selected FT window and the k-weighting. Because in the current version these parameters are not saved with the FT, it's highly recommended to do FT and BT in the same session. If you want to save intermediate data (which is by the way also recommended), the best will be to save the zero weighted  $\chi(k)$ . In order to avoid any misunderstanding, the rectangle window for the BT is pre-selected and all other windows are disabled. Therefore no window can be applied to the BT after the FT window has been removed. At present, the author is not aware of any advantages to do otherwise.

## 4.5.9 Phases and Amplitudes

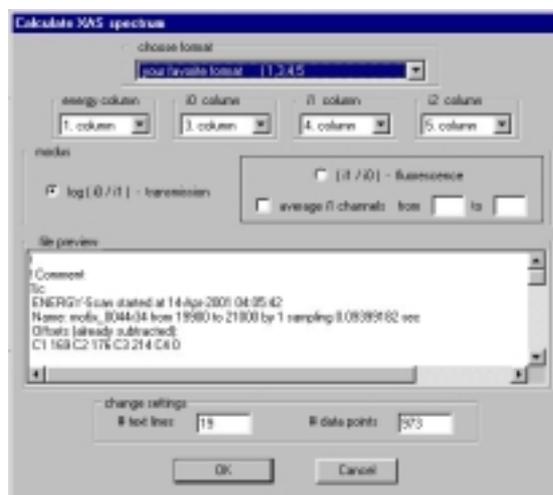
Extracts experimental phases and amplitudes from the Active X,Y-graph. Most likely this step will be the last one in the analysis of a reference compounds. Provided that the previous step was the back transformation of one well-distinguished peak in the FT, the Active Graphic Window will show the  $\chi(k)$  for this single shell. In order to obtain phase and amplitude for this single shell, select MODIFIED PHASE AND AMPLITUDE as well as the EDGE and enter the known structural PARAMETERS (coordination number and distance). Calculated phases and amplitudes can be saved for later use. For that, select SAVE and enter an appropriate name (without extension, WinXAS will set the extensions to \*.PHA and \*.AMP). **In addition to the phase and amplitude, the coordination number and the distance used to calculate a modified phase and amplitude are saved. These values are later retrieved in the XAFS refinement and, hence, this saves the time to input them again.**

The option SIMPLE PHASE AND AMPLITUDE displays the magnitude and the argument of the Active complex X,Y-graph. The Phases and Amplitudes dialog box can also be used to modify theoretical phases and amplitudes. In case, WinXAS recognizes that the Active X,Y-graph contains no complex data array, the program will assume that you want to modify a theoretical phase or amplitude and will change the dialog box accordingly.

## 4.5.13 Calculate Spectrum



This dialog box will pop up every time you open a multiple column ASCII file. It allows to calculate an absorption spectrum from columns corresponding to photon energy (E), first ( $I_0$ ) and second ( $I_1$ ) absorption signal. Select columns for E,  $I_0$ , and  $I_1$  in the respective list box and select if the spectrum was measured in transmission or fluorescence. Settings will be stored and set as default next time you open a multiple column file. Moreover, the same settings are used to AVERAGE XAS SPECTRA or to CREATE MULTIPLE COLUMN files.



If a reference absorption spectrum is included in the ASCII file, select the proper column for  $I_2$ . WinXAS later will use these settings in order to calculate the reference spectrum from  $I_1$  and  $I_2$  for energy calibration. This dialog box constitutes the interface of WinXAS to the numerous XAFS raw data formats existing at the different beamlines. However, in case your raw data is saved in a binary format, refer to the beamline staff to obtain software to convert the binary data into ascii.

## 4.5.13 Difference Spectra

A second spectrum can be subtracted from the Active X,Y-graph. The spectrum is read from another file and the file name has to be entered in the FILE NAME field. The second spectrum can be either interpolated to the Active X,Y-graph or it can be subtracted point by point.

### 4.5.12 E0-Normalization

The X-axis of the Active X,Y-graph can be normalized. The dialog box reads an E0 and then subtracts this E0 from the X-axis (results in E=0 at the absorption edge). If you previously have determined E0 for the Active Graphic Window, the dialog box contains this value as default.

### 4.5.10 AUTO-XAS

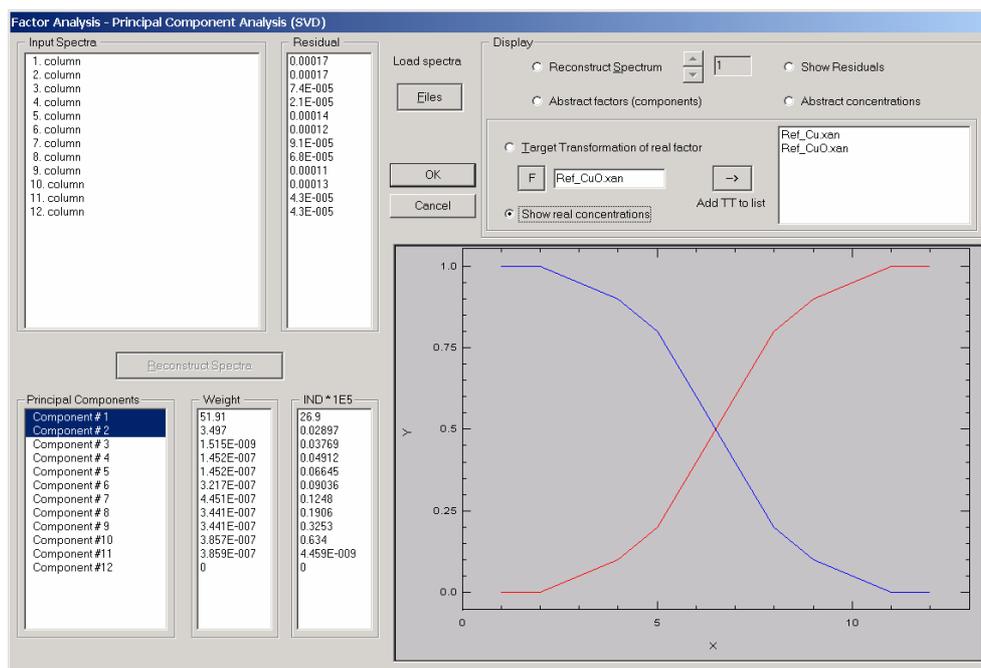


WinXAS performs a quick and rough automatic XAS analysis with the Active X,Y-graph. This item is enabled only for XAS spectra (in keV). The output of the analysis procedure are chosen to fit in the Active Graphic Window. Output data arrays are : background corrected and normalized XAS spectrum,  $\chi(k)$ , magnitude of FT ( $\chi(k)$ ). Details about each reduction step can be found in the RESULT WINDOW (E0,  $\mu(0)$  fit range, FT range, etc.). Of course, the results have to be handled with care, but I believe that everybody can judge for her/himself whether such a procedure is suitable for a given purpose or not.

### 4.5.13 PC Analysis



The principal component analysis (PCA, aka factor analysis) (some of the maths is described in T. Ressler, et al., **Environmental Science & Technology** 34 (2000) 950-958. and references therein) permits to determine the number of primary components in a set of experimental XANES or EXAFS spectra. Primary components refer to those, which contain the signal and, in principle, are sufficient to reconstruct each experimental spectrum by suitable linear combination. Secondary components refer to those, which contain only the noise.



The objective of a PC analysis of a **set** of experimental spectra (> 4 spectra) is to determine how many "components" (i.e. reference spectra) are required to reconstruct the spectra within the experimental error. Provided that first the number of "references" and second potential references have been identified, a linear combination fit (LC XANES FIT) can be attempted in order to quantify the amount of each reference spectrum in each experimental spectrum. By performing a PC analysis prior to XANES fitting, no assump-

tions have to be made as of the number of references and the type of reference compounds used. Thus, with the information from PCA, XANES fits can be performed with considerably less ambiguity.

The procedure is as follows:

- First thing to do in the PCA dialog box is to click on the FILES button and select the **N** files you want to include in the PC analysis (multiple select file open box, all files should be in one folder). After closing the file open box, the scroll boxes will fill up with numbers and the graphic window will show one red and one blue trace.
- The PC analysis (or better the singular value decomposition) is already done and now it is up to you to interpret its results. Shown are:
  - Input spectra* contains the **N** file names of the selected spectra.
  - Principal components* just shows a list of components numbered from 1 to **N**.
  - Weight* contains the weight of each component in a top to bottom order.
  - IND\*IE5* shows an indicator for each component that is meant to guide the decision as of which components are primary and which are secondary components (the indicator exhibits a minimum at the boundary between primary and secondary components. Refer to Malinowski book for details)
  - Residual* shows the residual (in %) between each experimental spectrum and the reconstructed spectrum. These values are supposed to be minimized until they do not change significantly anymore.
- As default the number of components used to reconstruct the experimental spectra is limited to those components that show significant weights. For the first spectrum the original data (red) and the reconstructed spectrum (blue) are displayed. To scroll through the reconstructed spectrum use the up and down arrows.
  - For none of the spectra the red and the blue curves are supposed to show significant differences. If in one or more cases they do not superimpose, the number of components used is insufficient and the next component in the *principal component* box needs to be added (note that it only makes sense to add principal components to the first one.). More often than not, however, you will have to decrease the number of components used. A good starting point is the minimum in the *indicator*. For that, highlight all those components in the *principal component* box you want to use for the reconstruction and press RECONSTRUCT. After that, scroll again through the reconstructed spectra and verify that in all cases the red and the blue traces properly superimpose. Also check the *Residuals* (plots residuals versus spectrum number) for spikes that may indicate missing components. This way you can iterate and try to identify minimum number of components needed to properly reconstruct the experimental spectra. This set constitutes the primary components.
  - Also, you can display the principal components (*PCs*) or their *mixing coefficients* (by clicking on the corresponding component in the *principal component* box). Often principal components that contain the signal (e.g. XANES) can readily be distinguished from those that contain only noise.
- As an intermediate step you may want to close the PCA window and have a look at the numerical results in the Results window.

First, a list of output files is displayed that contain some of the data generated by the PC analysis.

The next two blocks of numbers give the weights (as in the dialog box) and the mixing coefficients).

The third block contains the residuals for each spectrum assuming it was reconstructed with component #1, #1 and #2, #1, #2, and #3 etc. The columns can give interesting hints as to the composition of the corresponding spectra.

The last block contains some more indicators to decide on the numbers of primary components.  $S(R)$  is the sum of the residuals in data block #3;  $S(R*C_n)$  is the sum of the residuals times the number of components used. Similar to *IND* this indicator should go through a minimum at the boundary between primary and secondary components; *RE* is the estimated experimental error in the data. It should approach a minimum and change considerably only with the addition of primary components to the data construction. If the minima in *IND* and  $S(R*C_n)$  do not fall on the same principal component, this might indicate that the last component is only a minor constituent in the experimental spectra.

