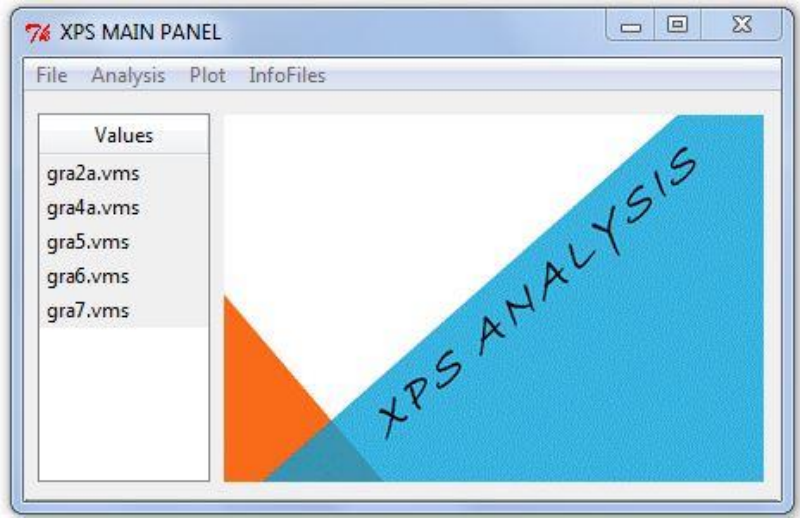
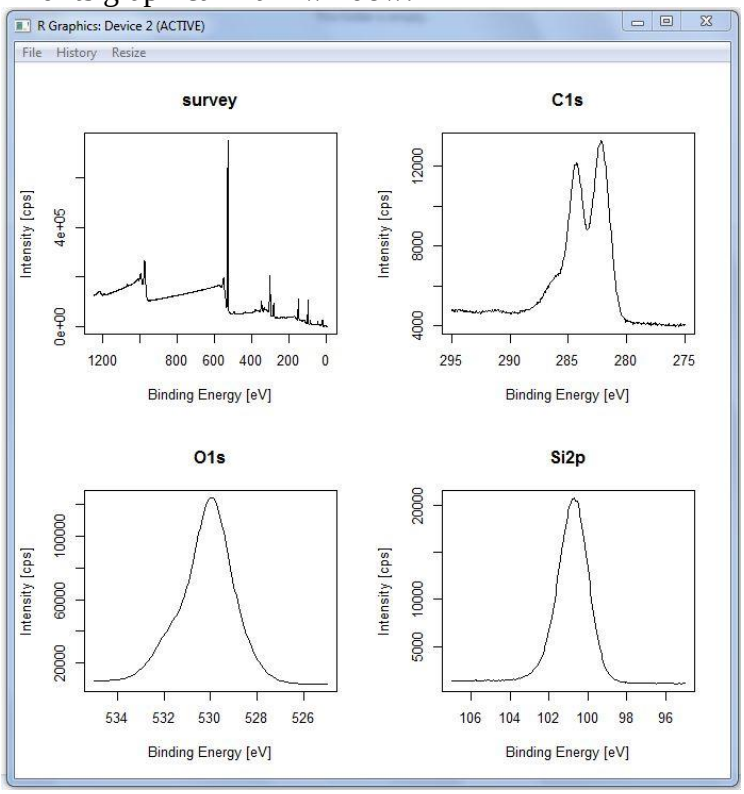
XPS ANALYSIS - the software to analyze XPS spectra
By G. Speranza

Make sure all the needed libraries are correctly loaded in the RStudio environment:
baseline, digest, grid, lattice, latticeExtra, memoise, minpack.lm, FME, NORMT3, signal, SparseM, wavelets, tcltk, tkrplot, gWidgets2, gWidgets2tcltk.
The R **xps()** command will run the XPS-Analysis software



And its graphical main window:



N.B. : in the following we will refer to the *active XPS-Sample* and *active CoreLine* as the datafile and coreline displayed in the graphical window which are going to be analyzed.

Menu description:

The XPS Main Panel shows four main menus:

- ***FILE;***
- ***ANALYSIS;***
- ***PLOT;***
- ***INFO & HELP.***

On the left-hand side of the main panel the window shows the name of the XPS-Sample data loaded in the software main memory to perform data handling and replotting of each of the XPS-Sample core line.

=> Double clicking on a name of the list will render it the active XPS-Sample. All the core line relative to the selected XPS-Sample will be shown in the graphic window

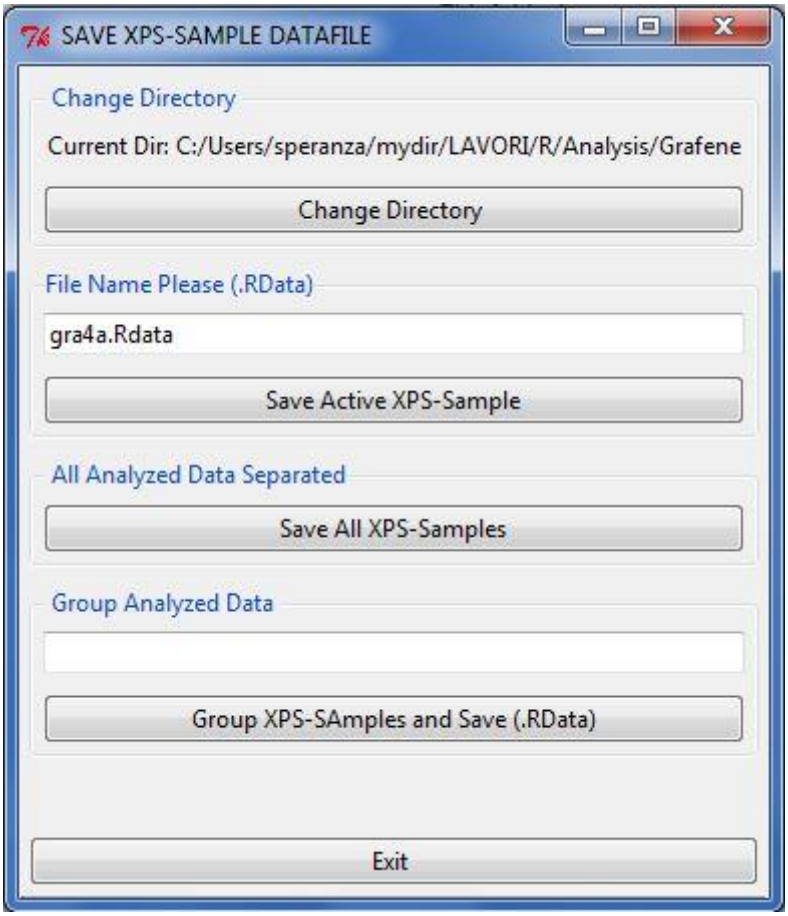
IMPORTANT: each of the xps() options activate an independent procedure which loads data from the software main memory, apply an operation. This affect data ONLY in the local memory. This changes are lost when exiting without saving.
Pressing the SAVE button will save changes in the main memory of the software making changes available for further processing. The effect of save is seen in the main graphical window where the processed spectrum is drawn and changes visible.

List of options

FILE	ANALYSIS	PLOT	INFO & HELP
Load VMS, PXT data	Spectrum selection	Plot	XPS Sample Info
Load PXT+RPL data	Analyze	Spectrum selection	Core Line Fit Info
Load Analyzed data	Extract from survey	Overlay	Help
Save Analyzed Data	Fit Constraints	Custom Plot	
Import Ascii	Fit Lev.Marq.	Annotate	
Export Ascii	Fit ModFit	Zoom & Cursor	
Split PXT data	Move Components	Graphic Device Options	
Remove Current XPS-Sample	Quantify	Set Analysis Window Size	
Set Working DIR	Energy Shift		
	Process Coreline		
	Smoothing		
	Reset Analysis		
	Change Spectrum Label		
	Element Identification		

***FILE menu*:**

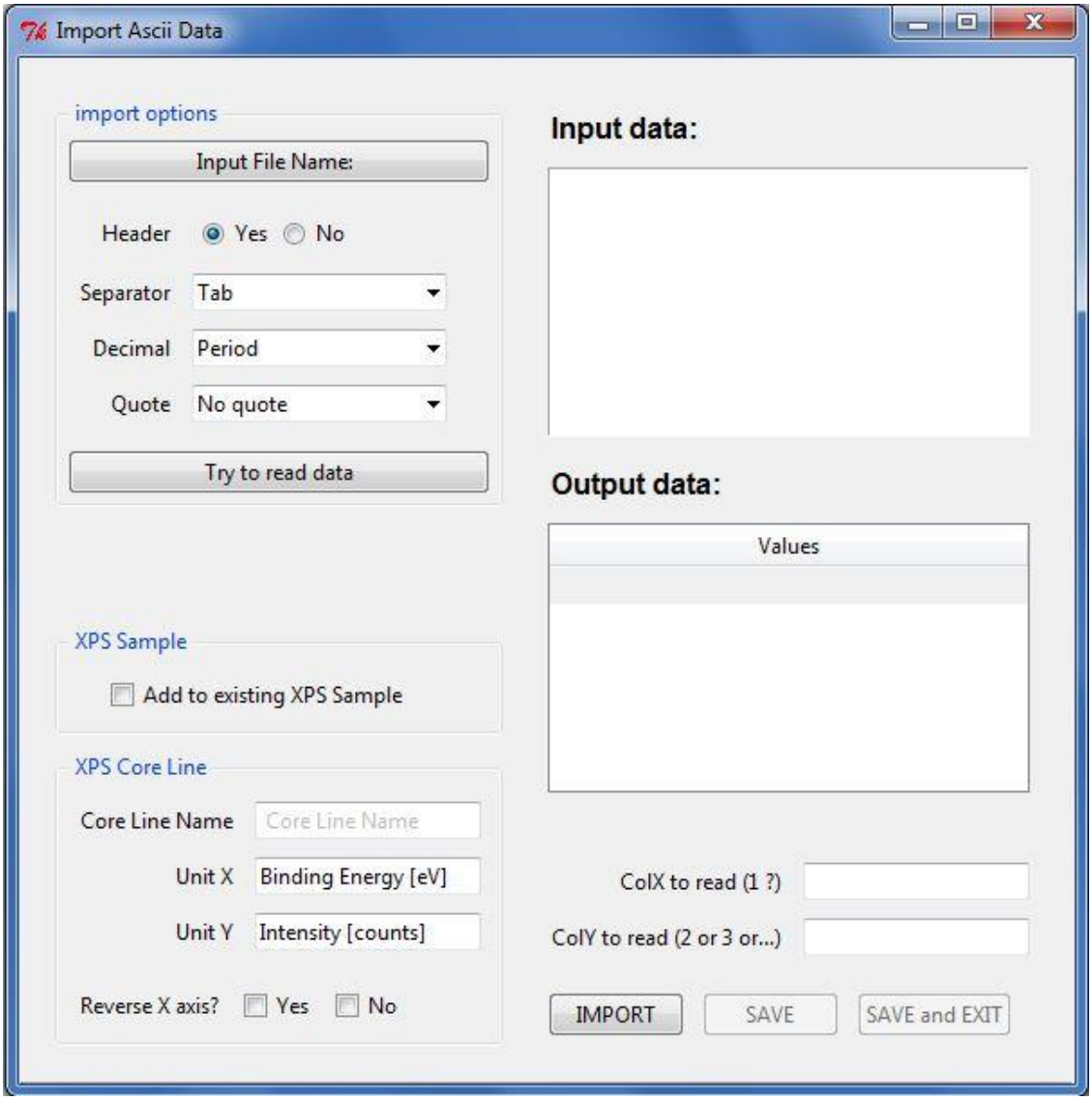
- ⇨ ***LOAD VMS, PXT DATA*:** load vamas and scienta .pxt datafile;
- ⇨ ***LOAD PXT+RPL DATA:*** load analyzed scienta .pxt files. This option reads analysis information which are contained in .rpl datafile. When the program opens the "*Select file*" window make sure that the RPL folder be present: the program will search for this folder to read the information regarding the analyzed spectra. Differently the program bloks.
- ⇨ ***LOAD ANALYZED DATA:*** load .RData or .RDS files containing spectra analyzed using the XPS ANALYSIS software.
- ⇨ ***SAVE ANALYZED DATA:*** save the analyzed data in the current working directory



- ***Change directory button*** to change the folder where to save the analyzed data;
- ***File Name Please*** the software give a default name which appears the window. You can change the name but the .RData extension should be maintained.
- ***Save Active XPS-Sample*** to save the current analyzed spectra;
- ***Save All XPS-samples*** to save all the analyzed XPS-samples (XPS data file loaded);

Group XPS-Samples and Save to group all the analyzed XPS-samples and save in just one file instead of separated files.

- ⇨ ***IMPORT ASCII:*** to load ascii (text) data files. This option will open the following window:



- ***Input File Name*** first the input ascii data file name is required to proceed with reading the ascii datafile. Once the name is given, a preview of the data is shown in the INPUT window

- Before reading data, the following format information are needed:
- ***Header:*** the ascii data file has an header?.
- ***Sparator:*** the kind of character used to separate data in the file TAB is the default;
- ***Decimal:*** the character used to separate the decimal digits from the integers. Period is the default;
- ***Quote:*** are the numbers written inside quotes (“xxx”, ‘xxx’)? No quote is the default.

- ***Try to read data*** button: On the basis of the format information given the program tries to read the ascii datafile. If information are correct, data will appear organized in columns in the OUTPUT window.
- ***Add to existing XPS sample*** you can add one or more columns to an existing XPS-sample loaded in the XPS-Analysis software;
- ***Core Line name:*** input the name of the column of data to be read. This name will be used by the software to identify these data;

- ***Unit X:*** units for the abscissa;
- ***Unit Y:*** units for the ordinate;
- ***Reverse X axis:*** the X axis has to be reverse (as for Binding energies) ?
- ***Col. X to read:*** which is the column describing the abscissas? (normally column number 1)
- ***Col. Y to read:*** which is the column of ordinates you want to read? (identify the second third forth… columns with 2, 3, 4);

- ***Import*** button: when ALL these data are given, press IMPORT to load the wanted columns of data. Data will be immediately displayed in them main graphic window.

Save button: to save read data in the software memory for further processing. Use this option if you wand to load more ascii data;

Save & Exit button: to save read data in the software memory for further processing and terminate the loading operation.

⇨ ***EXPORT ASCII:*** to export spectra and analyzed spectra in an ascii data file (data organized in a matrix columns)

Select CoreLine: select the coreline you want to export in ascii. Original spectrum and fit components (if present) will be exported. The datafile will be organized in columns as follow: orig. spectrum, baseline, fit comp. 1, fit comp. 2 ….., fit comp. N, envelop of the fit components (best fit);