#### Principal Components Analysis - Results

Multiple column file XFiles.dat, col: 37 ndp: 400

Output files generated in data directory:

```
* A_PCA_COMPONENTS.DAT -
  Principal Components
* A_PCA_RECON_DATA.DAT -
  Reconstructed data using 1st 12 components
* A_PCA_ORIGL_DATA.DAT -
  Original input data interpolated on same grid
* A_PCA_GROUP_PLOT.DAT -
  PCA Group Plot using 1st and 2nd Eigenvalue
```

#### SIGNIFICANT WEIGHTS / EIGENVALUES

```
Weight/Eigenvalue # 1 : 104.8592
Weight/Eigenvalue # 2 : 2.328854
Weight/Eigenvalue # 3 : 0.1036376
Weight/Eigenvalue # 4 : 0.0425444
```

#### MIXING COEFFICIENT MATRIX

```
-0.16455 0.30534 -0.12997 0.22614 -0.070716
-0.16455 0.3038 -0.21754 0.1134 0.15675
-0.16454 0.30281 -0.045632 0.24709 -0.050132
```

#### PCA RESIDUAL MATRIX AND SIGNIFICANCE INDICATORS

	Comp# 1	Comp# 2	Comp# 3	Comp# 4	Comp#
Spec # 1	2.75	0.0903	0.0705	0.0518	0.051
Spec # 2	2.75	0.102	0.0571	0.053	0.0498
Spec # 3	2.72	0.0763	0.0738	0.0567	0.0561
Spec # 4	2.64	0.108	0.0669	0.0666	0.0534
Spec # 5	2.53	0.0664	0.0564	0.0557	0.0555
Spec # 6	2.37	0.0606	0.0534	0.0532	0.0527
S(R)	48.7	3.44	2.71	2.45	2.33
S(R*Cn)	48.7	6.89	8.14	9.79	11.7
IND	1.1	0.533	0.521	0.537	0.562
RE(*1E2)	1.43	0.653	0.603	0.585	0.575

- If you have decided on the number of components contained in the set of experimental spectra, you may want to search for suitable reference spectra. This can be done with *Target Transform*. After selecting a reference spectrum (of course, carefully calibrated, normalized, and in the same energy range) the red trace shows the reference spectrum and the blue trace shows the transformed spectrum. In case the two superimpose within experimental errors, the corresponding reference is indeed included in the set of experimental spectra. Otherwise the red and blue traces will strongly deviate, indicating that this reference is not included in the experimental spectra. (A numerical residual of the match will be given in the Result window). This procedure should be repeated with as many references as available. In the best case, you will find as many perfect matches as you have determined primary components in the experimental spectra. The less fortunate among us will find either more or less good matches meaning that you have to try to distinguish good and perfect matches or that you have to hunt for more references.
- In addition to determining the concentration of the real factors by a least-squares fitting procedure, the Factor Analysis (Principal component analysis) dialog box permits the calculation of real factors (e.g. chemical species) from reconstructed spectra and target transformed references. This is an alternative procedure that offers several advantages compared to using a least-squares refinement of selected references (LC XANES fit). However, both procedures can be used to corroborate the results from either of them. The procedure in the Factor analysis dialog box is as follows: after target transformation of a suitable reference spectrum you can transfer the reference to the list of “real factors” by pressing the “Add to

list” button. After you have identified as many “real factors” (i.e. references) as there are primary components, you can select the “show real concentrations” button. The dialog box will display the evolution of the real concentrations as a function of spectrum number. Ideally, the real concentrations will vary between zero and one. This depends on the “match” between “real factor” and reference spectrum, though, and can be used to evaluate the suitability of the references chosen.

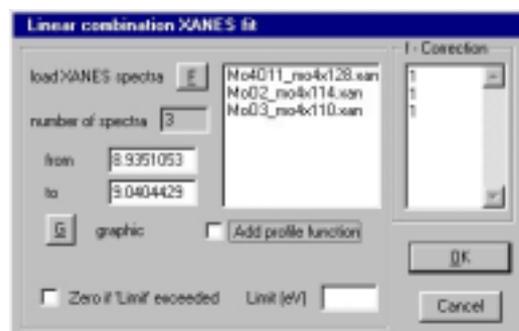
*Pitfalls and warning signs:* not every set of XANES spectra may be suited for PCA. Most important, you need at least twice as many spectra as primary components present in the set (i.e. for a mixture of three phases it is recommended to have at least six experimental spectra for PCA). Most clearly the failure of PCA can be noticed from the indicator IND. If it increases from the first component on, the analysis has failed.

In addition to separate files you may use the principal component analysis on a multiple column file (for data from time-resolved experiments, for instance). In this case the dialog box offers to take the individual columns from the file as input spectra and perform the PC analysis on them. This procedure may even be advantageous because it ensures that all spectra in the same range and interpolated onto the same energy grid. Multiple column files from experimental spectra can be generated using the “Create multiple column files” menu item (4.1.7).

### 4.5.13 LC XANES Fit



WinXAS will simulate an experimental XANES spectrum by a linear combination of various reference samples. This option allows to quantify species in multiple component mixtures from their fingerprint in the near edge region. The algorithm uses a least-squares procedure to refine the sum of a given number of reference spectra to an experimental spectrum. Two parameters are determined for each reference, i.e. the partial concentration  $c$  and an energy correction  $E$ . The latter is meant to correct for small differences in energy calibration of sample and references which may make a big difference in the fit. Follow the procedure given below:



Follow the procedure given below:

- Energy calibrate, background correct and normalize all reference spectra as careful as possible and save each reference spectrum to an individual file. Consistency matters, therefore use the same procedures within the same interval for references and sample.
- Calibrate, background correct and normalize sample spectrum just the same as the references.
- Go to XAFS-LC XANES FIT and select all reference spectra you want to include in the fit. Additional profile functions may be added if appropriate.
- A partial concentration of 0.25 and a shift of 1 eV are pre-set as initial value for each reference in the ENTER PARAMETER box. Press OK and start the refinement.
- When the fit is done, examine the parameters. Reference spectra which don't seem to be contained in the sample often will show negative partial concentrations or unreasonable energy shifts.

- Go to LC XANES FIT again and press REPEAT FIT. Fix the partial concentration and the energy shift of these references to zero and start the refinement again.

The "f-correction" values can be used to convert "XANES partial concentration" into weight percent (not necessarily the same). When suitable values are available (from mechanical mixtures, for instance) they can be input in to corresponding box. After the refinement WinXAS will convert the partial concentration into weight percent and display both values.

In addition to XANES data, the linear combination refinement option can be used for other experimental data as well (e.g. XRD, XPS, etc.). In those cases you need to tick the "XRD fit" button in the ENTER PARAMETER dialog box (otherwise, data is extrapolated to unity if experimental data exceeds the fitting range).

#### 4.5.14 Run FEFF

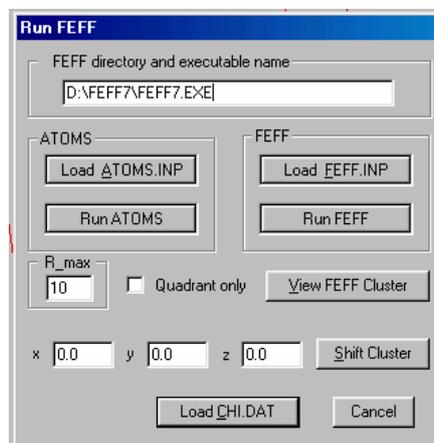


First of all, in order to use this menu item you have to have the ab-initio theoretical XAS code FEFF [8] installed somewhere on your PC.

(FEFF is not part of this package! For details on the latest version refer to the FEFF web site ([leonardo.phys.washington.edu/feff](http://leonardo.phys.washington.edu/feff)).

The FEFF version and the full path have to be entered in the corresponding input field. Once entered WinXAS will try to remember this location next time. The dialog box allows you to edit the FEFF.INP file (simply opens the program notepad.exe with the file feff.inp in the FEFF directory). If your INP file is saved somewhere else you will have to copy it to the FEFF directory). Furthermore, you

can edit the ATOMS input file ATOMS.INP and execute ATOMS (again provided that these files are in your FEFF directory). Pressing the RUN FEFF button to execute FEFF. After the FEFF calculation is done, close the dialog box by pressing LOAD CHL.DAT and the calculated theoretical  $\chi(k)$  is loaded and displayed.



In order to make sure that FEFF simulation and fitting of multiple scattering paths works without problems, it is recommended to position the absorber atom at the origin at ( $x=0$ ,  $y=0$ ,  $z=0$ ). This will be the default setting if you use ATOMS to generate the FEFF input file. However, you may want to modify the FEFF input file and make another atoms the central absorber atom. In this case you should displace the entire FEFF cluster by the xyz-coordinates of the new absorber atom (enter x, y, and z values and press "Shift Cluster"). This will place the new absorber atom at the origin at 0, 0, 0.

Additionally, the RUN FEFF dialog box offers a convenient interface to the free Molecular Viewing Program *RasMol* (by R. Sayle [9]). *RasMol* has to be installed in the WinXAS root directory. WinXAS creates a x,y,z-file from the FEFF input file and executes *RasMol* to display the corresponding cluster. If you do not have *RasMol* already, get the UC Berkeley enhanced version [9] and give it a try. It is a nice tool to view and examine your FEFF clusters in detail, determine bond length and angles, and more.

## 4.5.15 XAS Simulation (s)

### 4.5.16 XAS Fit (r)

XAS simulation and XAS fit basically use the same algorithms. The only difference is, that XAS FIT will try to refine the chosen XAS function to the Active X,Y-graph, whereas XAS simulations just displays the XAS function together with the current  $\chi(k)$ . However, it is recommended to simulate the XAS function prior to any refinement, in order to verify, that the initial parameters are appropriate. If a simulation was performed before and the XAS fit dialog box is re-entered in order to refine the current XAS function, the parameters of each function don't have to be entered again. In this case, press the button KEEP PARAMETERS

WinXAS offers two different approaches in order to refine a XAS function to the current  $\chi(k)$ . First, experimental phases and amplitudes can be used to refine the plane-wave single-scattering XAS formula. This is in the following referred to as 'conventional XAS' (this part of the dialog box also has to be used in order to perform a fit with theoretical phases and amplitudes from Teo & Lee, etc.). Second, theoretical phases and amplitudes obtained from FEFF calculations can be used.

The following XAS formula is used for refinement and simulation

$$\chi(k) = \sum_j \frac{N_j S_0^2 F_j(k)}{k R_j^2} \cdot e^{(-2k^2 \sigma_j^2)} \cdot e^{\left(\frac{-2R_j}{\lambda}\right)} \cdot e^{\left(\frac{2}{3} \sigma_j' k^4\right)} \cdot \sin\left[2kR_j + \delta_j(k) - \frac{4}{3} \sigma_j' k^3\right]$$

where backscattering amplitude  $F(k)$ , phase  $\delta(k)$ , and  $\lambda$ , photoelectron mean free path, are taken from the Feff output file *feffnnnn.dat* for the  $j$ -th scattering path (for experimental phases and amplitudes no photoelectron mean free path correction is used). Coordination number  $N$ , distance  $R$ , disorder parameter  $\sigma^2$ , and amplitude reduction factor  $S_0^2$  are free running parameters in the refinement (as well as optional, the 3<sup>rd</sup> and 4<sup>th</sup> cumulant  $\sigma'$  and  $\sigma''$ , respectively).

**A. Experimental phases and amplitudes:** Using the conventional plane-wave XAS formula with experimental phases and amplitudes is straightforward. Just select the appropriate absorption edge and enter the file names of experimental phases and amplitudes in the corresponding input box. For each shell to be refined, one phase and one amplitude file has to be selected. The selection has to be made in the right order. WinXAS will just read in the files from top to bottom and will not compare the names or check for consistency.