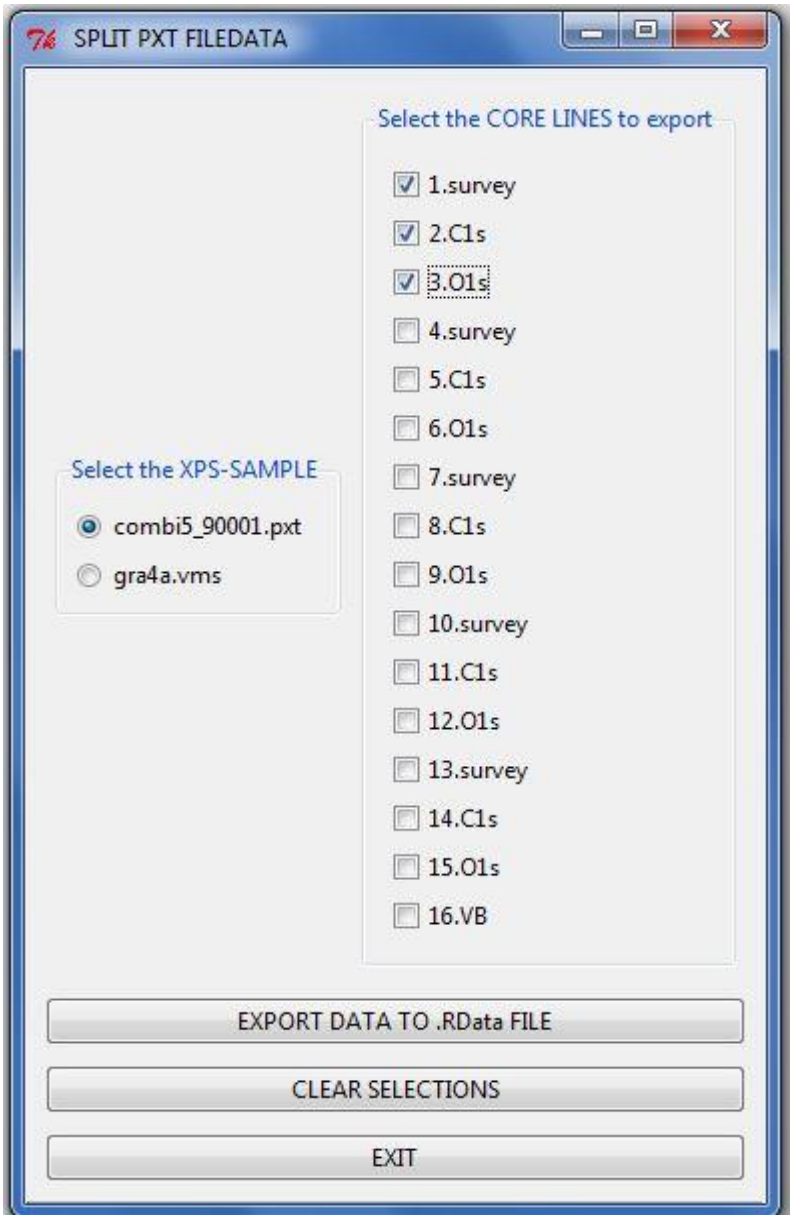
Select output format: here you select the kind of data separator and if Period or Comma will be used as separator for decimals;

Export Data button***:*** clicking the button a window interface will open where you can select directory where to save the data and filename;

Exit button***:*** to terminate the export operation.

⇨ ***SPLIT .PXT DATA:*** many times Scienta-PXT data files include spectra acquired on different samples. This option can be used to easily split such a data file in lists of spectra each one belonging to a given samples. Then one can save spectra in separated files.

First load the .PXT file to split then selecting this option a panel similar to the following will appear

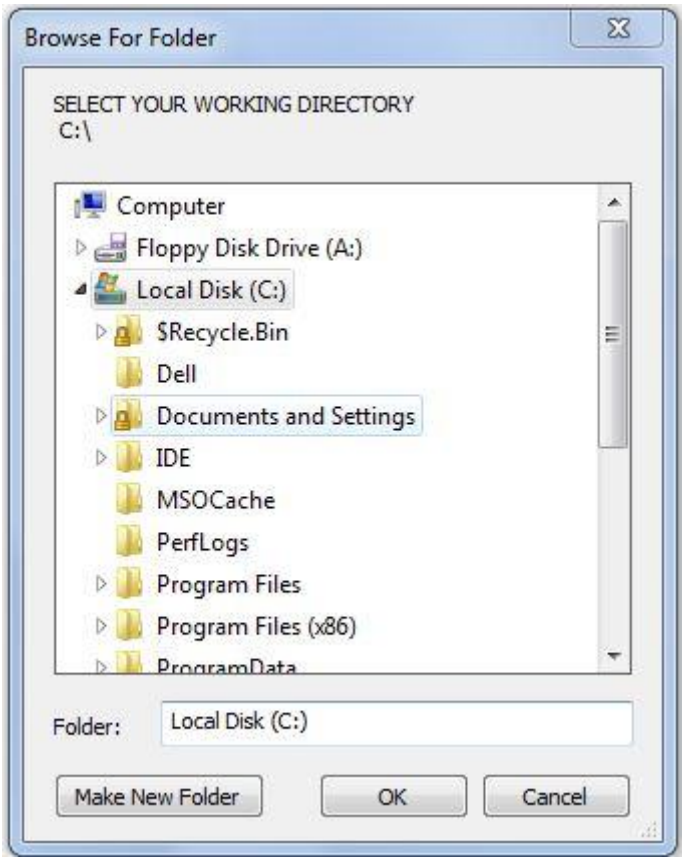


This example shows a typical Scienta datafile containing spectra from 5 different samples.

- ***Select the Data file to split:*** on the left side will appear the list loaded in the memory of the XPS-Analysis software. Select the one you want to split with the radio-button;
- ***Select the group of corelines to split:*** on the right side will appear the list of corelines belonging to the selected XPS datafile. A checkbox allows you to select the corelines you want to separate from the others. In the example the first three corelines are selected.
- ***Export data to .RData file*** button***:*** clicking this button you can save the selected corelines in a separated .RData file;
- ***Clear selection*** button***:*** clicking this button you reset the selection for a further data splitting;
- ***Exit*** button***:*** to terminate the splitting operation.

⇨ ***REMOVE CURRENT XPS-SAMPLE:*** you can remove the current XPS data from the list of loaded XPS-sample data (i.e. from the software memory);

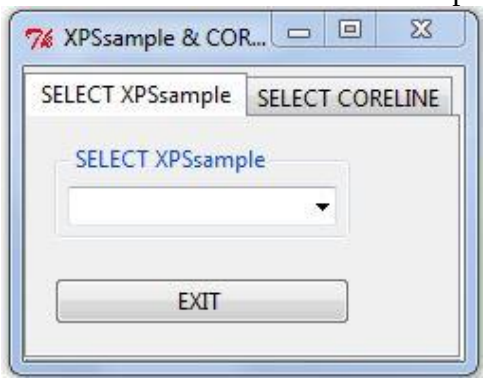
⇨ ***SET THE WORKING DIR:*** you can set the default working directory where you have the list of data-file to analyze;



An interactive window will appear and choice of the working-dir is done just clicking on the *LOCAL DISC C:* to select the proper folder.