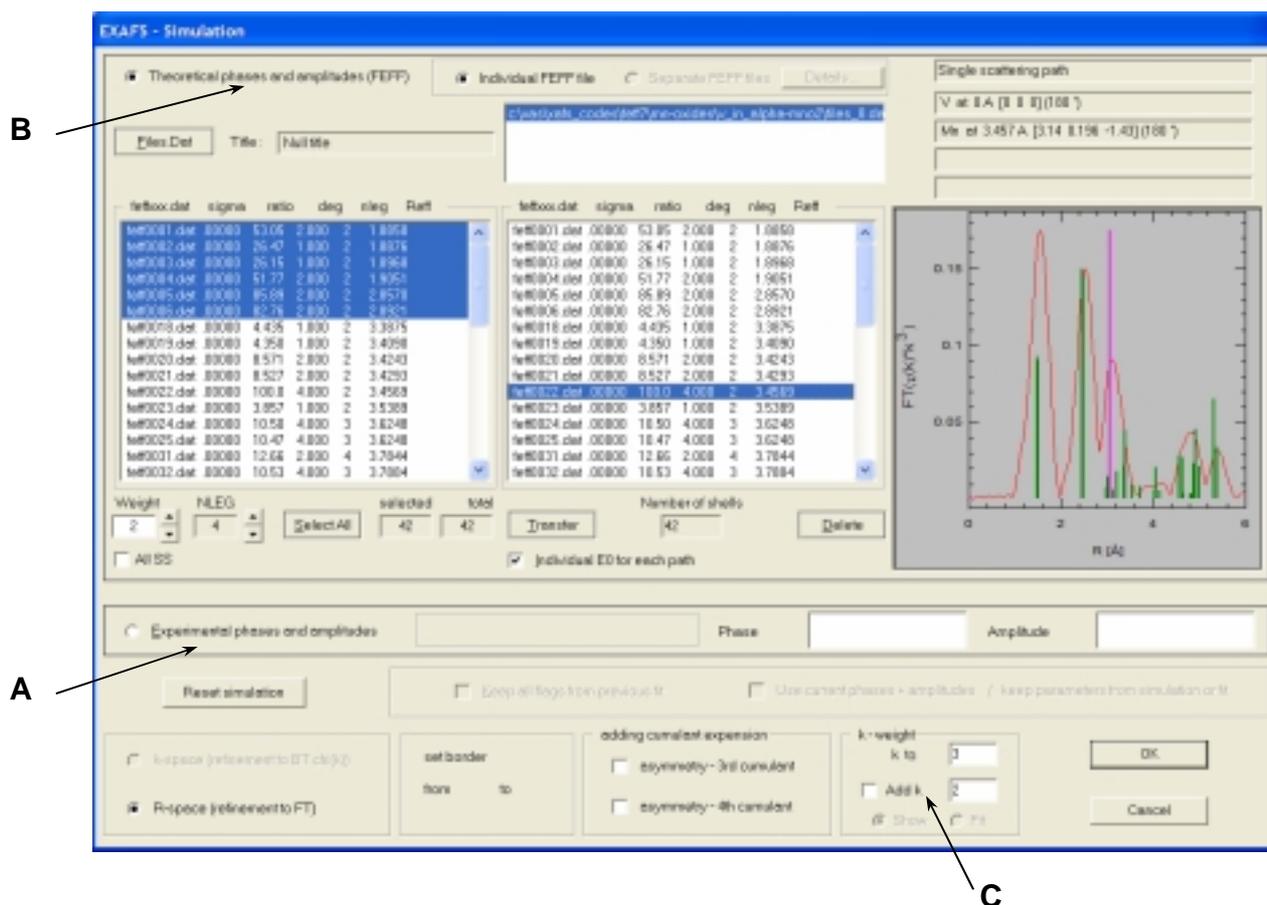


**B. Theoretical phases and amplitudes (FEFF):** In order to use the FEFF-Fit option, a theoretical FEFF calculation has to be performed beforehand. As one sort of output files, FEFF generates *feffnnnn.dat* files with phases and amplitudes for each scattering path included. These files are used for the WinXAS FEFF option and have to be generated in the FEFF6 ASCII format. In case you are using FEFF7 or later you will have to set the PRINT flag to 3 to get the "old" ASCII files (the new FEFF8 binary file is not interpreted yet).

```
*          mphase, mpath, mfeff, mchi
CONTROL   1          1          1          1
PRINT     1          0          0          3  (← this flag needs to be changed to '3')
```

After selecting the “Files.Dat” button, WinXAS will ask you to enter the location of a FILES.DAT or XMU.DAT file. These files contain names and parameters for each scattering path. The FILES.DAT and *feffnnnn.dat* files (and PATHS.DAT (FEFF7) or **PATH00.DAT (FEFF8)**) have to be in the same folder. WinXAS will then read the FILES.DAT file and display its content in a multiple selection list box together with some general info about the calculation (“Title”). Now it is up to you to select all scattering paths you want to include into the refinement (remember, multiple selection can be done with a combination of mouse and [SHIFT] and [CTRL] keys). **The paths selected will be displayed as blue bars in the graphic section. All files displayed can be selected with the “Select All” button. Furthermore, a weight filter and a NLEG filter (2 = single scattering path, 3 = triangular scattering path, etc.) can be used to display only a suitable sub-set of all *feffnnnn.dat* files.**

After you have selected all paths to be included, press the “Transfer” button and the selected paths will be transferred to the second list box. This step is mandatory to be able to start a XAFS refinement (note that only now the OK button is active!). All paths in the second list box will be displayed as green bars in the graphic section. Additionally, you may select single paths in the second list box to (i) delete them, (ii) obtain the corresponding path information in the top right corner, or (iii) simply see what path you are currently looking at from the magenta bar in the graphic section. In case you want to use paths from more than one FEFF calculation, press the “Files.Dat” button again and repeat the selection procedure.



The XAS refinement/simulation can be carried out in either k or R space. In order to perform a XAS refinement in R space, **a particular order of data arrays in the Active Graphic Window is required.** Provided

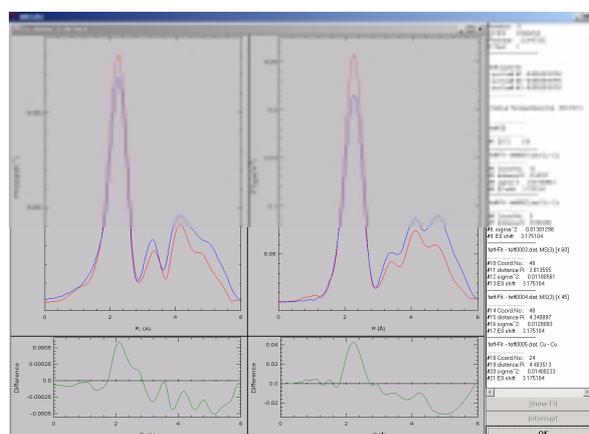
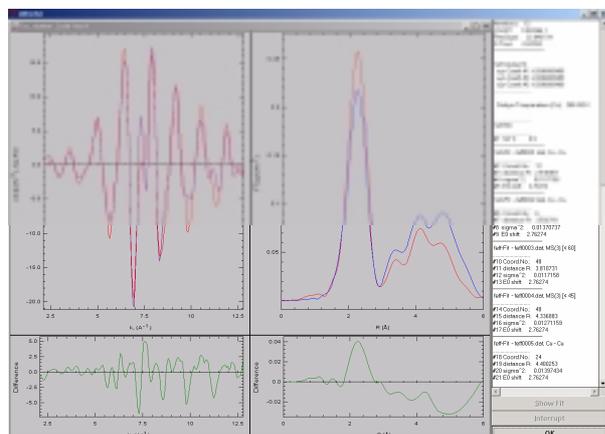
the Active X,Y-graph is the  $\chi(k)$ , this order results from: calculate the FOURIER TRANSFORM, display the magnitude of the FT with SHOW MAGNITUDE !

When you enter the XAS Fit dialog box, WinXAS will try to determine what kind of fit you want to carry out from the Active X,Y-graph. Therefore, if the Active X,Y-graph is a real data array, WinXAS will assume a  $\chi(k)$  and disable the R fit option. If the Active X,Y-graph is a complex data array, WinXAS will check whether the previous array holds the FT itself and the pre-previous array holds the corresponding  $\chi(k)$ . If all these requirements are met, WinXAS will activate the R space option. Otherwise, a corresponding warning will appear and the XAS Fit dialog box will be terminated.

Although the Number of shells box and k weighting box can be changed, they should already contain the appropriate figures. The weighting is set according to the weighting of the Active X,Y-graph and the number of shells is taken either from the number of *feffnnnn.dat* files you selected from a previous FEFF calculation or from the number of phases you entered in the list box. Higher order cumulant can be added to the XAS formula, independent from a conventional analysis or a FEFF refinement (the XAS formula including the third and fourth cumulant is shown above).

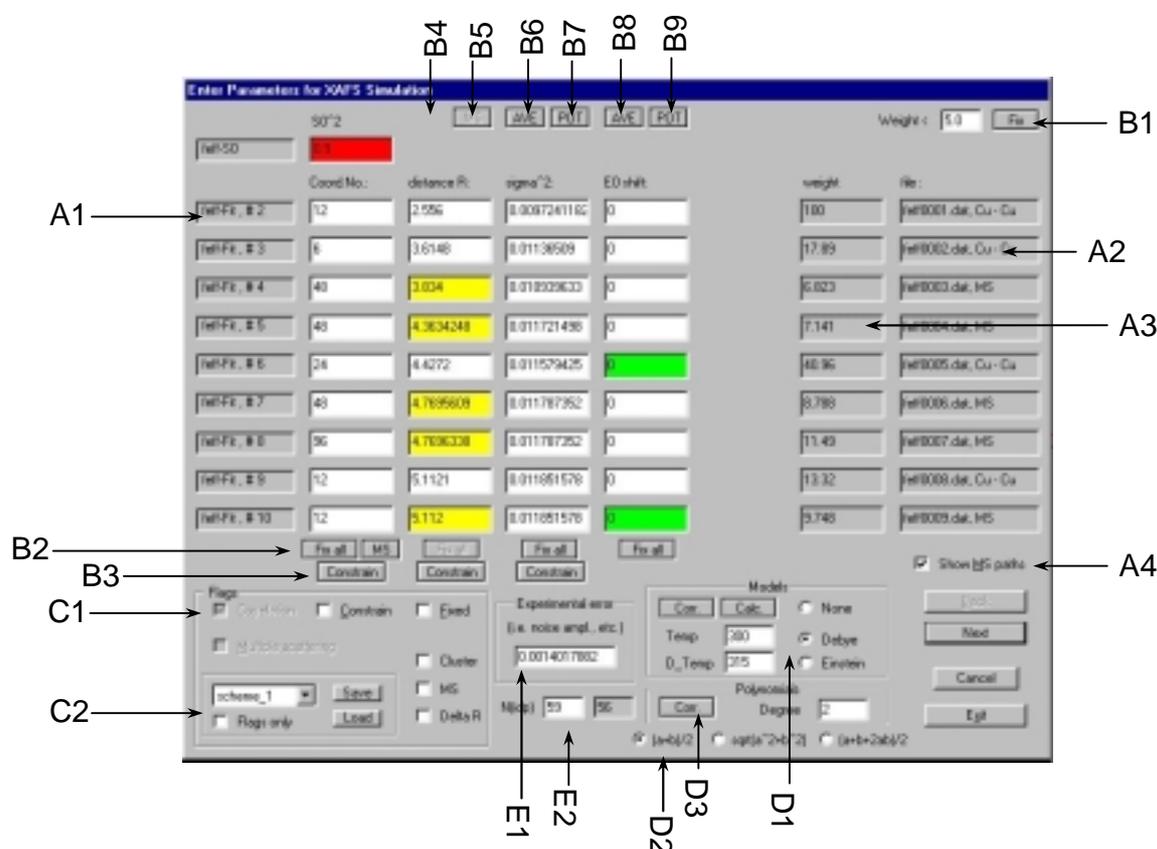


**C) The XAFS refinement box features an optional display of the experimental and theoretical  $\chi(k)$  in addition to the FT( $\chi(k)$ ) (default setting, left figure). Moreover, the refinement can be easily performed to differently weighted Fourier transformed  $\chi(k)$  (e.g. simultaneous refinement to  $\text{FT}(\chi(k)*k^1)$  and  $\text{FT}(\chi(k)*k^3)$ , right figure) (select “Add k” button and “fit” for refinement and “show” for display only). This should result in more stable converging XAFS refinements and may permit to reduce the correlation between characteristic XAFS parameters (e.g. CN and Debye-Waller factor).**



If everything is set properly, you can leave the dialog box. In the next step WinXAS will open the ENTER PARAMETER box (see [index](#)). In case you selected theoretical phases, WinXAS will take the parameters for each path from the XMU.DAT file and display them as initial parameters. For experimental phases and amplitudes the corresponding “\*.par” file is used. Additionally, in case XAS refinement was chosen, parameters can be fixed, constrained or correlated. Graphical display is not available at this point.