***ANALYSIS menu*:**

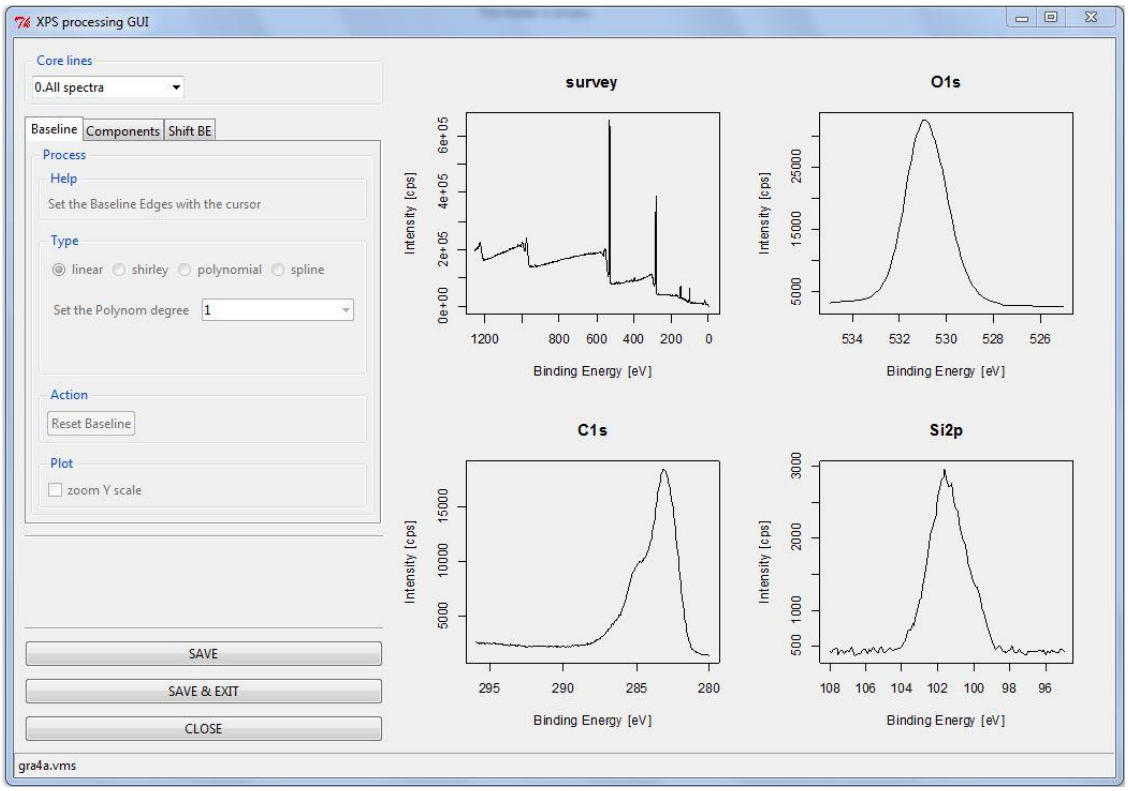
⇨ ***SPECTRUM SELECTION*:** option to select the actual XPS-sample/core line to analyze;



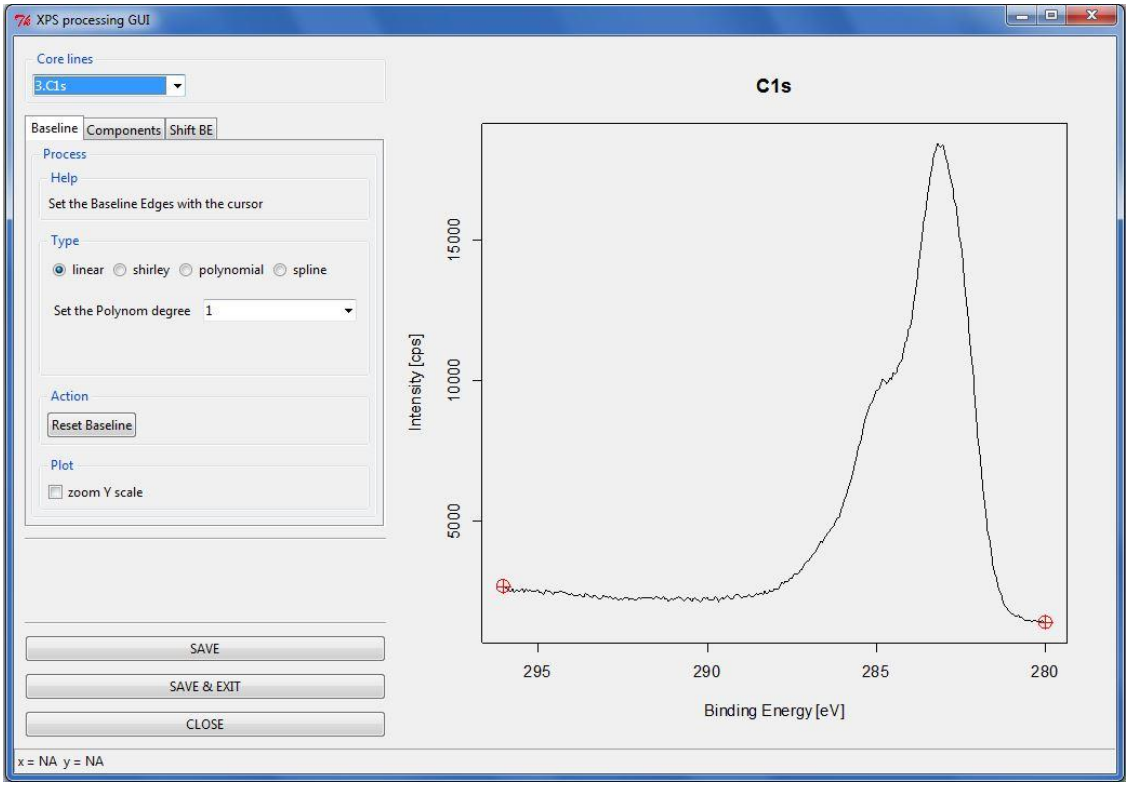
- ***Select XPS sample:*** to select the actual XPS Sample to analyze;
- ***Select Core line:*** to select the actual Core Line to analyze;
- ***Exit*** button***:*** to terminate the Spectrum Selection operation.

N.B. double clicking on the XPS-Sample name will activate a popup menu to select the active coreline

⇨ ***ANALYZE*:** option to perform peak fitting on a selected coreline. The *Analysis* option opens the following interactive window where all the spectra of the current XPS-sample are shown:

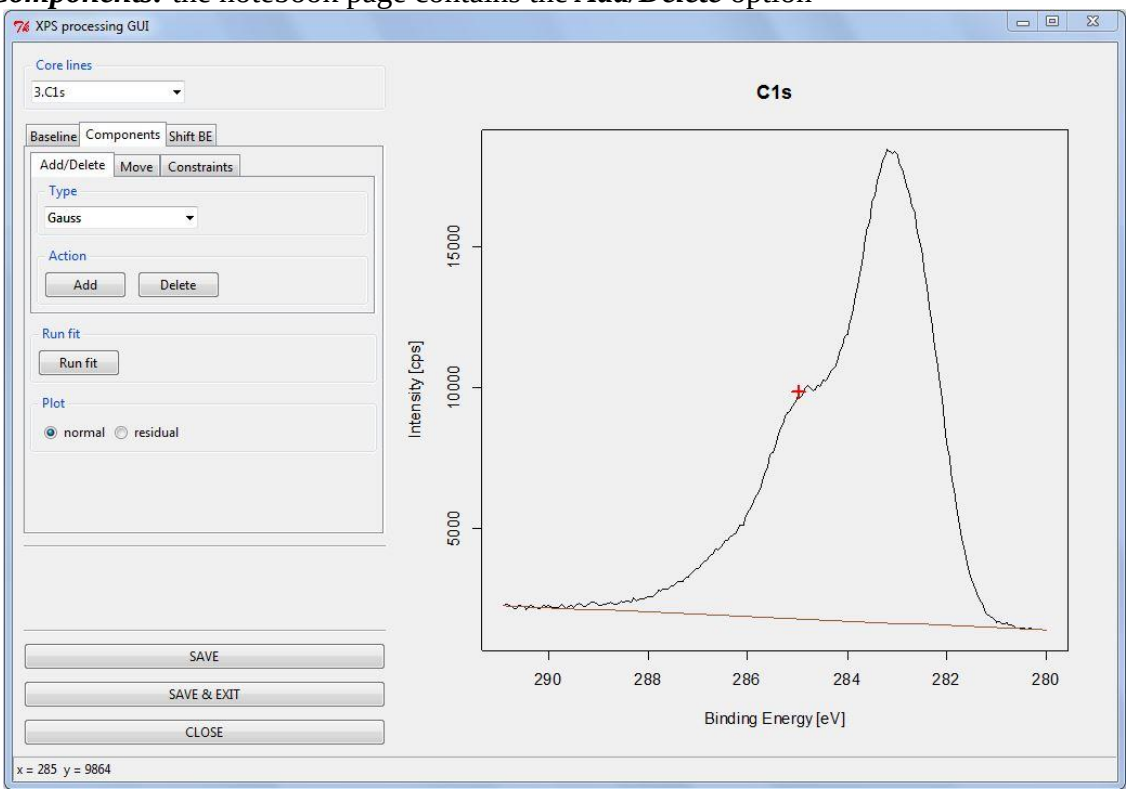


- ***Core Line (top left):*** to begin peak fitting a core line has to be selected. Only the selected core line (C1s in the example) will be then shown in the graphic window:



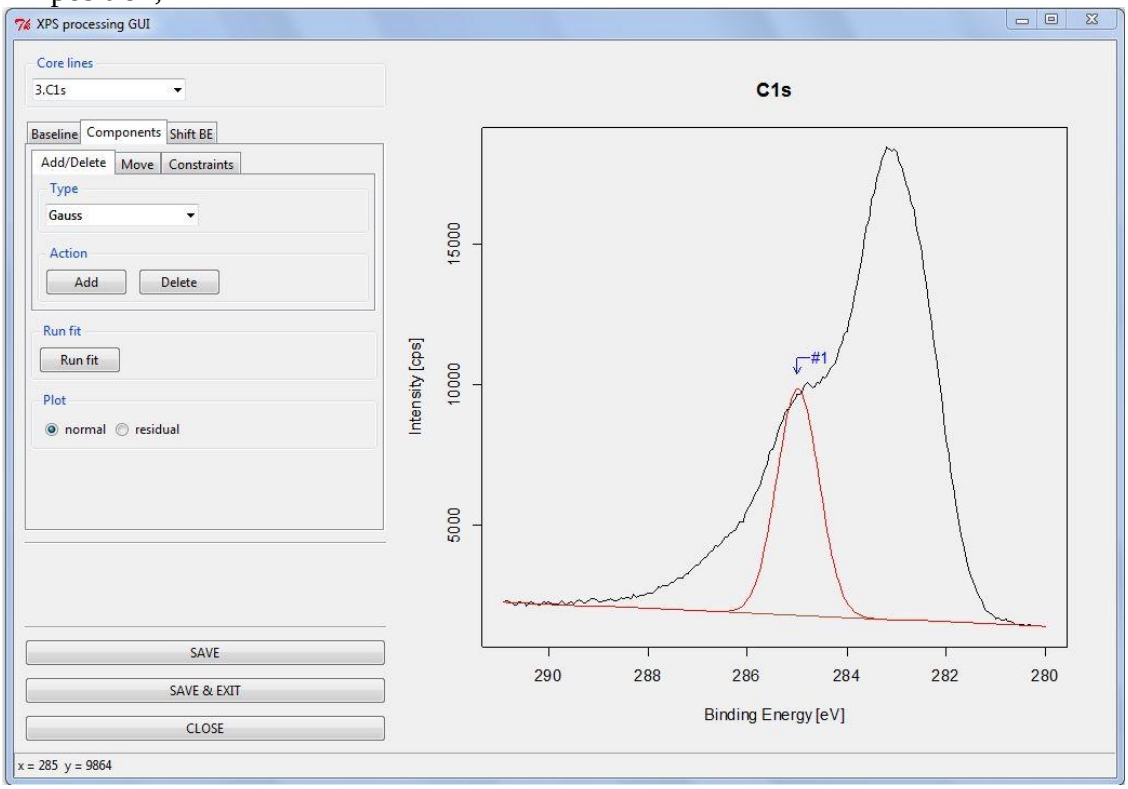
BaseLine: different kinds of baseline are available: Linear (default), Shirley, Polynomial, Spline. Select the desired baseline and define the edges of the fitting regions moving the red_cross cursor ⊗ at the ends of the spectrum. Immediately the baseline will be shown under the defined region-To-fit.

Components: the notebook page contains the ***Add/Delete*** option

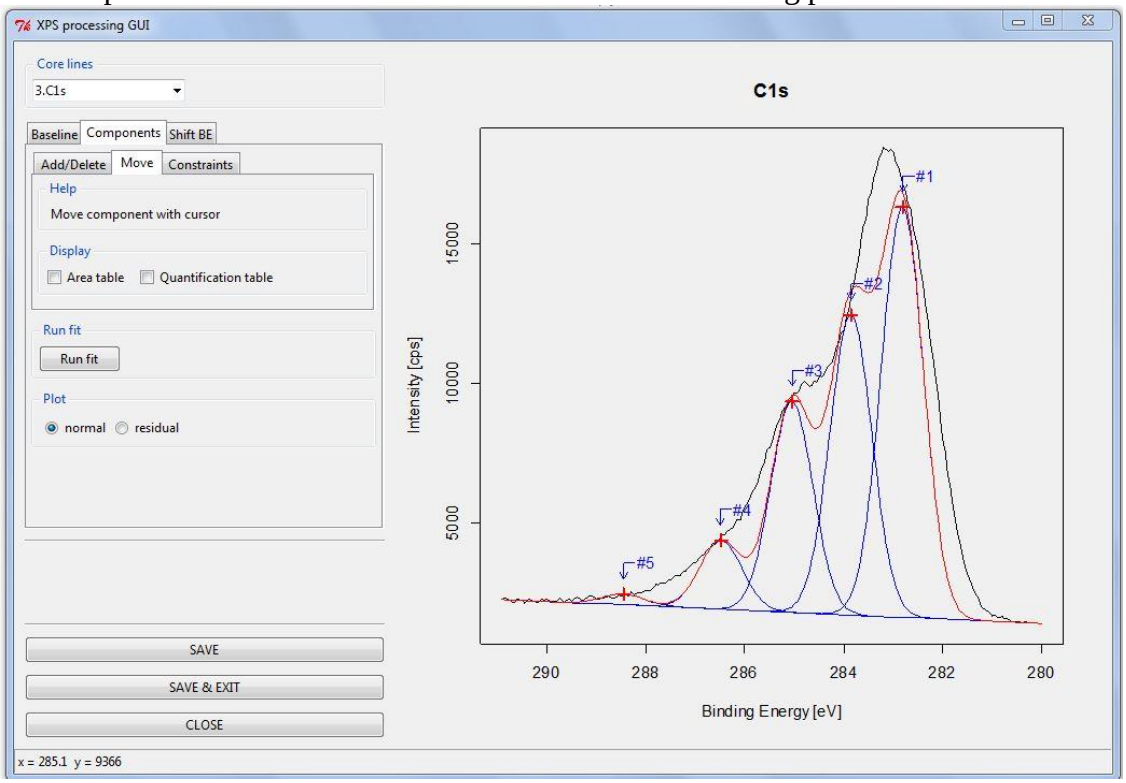


One the baseline is defined, fit components are added using the ***Component*** ➔ ***Add/Delete*** *page*

- ***Type:*** to select the function for the best fit procedure
- ***Component position:*** just click with the mouse on the desired position. A red cross will appear indicating position and intensity of the fitting component (see figure);
- ***Add:*** pressing this button the fitting function will be added to the spectrum in the chosen position;



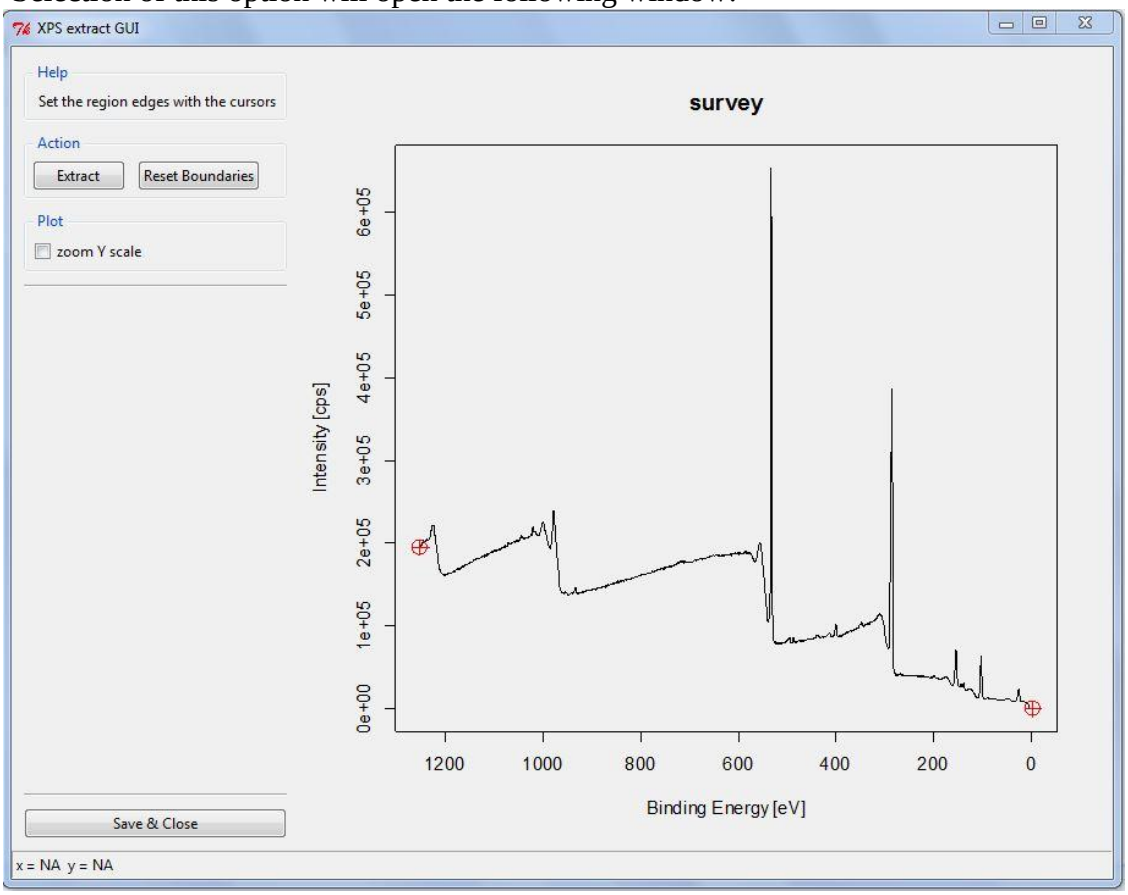
- ***Delete:*** pressing this button fitting components can be removed. Removing fitting components will cause the loss of constraints on the fitting parameters.



- Add as many fit component as required by the spectrum lineshape.
- ***Component*** ➔ ***Move*** *page:* it is possible to adjust component position just clicking near the red cross appearing on the top of each fit component. This will cause the component to shift in the new position identified by the mouse position.
- ***Run fit*** button***:*** starts the peak fitting procedure applying the Newton algorithm. <u>It is preferable to set fitting constraints and run the best fit using more appropriate options described below;</u>

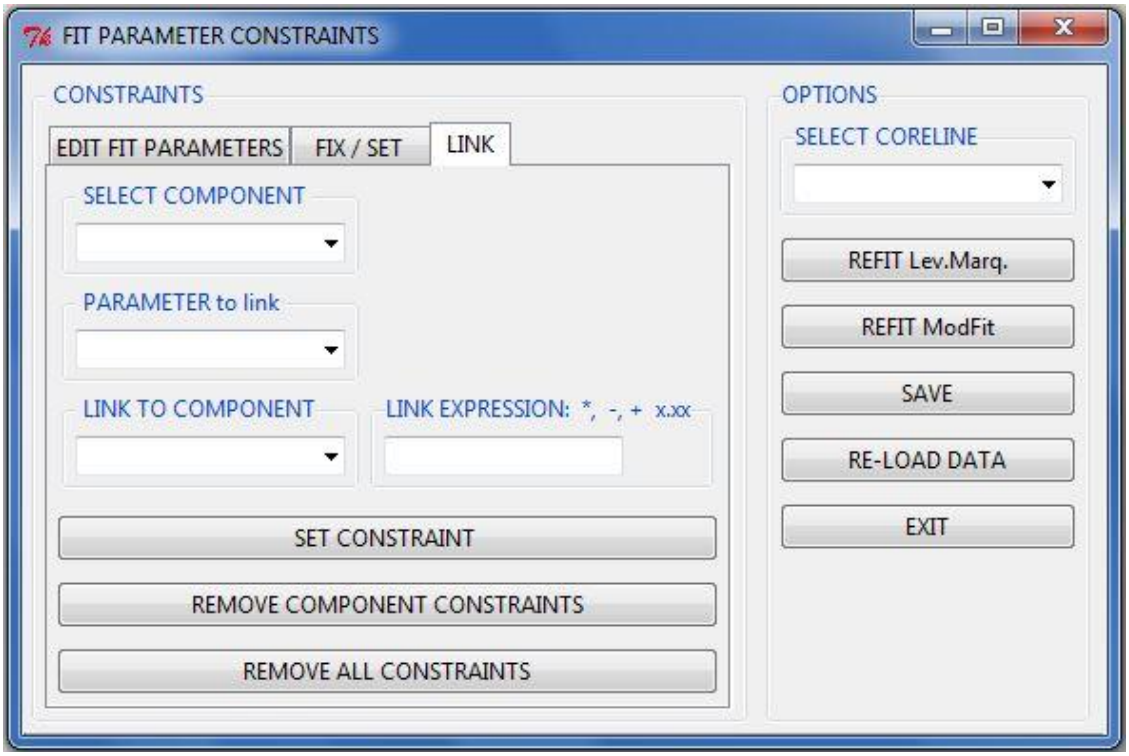
- ***Save*** button*:* to save the fitting start conditions and proceed with another coreline
- ***Save & Exit*** button*:* to save the fitting start conditions and exit the Analysis procedure
- ***Close*** button*:* to exit the Analysis procedure

⇨ ***EXTRACT FORM SURVEY*****:** option to extract spectral features not acquired separately. Selection of this option will open the following window:



- Click on the red-cross cursors ⊗ at the ends of the wide spectrum. Once you move the cursors, the graphic window will be updated upon new edge definition.
- Press the ***Extract*** button when the range fits with spectral feature you ant to extract from the wide spectrum;
- A window requiring the name of the spectral feature will be required;
- ***Reset Boundaries*** to reset ends and restart the range selection.
- ***Zoom Y-scale***: you can zoom the spectrum to increase the precision in identifying the feature when its intensity is very low, to better identify the region to extract;
- ***Save&Exit***: to add the new region in the current XPS-Sample, save and exit the extract operation;

⇨ ***FIT CONSTRAINTS*:** option to set constraints among the fitting components set for a given coreline. This option opens the following window:



The Constraints window is organized in a notebook composed by the three pages: *EditFitParameters, Fix/Set, Link* containing a set of options regarding the fit component parameters.

Link: this page is used to link a certain parameter of one component to that of another component:

- ***Select component:*** to select the fit component with the parameter you want to link;
- ***Parameter to link:*** to select the parameter to link;
- ***Link to Component:*** to link the previous parameter to that of this component;
- ***Link expression:*** here you can set the proportion between the two parameter
- ***Set Constraint:*** always press this button to set the actual constraint and proceed setting the next one;
- ***Remove component constraints:*** press this button to remove all the constraints for the selected fit component;
- ***Remove all constraints:*** reset the core line fitting conditions: all the constraints of each of the fitting components will be suppressed;

Example 1:

Link component = C5, parameter = *sigma*, Link to Component = C1, Link Expression = *0.5

Links the width *sigma* of component C5 to be 0.5* sigma of component C1

Example 2:

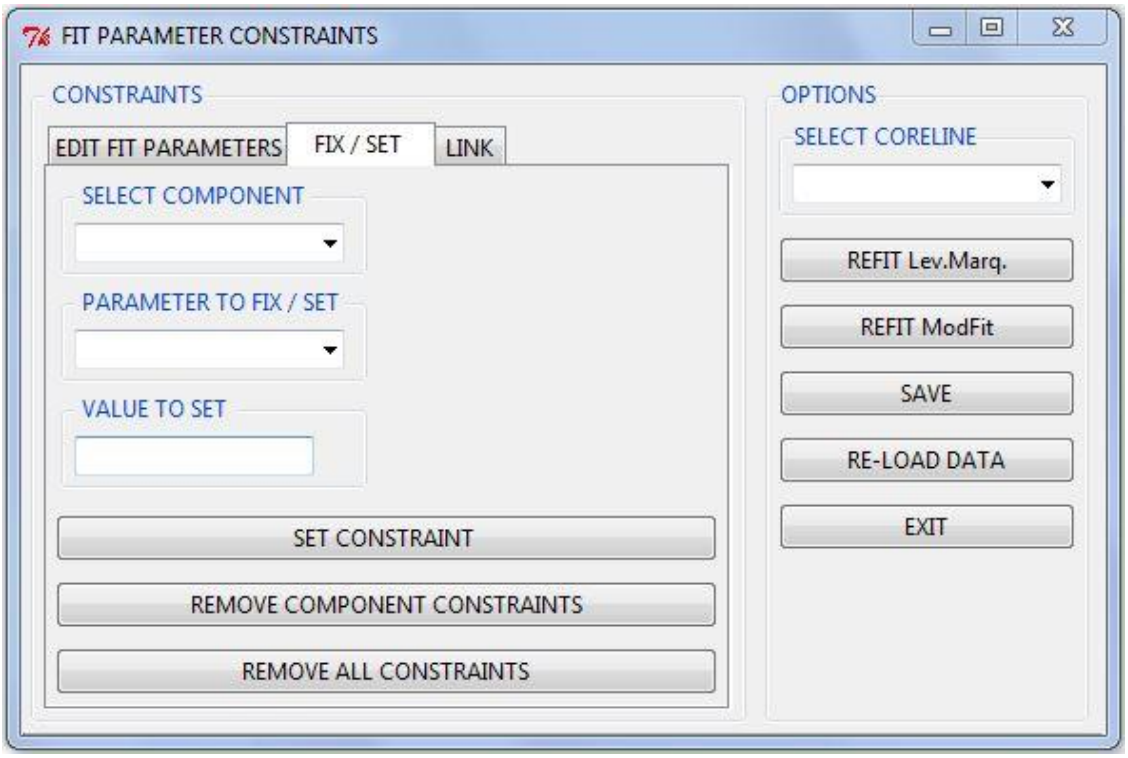
Link component = C5, parameter = *mu*, Link to Component = C1, Link Expression = +1.5

Links the position *mu* of component C5 to be 1.5 + position of component C1.

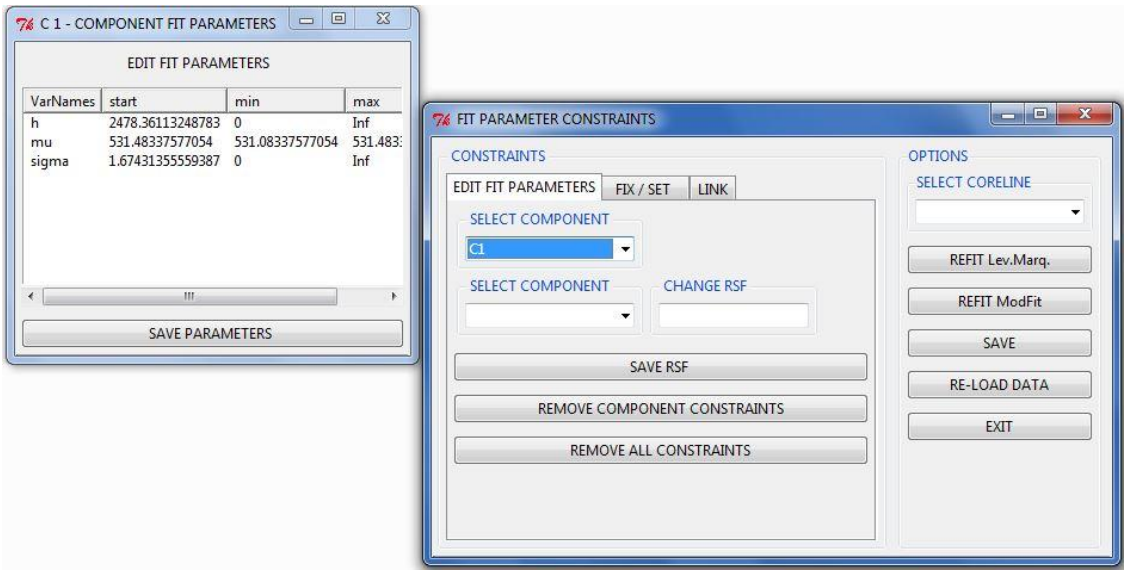
Fix Set: this page is used to fix or set the value of a certain fit parameter.

- ***Select component:*** to select the fit component with the parameter you want to link;
- ***Parameter to link:*** to select the parameter to Fix/Set;

- ***Value to Set:*** input the value for the selected parameter;
- ***Set Constraint:*** always press this button to set the actual constraint and proceed setting the next one;
- ***Remove component constraints:*** press this button to remove all the constraints for the selected fit component;
- ***Remove all constraints:*** reset the core line fitting conditions: all the constraints of each of the fitting components will be suppressed;



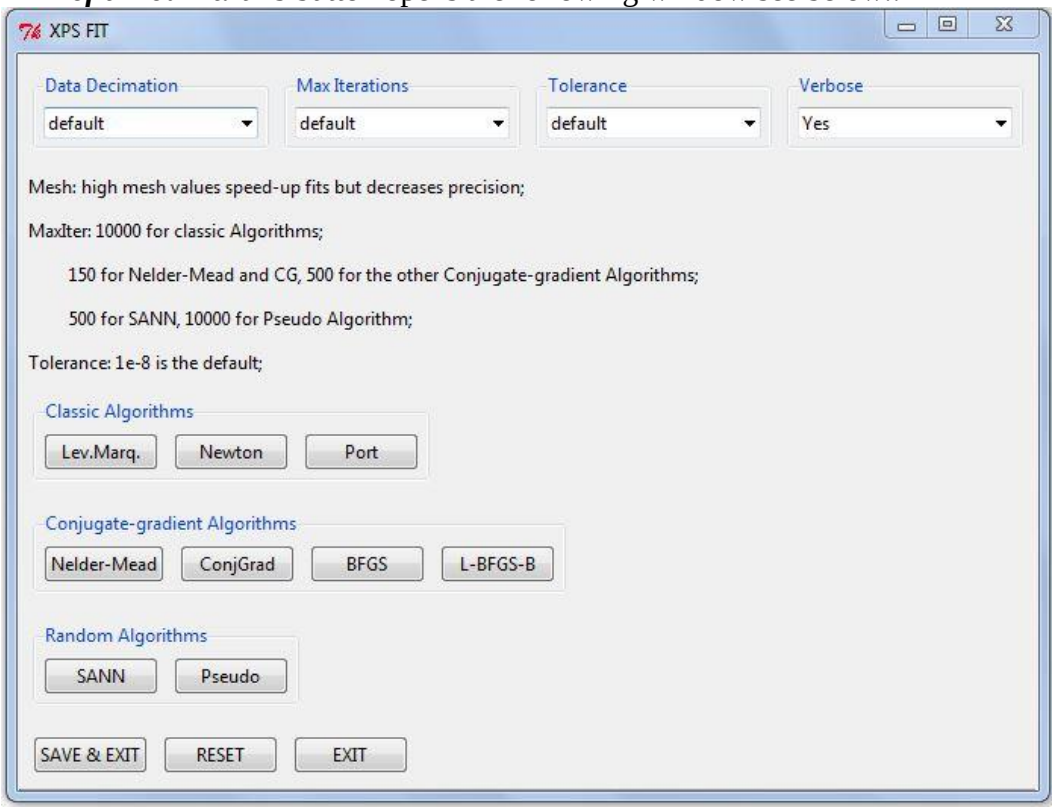
Edit Fit Parameters: this page is used edit the table of fitting parameter for each of the fitting components.