 For a XAFS refinement using FEFF phases and amplitudes a modified "Enter XAFS Parameter" dialog box will appear. Its options and potentials are explained below



### Display options

- A1 Name and number of function (number is needed for single parameter correlation)
- A2 Name of '*feffnnnn.dat*' file with either scattering pair (e.g. Cu-Cu) or MS (multiple scattering)
- A3 Relative weight of corresponding scattering path
- A4 Optionally, only SS paths can be displayed (convenient if all MS are correlated to SS anyway)

### Multiple parameter correlation options

- B1 All parameters of those scattering paths that have a weight below a certain limit are fixed in the refinement. This way paths with small weights can be included in the calculation without their free running parameters assuming meaningless values. (Medium reduction of  $N_{free}$ )
- B2 All parameter in one column can be fixed. MS attempts to correlate the CN of MS paths to that of the corresponding SS paths. Because this is not trivial, this option seeks to maintain a constant ratio of the SS paths CN to the MS paths CN (e.g.  $CN_0(SS\#1) = 6$ ,  $CN_0(SS\#2) = 12$ ,  $CN_0(MS) = 24 \rightarrow CN_0(SS\#1) = 4$ ,  $CN_0(SS\#2) = 10$ ,  $CN_0(MS) = 21.3$ )

- B3 All parameter in one column can be constrained to vary with a certain range. This does not reduce the number of free running parameters, but it prevents less significant scattering paths to assume physically meaningless values.
- B4 *XYZ* – all distances are correlated to one expansion coefficient. This means, that instead of refining all distances independently, MS and SS distances are calculated from their x,y,z coordinates taken from the FEFF calculation times an expansion coefficient. On the one hand, the number of free running parameters for the scattering path distances is reduced to a minimum. On the other hand, the refinement can still account for differences between the idealized structure used for the FEFF calculation and the “real” structure of the system studied. In contrast to a constant  $\Delta R$  value, the effect of the expansion coefficient increases with increasing distance.

The expansion coefficients for x, y, and z are saved in the distance box of the distances of the last three scattering shells (If only a limited number of shells is included in the refinement this procedure may result in problem. Sometimes including some more multiple scattering shells may help). Furthermore, the expansion coefficients can be refined independently to account for an anisotropic expansion. However, more than two free running expansion coefficients make no sense (strong correlation). (Strong reduction of  $N_{\text{free}}$ )

- B5 *MS* – the distances of multiple scattering paths are correlated to those of the constituent single scattering paths. To calculate the distance of an MS paths, the angle between the SS paths is assumed to be constant (angle is taken from FEFF calculation). The SS path distances run free and can be further correlated to each other (e.g. in the  $\Delta R$  mode to vary the same) or can be constrained not to exceed a certain range. (Medium reduction of  $N_{\text{free}}$ )
- B6 *AVE* – the Debye-Waller (DW) factors of the multiple scattering paths are calculated from the DW factors of the constituent single scattering paths. The DW factors of single scattering shells run free and can be further constrained or correlated to each other. On default, the DW factors of single scattering shells that contain the same backscattering element at very similar distances are set to vary the same (e.g. Mo–O shells at 1.91 Å and 1.97 Å). (Medium reduction of  $N_{\text{free}}$ )
- B7 *POT* – DW factors of single scattering shells are calculated from either the Debye or the Einstein model. In contrast to the *CORR* option, not only one Debye temperature is refined, but each element in the system (i.e. each potential in the FEFF calculation) has one Debye temperature assigned to it (for instance, for ZnO one Debye temperature is refined for all Zn backscatterer and one Debye temperature for the O backscatterer). Because the Debye model regularly overestimates the DW factors of light backscatterer (e.g. O, C, etc.), the refinement is considerably improved by using more than one Debye temperature, while the number of free running parameters remains low. (Strong reduction of  $N_{\text{free}}$ )

The DW factors of multiple scattering shells are calculated from the average of the corresponding single scattering shells. The formulas available are described in D2.

- B8 *AVE* – the  $E_0$  shifts of the multiple scattering paths are calculate from the average of the  $E_0$  shifts of the corresponding single scattering paths. The  $E_0$  shifts of the single scattering paths run free and can (and should be) further constrained or correlated. It should be taken into account that significantly different  $E_0$  shift for very similar scattering paths (e.g. Mo–O at 1.91

A and  $E_0 = -4$  eV and at 1.97 Å and  $E_0 = 6$  eV) may not be physically meaningful. (Medium reduction of  $N_{\text{free}}$ )

- B9 *POT* – instead of one  $E_0$  shift for all scattering paths (can be selected in XAFS Fit dialog box) a different  $E_0$  shift is assigned to each element (potential in FEFF calculation) in the system studied. This option sometimes improves a XAFS fit considerably, because it accounts for the different average valences of the elements in the sample. (Strong reduction of  $N_{\text{free}}$ )

### Single parameter correlation options

- C1 Single parameters can be correlated to other parameters, constrained, or fixed (usage see above). The tick boxes are also used to indicate the status of a particular parameter (refers to the input box that currently contains the “carret”). With the *Delta-R* option the calculation of the distance R can be toggled between 'R' and ' $\Delta R$ '. The latter offers advantages when all distances are to be constrained to vary within the same range, or when two distances are correlated to vary the same. (Minor reduction of  $N_{\text{free}}$ )
- C2 The present 'correlation scheme' can be saved and loaded. Three different schemes are available. Comes in handy, when different spectra are to be fitted with the same settings. In addition, a 'correlation scheme' can be loaded without the corresponding parameters. Useful if refined parameters are to remain the same and shall be fitted again with a saved scheme.

### Debye-Waller factor options

- D1 Debye-Waller (DW) factors can be calculated from the correlated Debye model or the Einstein model. *Temp* is the measurement temperature, *D\_Temp* the Debye temperature of system studied. *Calc* calculates the DW factor for all scattering paths using the selected model. *Corr* (a hidden B option :) correlates the DW factors of all scattering paths to the selected model (all DW boxes turn blue and the Debye temperature is copied into the first box) (i.e. in a refinement only the Debye temperature is varied (only one free running parameter for all DW factors)). The settings in this section of the dialog box are taken for option **B7**. (Strong reduction of  $N_{\text{free}}$ )
- D2 Except when all DW factors are *correlated* to one model, the DW factors of MS paths are calculated from an average of the corresponding single scattering paths. Three different formulas can be employed to calculate DW factors of MS paths (indicated in dialog box – a, b, c, etc. refer to the DW factors of the corresponding SS shells).
- D3 In addition to the models for DW factors, the DW factors of all SS paths can also be calculated from a polynomial (1<sup>st</sup>, 2<sup>nd</sup>, or 3<sup>rd</sup> degree (more is possible but not useful)) (MS DW factors are obtained from averaging the SS DW). This way the number of free running parameters can be reduced, while allowing an increased degree of freedom compared to the models.

### Experimental conditions

- E1 Estimate for experimental error (taken from noise amplitude in  $\chi(k)$ , needed for calculation of standard deviation).

- E2     Number of independent data points together with current number of free running parameters (latter should be significantly smaller than the former (~ factor of two))

The “Copy” button copies the value of the selected parameter to all parameters in the corresponding column. This may come in handy if you want, for instance, to copy the  $E_0$  value of the first path to all other paths.

The different correlation schemes or parameter constrains are symbolized by different colors of the input boxes. This way it should be fairly easy to notice not yet constrained parameters. Furthermore, of course, an eye should be kept on the number of free running parameters compared to the number of independent parameters. Note, that most of the correlation schemes are “irreversible” (same as single parameter correlation, see above). That means, if you, for instance, have selected the *AVE* correlation for the DW factors and you change your mind half way through, you will have to close the dialog box and start over again. However, individual parameters can be taken out of a general correlation scheme by un-ticking the *fixed* flag for this particular parameter. For instance, you may want to correlate all scattering path distances to one x,y,z extension coefficient, except of one single scattering distance, that is to run free in the fit. To achieve this, press the *XYZ* button to correlate all distances and, afterwards click on the distance that is to run free and undo the *fixed* flag.

Constrained and fixed parameter can be freed again and the constrains can be changed. These operations are reversible, in contrast to the correlation schemes.

In total, the “Enter XAFS Parameter” box for FEFF simulations and refinements is certainly the most complex box in WinXAS. Its complexity is mostly caused by the large number of options available, whose advantages or potentials may not be obvious right away. I would recommend to start out with simple examples (for instance, a theoretical  $\chi(k)$  of Cu metal calculated with FEFF) and then increase complexity (for instance, oxides or mixed oxides).

When all correlation schemes and constrains have been set, closing the parameter box (EXIT or OK) and WinXAS will either carry out the refinement or display the calculated  $\chi(k)$ , depending on the chosen menu item.

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## 4.6 DXAS

### 4.6.1 Introduction

Owing to the differences between the energy-dispersive set-up and the standard double crystal monochromator for X-ray absorption spectroscopy, the treatment of dispersive XAS data requires some additional reduction steps. Besides the features to handle the normally quite large amount of spectra, that is the calculation of XAS spectra from  $I_0$  and  $I_1$  and the energy calibration.

### 4.6.2 DXAS Calibration

#### 4.6.2.1 Set by Foil

Offers a possibility to calibrate an energy-dispersive XAS spectrum with a reference spectrum (see above for details). The following two requirements has to be met in order to obtain a successful DXAS calibration.

- i) The DXAS spectrum you want to calibrate has to look like a 'good' XAS spectrum (flat pre-edge, absorption edge, horizontal EXAFS). That means, prior to the calibration itself you have to cut an appropriate section (no junk points left or right), subtract the background and normalize the spectrum to an edge jump equal to one.
- ii) In order to use a reference spectrum it has to be added to a special WinXAS file named DEXFOIL.DAT (see **index**, ADD To DEXFOIL.DAT). At the beginning of the calibration procedure, WinXAS will look for this file in its root directory (the one you started it from). If it's not there, WinXAS will tell you so and terminate the calibration. In this case, you must first either generate your own dexfoil.dat file or copy an existing file to the root directory.

Eventually, the calibration dialog box will appear. First of all, you may want to choose a reference spectrum from the ELEMENT list box. After you have selected one reference spectrum WinXAS will try to determine some initial values for the second order polynomial coefficients. The underlying procedure is the following : First, the threshold energy for both spectrum and reference is determined as the maximum in the first derivative. Second, WinXAS searches for all maxima and minima in the EXAFS of both spectra from the roots in the 1st derivative. Afterwards the found extrema are stored in an array and a second order polynomial is refined with the array using a standard least-squares algorithm.

In a sort of feasibility test, WinXAS is able to tell whether a found extrema in the DXAS spectrum correspond to a wiggle in the reference spectrum and shall be used for the refinement or whether it may be just a glitch, noise, etc. If an extrema appears to be no XAS wiggle, the root search will be terminated at this point and only the so far found extremas will be used.

However, this procedure may not always result in sufficient starting values. Although WinXAS already tries the described procedure for different degrees of smoothing, *additional smoothing* of the DXAS spectrum prior to the calibration does the trick in many cases.

As a result of its efforts WinXAS will now display the reference spectrum (gray) together with your DXAS spectrum. If the 'auto-search' procedure came up with reasonable starting parameters, both spectra will already be quite well superimposed and there shouldn't be that much left to do. In case the procedure failed, you may have to make extended use of the four scroll bars shown to the left of the x,y-graph.

Here is how you can calibrate your DXAS spectrum by hand :

Each polynomial coefficient has its own scroll bar. The zero order polynomial corresponds to a simple shift of the entire spectrum in energy. It is used to superimpose both edges and should be adjusted first. Normally, WinXAS does quite well in determining this coefficient and there shouldn't be much to improve. The next scroll bar to use corresponds to the first order polynomial. It scales the reference spectrum linearly over the entire energy range. When you change the first order coefficient, WinXAS seeks to change the zero order accordingly. This guarantees, that your absorption edge stays in place and you don't need to adjust zero order every time you've changed the higher orders.

Well, if the energy-position correlation on your detector was linear, you would not need any higher orders. Unfortunately, this is quite often not the case. Therefore, if you can't get a got match with a first order polynomial, you will have to adjust the second order as well. As you will realize soon, this is a bit more diffi-

cult, in the sense, that you probably have to flip between 1st and 2nd order several times before the superimposition is satisfying. A deviation from linearity is most obvious in the high energy region of your spectrum. Even though the match in the XANES can be quite good, the further you move away from the edge the worse it gets. If you now change the 2nd order, the match will probably become worse of the entire range. The trick is, to 'over do' the 2nd order and to try to get a good match back with the 1st order. You may have to do this several times but sooner or later you will find the superimposition better and better until matching is achieved.

This makes three scroll bars. The fourth one only moves the entire reference spectrum up and down without any changes to the polynomial coefficients.

After you've achieved a sufficient calibration, you can close the dialog box. The coefficients are stored within WinXAS and can now be used to convert DXAS spectra to photon energy (see **index**, CONVERT DXAS).

### 4.6.3 Convert DXAS

Converts an energy-dispersive XAS spectrum from photo diodes to photon energy. The procedure applies a second order polynomial on the X axis of the Active X,Y-graph. The coefficients of this polynomial can be entered in the corresponding input fields. Provided a DXAS CALIBRATION was previously performed, these fields will already contain the polynomial coefficient as they were determined from the calibration procedure.

If a WinXAS Macro is recorded in order to analyze DXAS data, the procedure CONVERT DXAS should be used instead of DXAS calibration.

### 4.6.4 Show Spectra Header

Provided the file of the Active Graphic Window is a WinXAS binary multiple column file, information stored in the header of each column can be retrieved and plotted versus column number (see **index**, WINXAS BINARY FILE FORMAT for details).

### 4.6.5 Show Odd/Even

Extracts two x,y-graphs from an as-measured DXAS spectra (intensity versus diode number). The first array contains all odd, the second one all even diodes.

### 4.6.6 Calculate Spectra

The procedure allows you to calculate a XAS spectrum from separate I1, I0 and I(dark) files. Name and path of each file can be entered in the corresponding input box (use the buttons to browse hard disk). The XAS spectrum will be calculated from  $[\log((i1-idark)/(i0-idark))]$  and displayed in the Active Graphic Window. The i(dark)[background] box can be left blank.

Optionally, an asterisk (\*) can be used as place-holder in the i1 or i0 input box to indicate the calculation of more than one spectrum. (e.g. : I0\_FILE.DAT together with I1\_FILE\*.DAT will find (I1\_FILE1.DAT, I1\_FILE2.DAT, etc. ) and calculated the XAS spectrum. Spectra are saved with the I1 file name and the extension \*.XAS; I0\_FILE\*.DAT together with I1\_FILE\*.DAT will search for I1 and I0 files with the same number and calculate the XAS spectrum.

The following advanced options are available :

- **CONVERT BL8 FORMAT** : expert users only - converts files from the ESRF's BL8 format to a WinXAS format prior to calculating the XAS spectrum (*currently disabled*).
- **GENERATE DEX FILE FORMAT** : this option allows you to create a HASYLAB/DEXAFS multiple column file and take full advantage of all WinXAS features for the analysis of DXAS data (see **index**, energy calibration and automatic analysis).
- **GENERATE MULTIPLE COLUMN FILE** : in case an asterisk is used in the I1 input box, the resulting XAS spectra can be stored in a WinXAS multiple column file, instead of being written to separate \*.XAS files (not available with the GENERATE DEX option).

### 4.6.7 Add to DEXFOIL.DAT

The WinXAS file DEXFOIL.DAT is used for the energy calibration of DXAS data (see **index**, DXAS calibration, SET BY FOIL). It is an ASCII file and contains as many reference spectra as you want to add in a eight column format. Before you are able to use a reference file for calibrating DXAS spectra you have to add it to DEXFOIL.DAT. The procedure is the following :

OPEN the reference spectrum as the Active Graphic Window. Afterwards subtract the background and normalize the spectrum to an edge jump equal to one. The reference spectrum should look like a XAS spectrum from the books (flat pre-edge, absorption edge, horizontal EXAFS). If you trust it and you really want to calibrate all your following experiments with it, select ADD To DEXFOIL.DAT.

WinXAS will ask you for a name (Cu K for instance) and than add the spectrum to "dexfoil.dat". The next time you go to DXAS CALIBRATION the name (Cu K) will appear in the list box and you can calibrate your DXAS spectra.

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## 4.7 TIME-RESOLVED

### 4.7.1 Automated Analysis

This feature offers the possibility to perform an automated analysis on the multiple-column file of the Active Graphic Window. This procedure can be selected for any multiple column file. Additionally, it contains some particular options for DXAS multiple-column files. The general features are described first, followed by the more specialized DXAS options.

The procedure will apply the chosen data-reduction steps in a serial manner, starting at column (START AT ...) through column (LAST COLUMN....) in a step width of STEPS. First of all, you have to enter the column numbers in the according input fields. Note that column #1 normally contains the X column and that it makes less sense to exceed the number of columns in your file.

Provided you have chosen a larger step width than one, you can have your spectra averaged. That means instead of taking columns 2, 10, 18, 26, etc. the procedure will average spectra 3 through 10 and 11 through 18, etc.

In the next step you have to choose what sort of result your data analysis will come up with. Let me try to explain this on two examples :

- i) You want to extract the  $\chi(k)$  of your XAS spectra. Your WinXAS Macro will therefore contain steps like background correction, E0 determination, Conversion into k space,  $\mu(0)$  fit and removal

of the k-weighting. However, eventually your Macro comes up with the  $\chi(k)$  as the Active X,Y-graph of your Active Graphic Window. If you now apply this Macro on your multiple-column file in an Automatic Analysis, the result you want to obtain is a new multiple-column file with all the  $\chi(k)$ s neatly arranged one after the other. For that you have to press the button SAVE RESULTING DATA ARRAY, because the output you want to save is a new array (the  $\chi(k)$  in our example).

- ii) In the 2nd example you want to determine the height of a 'white line' and how it changes with reaction time. Therefore, your WinXAS Macro will contain something like Background correction, Normalization, Cut out a section around the 'white line', Search Maximum in this section. Eventually, your Macro will store the value for the 'white line' height in the result window and the Active X,Y-graph will show the section out of your spectrum. Provided now, you would do the same as in (i) you would end up with a new file containing all the sections from your spectra. That's not what you need.

In order to save the ordinate value of the MinMax search, you have to press the button SAVE RESULTS AND PARAMETER. In this case, all numerical results of the last performed analysis step are saved to a multiple-column ASCII file. The first column contains the spectrum number, the following the results. For the example above only the 2nd column is of interest. It contains the 'white line' height of each spectrum. In case, more than one numerical value result from the last step they will be saved in the subsequent columns. This way, for instance, parameters of profile functions can be saved, etc.

If everything is complete, close the dialog box with OK. Before the analysis can be carried out, WinXAS asks you to choose a Macro, which you have defined before. Afterwards, the analysis will start and WinXAS will visualize its progress on the screen.

The following refers to the analysis of DXAS files (see DXAS section for details on the WinXAS energy-dispersive file format).

If your file is a valid DXAS multiple-column file you can have WinXAS calculating an absorption spectrum (i.e.  $(i1-id)/(i0-id)$ ) for each column (i1) prior to applying the Macro (DEXAFS SPECTRA button). Additionally, WinXAS can perform an interpolation between  $I_0$  measured at the beginning and the end of an experiment for each column. This new  $I_0$  is then used to calculate the absorption spectrum ( $I_0(1)-I_0(2)$  INTERPOLATION). WinXAS assumes  $I_0$  to be stored in the 2nd and the (N-2)th column. If this is not the case whatsoever, these settings can be changed in POSITION OF  $I_0$  COLUMNS.

## 4.7.2 Multiple Column Plot

The Multiple Column Plot option allows you to plot up to 100 spectra in the Active Graphic Window. For that, the file of the Active Graphic Window has to be a WinXAS multiple column file. The procedure will read all chosen columns from this file and display them in one plot. If you need to plot a larger number of single spectra that are not contained in one multiple column file, refer to CREATE MULTIPLE COLUMN FILE for details on how you can obtain a suitable WinXAS file.

As the first step you have to select all columns that shall appear in your plot. There are two different ways to do so. If you want to plot all columns or every second or third, you click FIXED STEPWIDTH and

enter 1, 2, or 3, respectively. Afterwards, you can leave the list box alone. However, if you want to plot just a range of your file or only a few columns you have to select these columns in the DATA COLUMNS list box (recall the rules for multiple selection in WINDOWS : in order to select a whole range : click the start column with the mouse, than press the [SHIFT] key and click the end column with the mouse, all columns between start and end should be highlighted now; in order to make multiple selections with your mouse keep the [CTRL] key pressed while selecting single columns, this way more than one column can be activated or deactivated).

Concerning the appearance of your spectra, the following options are available :

**DISPLACE CURVES** will plot all spectra in one X,Y-graph with a slight displacement. By default the spectra will be plotted from bottom to top. In order to change this press INVERSE PLOT.

**PSEUDO 3D EFFECT** will plot your spectra versus a third (Z) axis (equidistant). The inscription of the Z axis can be set by BOTTOM BORDER and TOP BORDER. By default spectra are plotted from the front to the back. In order to inverse the plot press INVERSE PLOT (Note that bottom border should be larger than top border in this case).

If you want to get rid of the multiple column display again, just deactivate the COMBINE button.

### 4.7.3 Create Multiple Column File

same as CREATE MULTIPLE COLUMN FILE in the FILE menu (see **index**).

### 4.7.4 Average Columns

Opens the AVERAGE COLUMNS dialog box. The box simply allows you to average columns from a multiple column file. For that, this procedure can be used on any multiple column file.

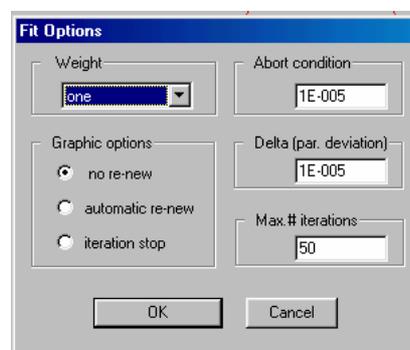
In case the file happens to be a valid DXAS file (e.g. from HASYLAB or the ESRF) you can additionally calculated the corresponding XAS spectrum from the averaged columns. Therefore, an I01 / I02 interpolation is carried out for each spectrum prior to the summation. In order to enable this option to result in a useful spectrum, the multiple-column file format of course has to follow the conventions for energy-dispersive WinXAS multiple-column files (as described in the DXAS section of this manual).

## 4.9 OPTIONS

### 4.9.1 Fit Options

Some options regarding the LEAST-SQUARES refinement (see **index**) with WinXAS can be changed.

- **Weight:** Several weighting schemes can be applied in order to emphasize parts of the spectrum differently. (e.g. peaks can be weighted higher than the background, or vice-versa).
- **Graphic Option:** During the refinement the Graphic Window can



be displayed only at the beginning and the end of each fit (NO RE-NEW) and after each iteration either automatically (AUTOMATIC RE-NEW) or after user input (ITERATION STOP).

- **Fit Results:** In addition to normal Fit Results (parameters, etc.), a Fit History (evolution of parameters during the fit) and the correlation matrix can be stored in the RESULT WINDOW (see **index**) (FIT RESULTS section),

## 4.9.2 EXAFS Options

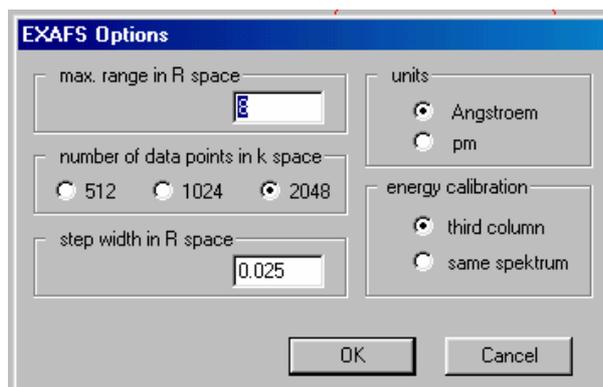
Some general options concerning XAS analysis can be changed in the EXAFS OPTIONS dialog box. First of all, forget about the Å and pm option. Because obviously nobody seems to care about the 'new' units, I didn't bother to implement them either. This may change in the future.