The component fit parameter window summarizes all the fitting parameters of the correspondent core line and it is editable. Just cliking on the desired parameter you can change the value or its limits. Press enter to input the parameter and, in case, change the next. Then pess the button *Save Parameters* to save the changes in the main memory of the software.

Common to all the three pages are the following options:

- ***Refit Lev.Marq.:*** pressing this button runs the fit using the Levenberg Marquardt algorithm;
- ***Refit ModFit:*** this button opens the following window see below.
- ***Save*** button***:*** the fit constraints MUST be saved before running the best fit algorithms;
- ***Reload*** *button:* loads the actual coreline and fit information from main memory. This allows the use of other routines such as move component to optimize fits and bond_stoichiometries;
- ***Refit ModFit:*** this button opens the following window see below.:



It could happen there are local minima preventing the convergence of the Levenber-Marquardt algorithm. In this case it is possible to refit the same feature using the *ModFit* interface which is more robust. The *ModFit* interface allows using also other fitting algorithms as shown in the window.
N.B. Depending on the algorithm chosen and on the number of data to be fitted it could be reasonable to *decimate* the set of data. Select the decimation level (for ex. 3 means 1 data over three), the number of iteration and the tolerance. (indications are shown in the window).

=> *Classic algorithms:* Levenberg-Marquardt which is handled in more robust way (although slower), Newton and Port are based on the minimization of the Squares of the Differences. In this case *Decimation=NO, MaxIteration=10000, Tolerance=1e-8.*

=> *Conjugate-Gradient Algorithms:* General-purpose optimization based on Nelder–Mead, quasi-Newton and conjugate-gradient algorithms. In this case *Decimation=Yes* in case of consistent number of data to fit, *MaxIteration=150 - 500, Tolerance=1e-8.*

Method Nelder and Mead (1965), that uses only function values and is robust but relatively slow. It will work reasonably well for non-differentiable functions.

Method "BFGS" is a quasi-Newton method (also known as a variable metric algorithm by Broyden, et al. 1970) uses function values and gradients to build up a picture of the surface to be optimized.

Method "L-BFGS-B" is that of Byrd *et. al.* (1995) which allows *box constraints*, that is each variable can be given a lower and/or upper bound. The initial value must satisfy the constraints. This uses a limited-memory modification of the BFGS quasi-Newton method. If non-trivial bounds are supplied, this method will be selected, with a warning.

=> *Pseudo Algorithms:* random based algorithm, VERY slow but convergence is assured. *Decimation=Yes* in case of consistent number of data to fit, *MaxIteration=500(Sann) 10000(Pseudo), Tolerance=1e-8.*

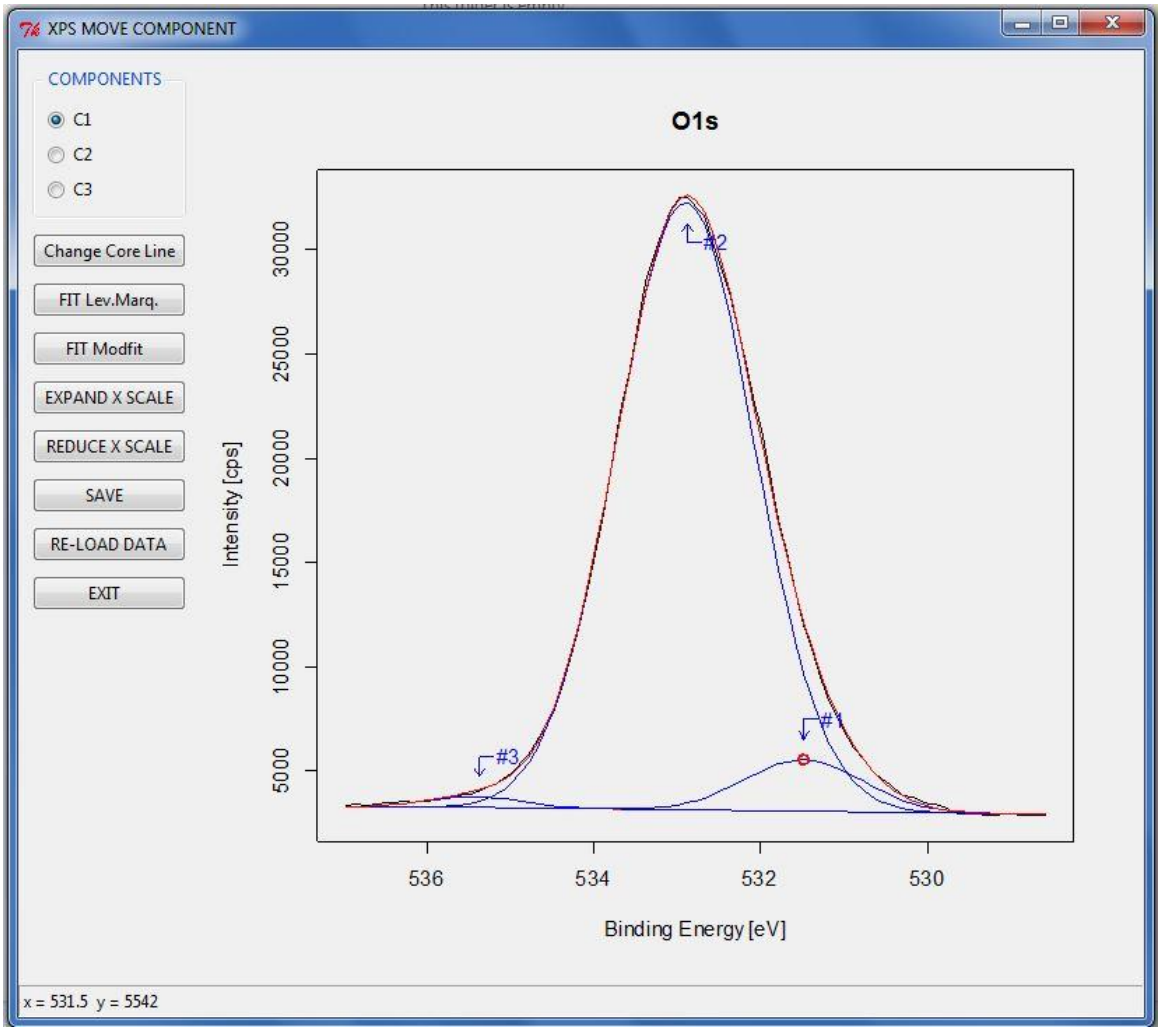
Method "SANN" by Belisle (1992). Simulated-annealing belongs to the class of stochastic global optimization methods. It uses only function values but is relatively slow. It will also work for non-differentiable functions. This implementation uses the Metropolis function for the acceptance probability.

Method “Pseudo” fits a model to data, using the pseudo-random search algorithm of Price (1977), a random-based fitting technique.

⇨ ***FIT LEV.MARQ.*:** option to run the Levenberg Marquardt algorithm to fit spectral data. See the *Analysis* option for more details.

⇨ ***FIT MODFIT*:** option to run the ModelFit interface to fit spectral data. See the Constraints option for mode details;

⇨ ***MOVE COMPONENTS:*** this option enables the possibility to adjust the position and the intensity of each fit component. It opens the following window:



The window is divided in two parts: an interactive graphic window on the right and a series of buttons on the left side.

- ***Select Component:*** radio buttons enable the choice of the fit component one want to change.
- ***Mouse pointer:*** just going with the mouse on the graphic window the mouse pointer changes from the classical mouse arrow to cross +. The cross indicate the new position for the selected component which is identified by the red circle in the graphic window. Clicking with the + pointer will make the red circle to be placed in the new position and the correspondent component to be redrawn.