The 'Maximum Range in R-Space' concerns the range in which the Fourier Transform is displayed in Å. It is set to 8 Å by default, but you can change it to almost everything you want. Actually, less is often convenient if you want to perform a XAS fit in R space and need a closer look at some FT peaks. (the ZOOM functions won't work; that's the way to do it)

The 'Number of Data Points in k Space' and 'Step Width in R Space' are also related to the XAS Fourier Transform. Literally, the more data points you want in your FT (small step width), the more data points in k space should be transformed. But you may want to play around with this options a little bit on your own and discover, what actually remains from your original  $\chi(k)$  if you choose something like step=0.01 and 1024 data points! And why actually measuring your XAS spectrum with equidistant data points in the k-space is not a bad idea at all.

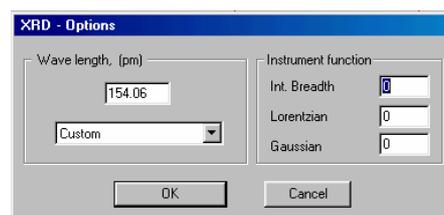
The last option concerns the Energy Calibration of your XAS spectra. Commonly, this is done with a reference spectrum where the threshold energy of the absorbing element is well know / tabulated (metal foil is not bad!). For convenience it makes sense to store the reference spectrum as third column in your XAS file. If this is the case and you choose ENERGY CALIBRATION (see **index**) from the XAS menu, WinXAS will try to load the third column of your file and display it. After E0 is determined and the tabulated value is entered, WinXAS will correct the sample spectrum accordingly. Anyway, in some particular cases you may want to calibrate your spectrum with some feature in the same spectrum, such as a second absorption edge, a monochromator glitch of known energy, etc.

In these cases you need to select SAME SPECTRA in order to prevent WinXAS from loading the third column and to allow you to calibrate the sample spectrum in the way you want to.



## 4.9.3 XRD Options

Experimental wavelength and instrumental function (integral breadth (peak area / peak height)) can be changed. These values are used to calculate particle size and strain from Gaussian or Lorentzian profile fitting to XRD data.



### 4.9.3 Graphic Options

Lets assume that at least some of the options are self-explanatory: DISPLAY OPTIONS; COLORS; LINE STYLE; CIRCLE and TRIANGLE size; LINE WIDTH of FRAME, FUNCTION, DATA ARRAY and AXIS; NO X or Y AXIS DESCRIPTION;

**DISPLAY SINGLE FUNCTION:** provided the profile function of the Active Graphic Windows consist of more than one single function, this button is enabled and can be used to switch the display of all single functions on and off. (available also from BUTTON WINDOW !)

**DISPLAY FUNCTION AT DATA POINTS ONLY:** if this button is checked, the profile function will only be calculated at the data points of the Active X,Y-graph. This option is set as default for XAS functions, but can also be used for all other profile functions.

**3D-ANGLE:** changes the angle of the Z-axis with respect to the X-axis for 3D representations (available also from BUTTON WINDOW !).

**SCALING FACTORS:** there is one factor for each axis and it determines how many numbers are printed on each axis. The scaling factor and much more can be changed interactively in the dialog box CHANGE X,Y-GRAPH SCALING and may vanish one day from this box (see GRAPHIC WINDOW or click outside the graph in the active Graphic Window).

**FRAME:** each x,y-graph of the Active Graphic Window is surrounded by a FRAME. That holds for output graphics too. If this is not desired, the frame can be switched of here.

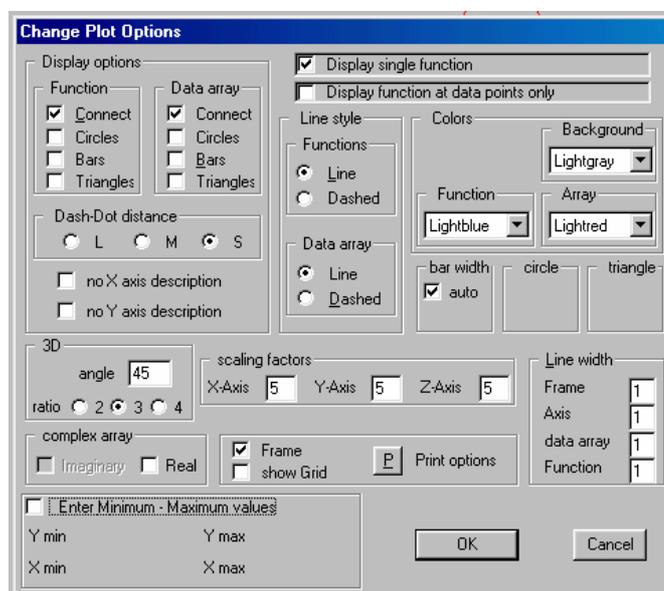
**GRID:** switches display of a GRID in the Active Graphic Window on and off. (available also from BUTTON WINDOW !)

**PRINT OPTIONS:** see [index](#)

**COMPLEX ARRAY:** for a complex data array the display of either the imaginary or the real part can be switched on and off (available also from BUTTON WINDOW !)

**ENTER MINIMUM MAXIMUM VALUE:** this option allows the output of the Active X,Y-graph in a pre-defined range on the Y-axis. It may be useful, if you don't want the x,y-graph to occupy the entire area of the window, which is does by default.

**DASH-DOT DISTANCE:** this option is sort of a crutch. The build-in WINDOWS functions don't enable a program to draw a dashed or dotted line with a line width of more than one pixel. It will always appear as a solid line. In this case WinXAS has to plot the array on its own. Depending on the slope of the graph, the distance between dots or dashes might not always be appropriate (too close or too far away). In order to adjust the distance between consecutive dots choose Large, Medium or Small.



### 4.9.4 Print Options

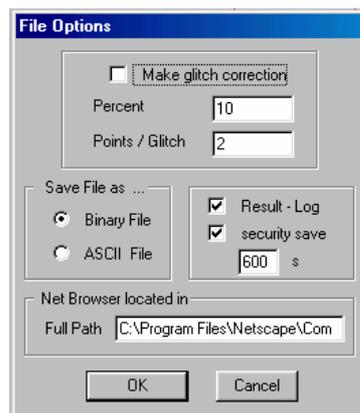
Some PRINT features can be changed in this dialog box. First of all, you can choose between PORTRAIT or LANDSCAPE orientation and in the former case also between different sizes.

Additionally, you can determine whether the current background color shall be used for printing or the background shall be white. The later is the default setting for WinXAS.

### 4.9.5 File Options

Some file input/output options are available.

- i) The default setting for the SAVE FILE item can be changed from BINARY to ASCII. This is not recommended. If only once in a while a spectrum has to be saved as ASCII, please use SAVE ASCII FILE (see above).
- ii) Result Log and Security Save can be activated or de-activated. Besides the normal Result Window, Result Log writes a complete history of all operations and numerical results to a file (RESULT.DAT). This file can be used to retrieve information in case WinXAS crashes. IMPORTANT : the file is overwritten each time you start a new session ! Therefore, if WinXAS happens to crash, rename or print RESULT.DAT before you restart WinXAS.



Security Save stores all active X,Y-graphs of all Graphic Windows to files named NUM-SAVEn.MES. Again, in case WinXAS crashes (which is by the way highly unlikely, of course !) the last active data arrays can be restored. WinXAS will prompt you to do so when its restarted after a 'non-proper termination'. Again, these files are overwritten with each new session.

- iii) WinXAS can remove glitches automatically during the FILE OPEN procedure. This algorithm seeks to determine and remove sharp, regular spikes, peaks or glitches in your spectrum. Whether a sharp features is taken as a glitch depends on the values in the boxes PERCENT and POINTS/GLITCH. The former determines how much a data point has to exceed its neighboring points in order to be recognized as a glitch. The latter restricts glitches to a certain number of points. This means, all sharp features with more than POINTS data points will not be removed. In order to remove a glitch, the array is interpolated between the neighboring data points. In general, this procedure works quite well for reasonably distinguished spikes of one, two, or three data points. It works less good for broader features or 'derivative-like' glitches.

### 4.9.8 Default Font

Allows you to change the settings for the WinXAS default fonts. The Start-up font is used as default every time a new Graphic Window is opened. Additional to font size (axis inscription, axis scaling, capital and legend) some plot options can be set. That is line width of axis, frame, graph and function and frame on/off, etc. (the etc. refers to changes in future versions).

In order to change between both default fonts use the FLIP FONT item in the local menu of the Active Graphic Window. The option may come in handy if you want to use different fonts for data processing on screen and printer output or copying to the clipboard.

### 4.9.9 Inscribe Axis

Opens a similar named dialog box where you can enter or change the inscription of the Active X,Y-graph together with the current font.

The four combo boxes at the top refer to the corresponding axis. A new inscription can be entered or an existing one can be chosen from the list. Inscriptions can be aligned either left, middle or right. This actually is the only place where you can enter new inscriptions. A more clever way to choose existing ones is via the selection boxes in the **BUTTON WINDOW** (see **index**).

The Legend combo box allows you to place any inscription directly inside the graph (that's why it's plotted here). The way to get it there is :

- write the inscription into the combo box input field.
- take the mouse, move its arrow inside the graph and (surprise, surprise) drag the little gray rectangle to the position where you want to place the inscription. An existing inscription can be detached by simply clicking on it and move the rectangle to its new position. In parallel, the corresponding string will appear in the combo box for changes.

The **FONT** button allows you to change some features concerning the appearance of the currently selected font family (font can be selected from the **BUTTON WINDOW** (see **index**) as well as different sizes). Changes can be made to each inscription font separately (in contrast to the Button Window). You can choose between bold, italic and/or underline and different sizes for each font.

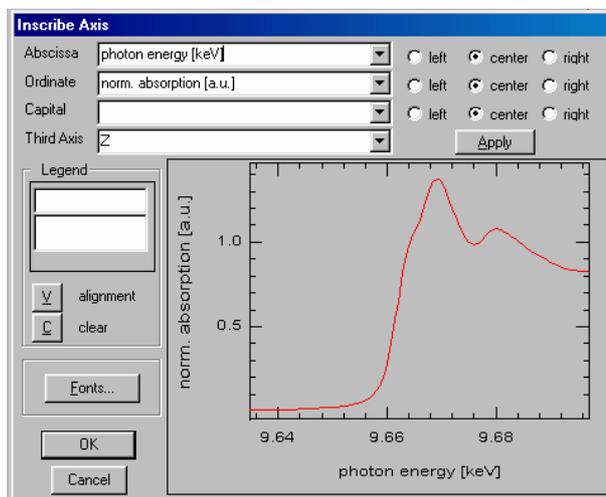
One more fancy feature of the WinXAS inscription capabilities concerns sub- or super-script characters (like in  $\text{H}_2\text{O}$ , or  $\text{\AA}^{-1}$ ) and Greek or math symbols. Including these characters in the axis titles can be achieved using the following tags :

- @ writes the following character down by 1/3 of the character height. Curly braces can be used to define a longer string. (e.g.  $\text{H}@2\text{O}$  results in  $\text{H}_2\text{O}$ ,  $\text{C}@\{60\}$  results in  $\text{C}_{60}$ )
- ~ writes the following character up by 1/3 of the character height. Curly braces can be used to define a longer string. (e.g.  $\text{\AA}\sim\{-1\}$  results in  $\text{\AA}^{-1}$ ,  $\text{k}\sim2$  results in  $\text{k}^2$ , and  $\text{SO}@4\sim\{2-\}$  results in  $\text{SO}_4^{2-}$ )
- ^ writes the following character as its **SYMBOL** analogue. Refer to the **WINDOW Character Map** to see which characters correspond to which symbols (e.g. c corresponds to  $\chi$ , hence  $\wedge\text{c}(\text{k})$  results in  $\chi(\text{k})$ ).

WinXAS inscriptions are stored in a file named **NUMERIC.INS** which looks like this :

```
photon energy [keV]#k [+~{-1}]#R [+#time [min]#time [h]#
absorption [a.u.]#norm. absorption [a.u.]#^c(k)*k~2#FT(^c(k)*k~2)#
```

The first line contains X-axis inscriptions, 2nd line Y- and Z-axis and 3rd line the capitals. The format is obvious, each title is separated by a #, the number of titles can be up to 10. Changes to this file can be easily made with any **WINDOWS** editor (see **EDIT INSCRIPTION FILE**).



As you may have already realized, there are some characters than can not appear in WinXAS axis inscriptions. These are @, ~, ^, and #.

### **4.9.10 Edit Inscription File**

The WinXAS inscription file (NUMERIC.INS) can be loaded into the standard WINDOWS edit (notepad.exe) and changed (see above for details on file format). In case notepad.exe is not installed on your computer, WinXAS will tell.

## **4.10 WINDOW**

### **4.10.1 Arrange**

Arranges all open WinXAS windows side by side.

### **4.10.2 Result**

Opens or displays the WinXAS Result Window (see RESULT WINDOW for details).

### **4.10.3 Edit**

Opens or displays the WinXAS Edit Window (see EDIT WINDOW for details).

### **4.10.4 Change Parameters**

Opens the CHANGE PARAMTERS dialog box (see CHANGE PARAMTERS).

### **4.10.5 Minimize**

Minimize the Active Window to an ICON and displays the icon at the bottom of the WinXAS desktop. Double-click on the icon to restore the window.

### **4.10.6 Maximize**

Maximizes the Active Window to the entire size of the WinXAS desktop. Choose MAXIMIZE again to display the Active Window in its previous size.

### **4.10.7 Change**

Activates the next WinXAS window and displays it on top. If the ARRANGE item has been chosen before, only the title bar of the current Active Window will be highlighted without further obvious changes.

### **4.10.8 Local Menu**

Displays the local menu of the currently active window. Each WinXAS window (see above) has its own local menu which offers a convenient short-cut to often-used functions. The local menu can also be reached by pressing the right mouse button inside the corresponding window. Please refer to the different WinXAS windows for details.

### 4.10.9 Start WinXAS Assistant

Starts the WinXAS Assistant dialog box for online help and a guided tour through WinXAS's capabilities. Just follow the instructions displayed in the Assistant example window.

### 4.10.10 McMaster Window



The McMaster dialog box displays x-ray data for the majority of chemical elements and calculates x-ray cross-sections and absorption coefficients for a given element and photon energy (in keV). This box is based on the program 'Mucal' by Pathikrit Bandyopadhyay and converted to C by Boyan Boyanov (boyan@tmnxt1.iit.edu), and is using McMaster data in the May 1969 edition.

In addition, the absorption in ion chambers filled with different gases can be calculated from the length of the chamber and the gas phase composition (mixture of two gases possible). If ion chambers are used with less than 1000 mbar pressure, "fill" the remaining gas volume with He (e.g. for 300 mbar of Ar, use 30 % Ar and 70 % He).

Z	mol. weight	density [g/cm <sup>3</sup> ]
29	63.54	8.94

absorp. coeff. [1/cm]	mass abs [cm <sup>2</sup> /g]
2428.4	271.64

K-edge:	8.979	photoelectric x-section:	269.897
L1-edge:	1.1	coherent x-section:	1.66754
L2-edge:	0.952	incoherent x-section:	0.07295
L3-edge:	0.932	total x-section(cm <sup>2</sup> /g):	271.638
M-edge:	0.12	conversion factor:	105.5
k-alpha1:	8.047	l1-edge jump(fractional):	1.16
k-beta1:	8.904	l2-edge jump(fractional):	1.41
l-alpha1:	0	l3-edge jump(fractional):	2.874
l-beta1:	0	k fluorescence yield:	0.44
		l1 fluorescence yield:	0.0016
		l2 fluorescence yield:	0.01
		l3 fluorescence yield:	0.011

Ion chamber absorption

Length, (cm)  Absorption, (% of I0)

Gas #1   % Gas #2   %

## 5. Credits

The author wishes to thank the following colleagues for valuable technical discussion:

J. Ehrich, H. Esemann, M. Fröba, F. Girgsdies, M.M. Günter, M. Hagelstein, R.E. Jentoft, U. Hatje, N. Hilbrandt, O. Kirilenko, B.L. Kniep, K. Lochte, W. Metz, W. Meyer, W. Niemann, J. Osswald, E. Rödel, J. Röhrer, A. San-Miguel, B. Scholze, A. Szizybalski, J. Wienold, J. Wong.

## 6. References

### WinXAS Publications

#### *General*

T. Ressler, **J. Synch. Rad.**, 5, 118 (1998). (Please cite when you have used WinXAS in published work)

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T. Ressler, J. Wienold, R.E. Jentoft, **Solid State Ionics**, 141-142, 243 (2001).

#### *XANES Analysis (LC fitting, PC Analysis)*

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T. Ressler, et al., **Environmental Science & Technology** 34 (2000) 950-958.

#### *Time-resolved and/or DXAS Studies*

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T. Ressler, M. Hagelstein, U. Hatje, and W. Metz, **J. Phys. Chem. B**, 101, 34, 6680 (1997).

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T. Ressler, J. Wienold, R.E. Jentoft, M.M. Günter, **Topics in Catalysis**, 18, 45 (2002).

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## 7. Appendix

### 7.1 WinXAS Binary File Format

Each WinXAS binary file starts with a general header consisting of 50 short integer values (4 bytes each) and 150 char values (1 byte each). Afterwards, each data column again consists of a header (20 short integer values) and the data itself. The data values can be either short integer or float. The data type has to be indicated in the file's general header.

In the following the reserved values in the general file header and the individual column header are described. The values indicated as FREE can be used without problems, other values not used so far may become occupied in the future.

Some values are mandatory in order to enable WinXAS to open the file. These values are marked as **bold** in the following. For instance, if these values are set with all other values set to ZERO, WinXAS will open the file as a binary file with one X column and float data values.

<b>General file header</b>		<b>Individual column header</b>	
<i>50 Integer:</i>		<i>20 Integers:</i>	
#	meaning	#	meaning
-----		-----	
<b>0.</b>	<b>6666, indication for</b>	0.	spectrum number
<b>1.</b>	<b>9999, binary file</b>	1.	time
2.	1 : integer data values 0 : float data values	2.	temperature
...	(not used so far)	...	
<b>10.</b>	<b>number of data points</b>	5. - 15.	FREE
<b>11.</b>	<b>number of columns</b>	18.	0 : all columns with same number of data points non zero : number of data points in next column
12.	0 : normal data file 1 : complex data file	19.	used
13.	0 : one X column 10 : individual X columns (not used so far)	0. - [# data points -1]	(integer or float values)
20. - 29.	used		
30. - 49.	FREE		
 150 Char:			
0. - 149.	FREE for comments, etc.		

# WinXAS Accelerator F-Keys

(Print, Cut, and Paste to your keyboard)

✂-----

<b>Help</b>	<b>Section</b>	<b>Save</b>	<b>Open</b>		<b>Max.</b>	<b>Change</b>	<b>Show All</b>	<b>Function</b>		<b>Edit</b>	<b>E-calib</b>	<b>XANES</b>	<b>XAS-fit</b>
	<b>Arrange</b>	<b>ASCII</b>	<b>Load</b>	Shift	<b>Menu</b>	<b>Print</b>	<b>Combine</b>	<b>Data</b>	Shift	<b>Result</b>	<b>2-Poly</b>	<b>μ<sub>0</sub>-Fit</b>	<b>Simul</b>
<b>Variables</b>	<b>Play M.</b>	<b>Rec. M.</b>	<b>Hide</b>	Ctrl	<b>Zoom</b>				Ctrl		<b>Set E<sub>0</sub></b>	<b>FT</b>	<b>FEFF</b>

✂-----

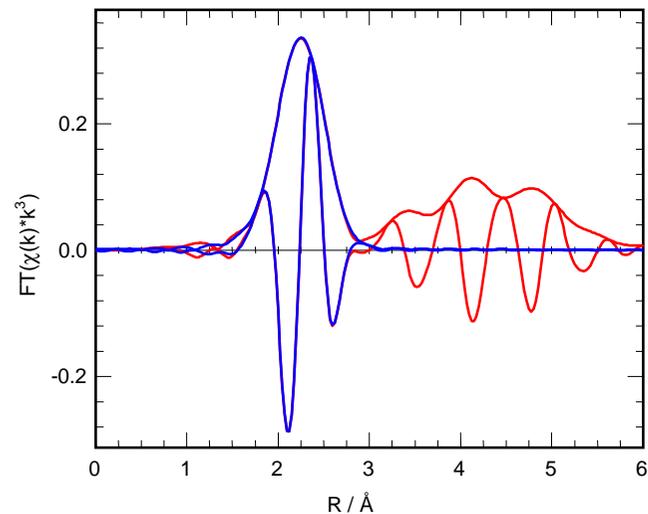
<b>F1</b>	<b>F2</b>	<b>F3</b>	<b>F4</b>		<b>F5</b>	<b>F6</b>	<b>F7</b>	<b>F8</b>		<b>F9</b>	<b>F10</b>	<b>F11</b>	<b>F12</b>
-----------	-----------	-----------	-----------	--	-----------	-----------	-----------	-----------	--	-----------	------------	------------	------------

## Index

Introduction	WinXAS buttons	Graphic window	Edit window	Result window	Online help	Status line
<b>WinXAS menu</b>						
<b>FILE</b>	<b>EDIT</b>	<b>SHOW</b>	<b>NUMERIC</b>	<b>XAFS</b>	<b>DXAS</b>	<b>OPTIONS</b>
Open	Function → x,y-graph	Function	Least-Squares Fit	Energy calibration	DXAS Calibration	Fit Options
Load	Deglitching	Data array	Restore parameters	Background Correction	Convert DXAS	EXAFS Options
Average Spectra	Paste x,y-graph	Choose Function	Confidence limits	Normalization	Show Spectra Header	Graphic Options
Save File	Copy x,y-graph	Enter Parameter	Automatic F Test	Conversion	Show Odd/Even	Print Options
Save ASCII File	Modify Ordinate	Change Parameter	2 D confidence limits	Set-E	Calculate Spectra	File Options
Average spectra	Modify Abscissa	Change Border	Smoothing	μ() Fit	Add to DEXFOIL	Default Font
Create MC File	Noise Generator	Save Parameter	Integration	k-Weighting	<b>TIME-RES.</b>	Inscribe Axis
Save MC to ascii	Write Feff file	Load Parameter	Differentiation	Fourier Transformation	Automatic Analysis	Edit Inscription File
Extract MC files	Show FT Magnitude	Zoom	Roots	Phases Amplitudes	Multiple Column Plot	<b>WINDOWS</b>
Print	Extract Imaginary Part	Section	Interpolation	Calculate spectrum	Create MC File	Arrange
Printer set-up	Copy to Clipboard	Original	Fourier Transformation	Difference Spectra	Average Columns	Result
Edit	Open New Window	Show all x,y-graphs	Convolution	E-Normalization	<b>XRD</b>	Edit
File Information		Combine x,y-graphs	Level-out Polynomials	Auto-XAS	Peak Search	Change Parameter
About		Previous	Linear Regression	Factor (PC) analysis	Fourier Synthesis	Minimize
Convert data		Next	Search Min-Max	LC XANES Fit	Stokes Deconvol.	Maximize
Exit		Start Macro		Run FEFF	Kinetic Calcul.	Change
		Start Macro recorder		XAS Simulation	Isoconversional Anal.	Local Menu
				XAS Fit	XRD-Structure fit	WinXAS Assistant
<b>Appendix</b>						
Credits	References	WinXAS binary file format	Examples			

**Examples for application of confidence limits and F test in XAFS data analysis:**

i) Cu metal foil, Cu K edge XAFS spectrum,  
 theoretical phase and amplitude calculated for first Cu – Cu shell with FEFF 7.  
 (R range 1.7 - 2.9 Å, k range 2.1 - 12.8 Å<sup>-1</sup>, residual 1.05, N<sub>ind</sub> = 10, N<sub>free</sub> = 4)



Showcase example: very good fit, clearly independent parameters (all F=0) and very small confidence limits for all parameters refined.

```
-- Automated F-test for current fitting parameters - Original R value: 1.047
Par #02: 11.66      - F 0      , R: 1.882 (R: 1.047, Par: 12.826 , Var: 10 %) : independent
Par #03: 2.5437    - F 0      , R: 21.52 (R: 1.047, Par: 2.5946 , Var: 2 %) : independent
Par #04: 0.0081079 - F 0      , R: 3.535 (R: 1.047, Par: 0.0097295, Var: 20 %) : independent
Par #05: 3.9593    - F 0      , R: 2.148 (R: 1.047, Par: 4.7512 , Var: 20 %) : independent
(1)      (2)      (3)      (4)      (5)      (6)      (7)      (8)
```

- (1) # of free running parameter in refinement corresponds to parameter list
- (2) fit parameter obtained from original refinement
- (3) F test parameter and (8) the corresponding significance estimate
- (4) residual obtained from fit with value of varied parameter ((6) varied by X % (7) with respect to original fit) kept invariant in the refinement
- (5) residual obtained from allowing the modified parameter (6) to vary in fit (should be the same as original residual, otherwise local minimum).

```
-- Confidence limits of current fitting parameters -
```

```
Variation of residual within 95 %
Par #02: 11.66015 +- 0.157
Par #03: 2.543684 +- 0.000554
Par #04: 0.008107939 +- 0.000105
Par #05: 3.959325 +- 0.108
```

Acceptable variation of residual (e.g. 95 %) can be changed in “Fit Options”.

ii) Molybdenum dioxide, MoO<sub>2</sub>, Mo K edge,

theoretical phases and amplitudes calculated with FEFF 7.

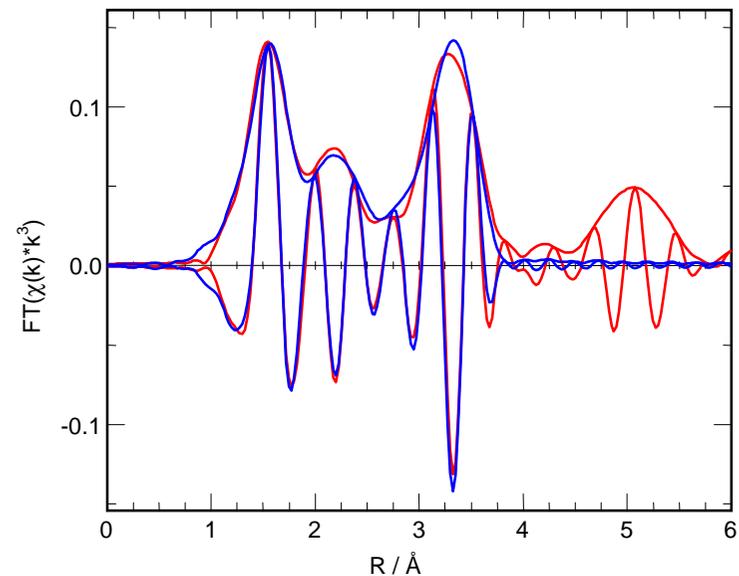
(R range 1.0 - 4.0 Å, k range 2.2 - 15.5 Å<sup>-1</sup>, N<sub>ind</sub> = 27, N<sub>free</sub> = 11)

(Only single scattering paths (8) considered, MS paths omitted for clarity.)

Results of first try to refine MoO<sub>2</sub> model structure to XAFS data.

(R model corresponds to crystallographic distances)

Pair	CN	R, model	R	sig <sup>2</sup>	E0
Mo-O	2	1.97	1.93	0.000393	-2.75
Mo-O	2	1.99	1.998	0.000393	-2.75
Mo-O	2	2.07	2.059	0.000393	-2.75
Mo-Mo	1	2.51	2.518	0.00305	-2.75
Mo-Mo	1	3.11	3.117	0.00305	-2.75
Mo-Mo	4	3.68	3.655	0.00305	-2.75
Mo-Mo	2	3.71	3.736	0.00305	-2.75
Mo-Mo	2	3.79	3.735	0.00305	-2.75



Issues:

- \* significance of free running Mo – O distances in first (slightly distorted) shell and confidence limits
- \* significance of free running E<sub>0</sub> in refinement and confidence limits
- \* reliable σ<sup>2</sup> parameters of Mo-O and Mo-Mo paths
- (\* significance of independent σ<sup>2</sup> parameters of various Mo-O paths, for instance) (not shown)

a) First try:

(all three Mo-O paths running free, all Mo-Mo paths free, single  $E_0$  for all paths, one  $\sigma^2$  for Mo-O paths, and one  $\sigma^2$  for Mo-Mo paths, CN fixed,  $S_0^2$  fixed)

```
-- Automated F-test for current fitting parameters - Original R value: 7.915
Par #03: 1.93 - F 0.52 , R: 8.167 (R: 7.915, Par: 1.9686 , Var: 2 %) : maybe dependent
Par #04: 0.00039261 - F 0.72 , R: 8.284 (R: 7.915, Par: 0.00062819, Var: 60 %) : maybe dependent
Par #05: -2.7517 - F 0.47 , R: 8.491 (R: 7.915, Par:-3.302 , Var: 20 %) : largely independent
Par #07: 1.9983 - F 0.74 , R: 8.016 (R: 7.915, Par: 2.0383 , Var: 2 %) : maybe dependent
Par #11: 2.0589 - F 0 , R: 9.298 (R: 7.915, Par: 2.1001 , Var: 2 %) : independent
Par #15: 3.1166 - F 0 , R: 11.5 (R: 7.915, Par: 3.1789 , Var: 2 %) : independent
Par #16: 0.0030543 - F 0 , R: 10.87 (R: 7.915, Par: 0.0036652, Var: 20 %) : independent
Par #19: 2.5182 - F 0 , R: 14.15 (R: 7.915, Par: 2.5686 , Var: 2 %) : independent
Par #23: 3.6554 - F 0 , R: 9.758 (R: 7.915, Par: 3.7285 , Var: 2 %) : independent
Par #27: 3.7363 - F 0 , R: 8.304 (R: 7.915, Par: 3.8111 , Var: 2 %) : independent
Par #31: 3.7355 - F 0 , R: 8.29 (R: 7.915, Par: 3.8102 , Var: 2 %) : independent

-- Confidence limits of current fitting parameters - Variation of residual within 95 %
Par #03: 1.930005 +- 0.0969
Par #04: 0.0003926089 +- 0.000253
Par #05: -2.751671 +- -0.48
Par #07: 1.998318 +- 0.054
Par #11: 2.058897 +- 0.0133
Par #15: 3.116577 +- 0.00895
Par #16: 0.003054334 +- 0.000128
Par #19: 2.518219 +- 0.00574
Par #23: 3.655393 +- 0.0141
Par #27: 3.736336 +- 0.0327
Par #31: 3.735466 +- 0.0328
```

- \* High F test parameters and high confidence limits are obtained for three independent Mo-O distances and  $E_0$  parameters. Independent parameters are not significant and unreliable. Apparently, they need to be fixed or constrained in refinement.
- \* Mo-Mo paths appear mostly reliable with acceptable confidence limits. Mo-Mo paths at  $\sim 3.7 \text{ \AA}$  may be uncertain.

b) Second try:

(two independent Mo-O paths, all Mo-Mo paths free, single  $E_0$  for all paths, one  $\sigma^2$  for Mo-O paths, and one  $\sigma^2$  for Mo-Mo paths, CN fixed,  $S_0^2$  fixed)

```
-- Automated F-test for current fitting parameters - Original R value: 8.085
Par #03: 2.0171      - F 0      , R: 12.15 (R: 8.085, Par: 2.039      , Var: 2      %) : independent
Par #04: 0.0022393  - F 0      , R: 15.11 (R: 8.085, Par: 0.0043697, Var: 20     %) : independent
Par #05: -3.2199    - F 0.32   , R: 8.691 (R: 8.086, Par:-3.696      , Var: 20     %) : largely independent
Par #11: 1.9398     - F 0.54   , R: 8.392 (R: 8.183, Par: 2.0628     , Var: 4      %) : maybe dependent
Par #15: 3.1154     - F 0      , R: 12.56 (R: 8.085, Par: 3.178      , Var: 2      %) : independent
Par #16: 0.0030204  - F 0      , R: 11.04 (R: 8.085, Par: 0.0036089, Var: 20     %) : independent
Par #19: 2.5169     - F 0      , R: 14.95 (R: 8.085, Par: 2.567      , Var: 2      %) : independent
Par #23: 3.6534     - F 0      , R: 8.884 (R: 8.084, Par: 3.7268     , Var: 2      %) : independent
Par #27: 3.7345     - F 0      , R: 9.202 (R: 8.086, Par: 3.8098     , Var: 2      %) : independent
Par #31: 3.734      - F 0      , R: 9.206 (R: 8.085, Par: 3.8094     , Var: 2      %) : independent

-- Confidence limits of current fitting parameters - Variation of residual within 95 %
Par #03: 2.017069    +- 0.00352
Par #04: 0.002239207 +- 0.000206
Par #05: -3.219888   +- -0.462
Par #11: 1.939823    +- 0.102
Par #15: 3.115384    +- 0.00927
Par #16: 0.003020411 +- 0.000131
Par #19: 2.516909    +- 0.0055
Par #23: 3.65338     +- 0.0476
Par #27: 3.734497    +- 0.026
Par #31: 3.73404     +- 0.0259
```

\* Considerable F test parameters and high confidence limits are also obtained for two independent Mo-O distances and  $E_0$  parameters. Parameters are still not significant and unreliable. Apparently, they need to be further fixed or constrained in refinement.

\* Mo-Mo paths appear mostly reliable with acceptable confidence limits. Mo-Mo paths at  $\sim 3.7 \text{ \AA}$  may be uncertain.

c) Third try:

(one independent Mo-O paths, all Mo-Mo paths free,  $E_0$  set to zero and fixed, one  $\sigma^2$  for Mo-O paths, and one  $\sigma^2$  for Mo-Mo paths, CN fixed,  $S_0^2$  fixed)

```
-- Automated F-test for current fitting parameters - Original R value: 9.025
Par #03: 2.0029      - F 0      , R: 15.12 (R: 9.025, Par: 2.043      , Var: 2      %) : independent
Par #04: 0.0038144  - F 0      , R: 10.53 (R: 9.025, Par: 0.0045772, Var: 20     %) : independent
Par #15: 3.1219     - F 0      , R: 13.24 (R: 9.025, Par: 3.1843     , Var: 2      %) : independent
Par #16: 0.0030157  - F 0      , R: 11.12 (R: 9.025, Par: 0.0036188, Var: 20     %) : independent
Par #19: 2.5242     - F 0      , R: 15.33 (R: 9.011, Par: 2.5747     , Var: 2      %) : independent
Par #23: 3.6794     - F 0      , R: 9.297 (R: 9.011, Par: 3.753      , Var: 2      %) : independent
Par #27: 3.7134     - F 0      , R: 9.904 (R: 9.025, Par: 3.862      , Var: 4      %) : independent
Par #31: 3.7873     - F 0      , R: 9.869 (R: 9.025, Par: 3.863      , Var: 2      %) : independent
```

Pair	CN	R, model	R	sig <sup>2</sup>	E0
Mo-O	2	1.97	2.00	0.00381	0
Mo-O	2	1.99	2.00	0.00381	0
Mo-O	2	2.07	2.00	0.00381	0
Mo-Mo	1	2.51	2.52	0.00302	0
Mo-Mo	1	3.11	3.12	0.00302	0
Mo-Mo	4	3.68	3.68	0.00302	0
Mo-Mo	2	3.71	3.71	0.00302	0
Mo-Mo	2	3.79	3.79	0.00302	0

```
-- Confidence limits of current fitting parameters -
Variation of residual within 95 %
Par #03: 2.002916      +- 0.0039
Par #04: 0.003814353  +- 0.000243
Par #15: 3.12187      +- 0.00989
Par #16: 0.003015651  +- 0.000151
Par #19: 2.524178     +- 0.0054
Par #23: 3.679366     +- 0.0236
Par #27: 3.713439     +- 0.0167
Par #31: 3.787251     +- 0.0152
```

\* All parameters independent with acceptable confidence limits. Notice the much improved Mo-Mo at  $\sim 3.7 \text{ \AA}$  and the good agreement with the model structure. Alternatively, instead of varying the distances of the Mo-O paths the same, the  $\Delta R$  values with respect to the crystallographic distances could be varied the same ( $\rightarrow$  indeed slight improvement of residual).

Notes: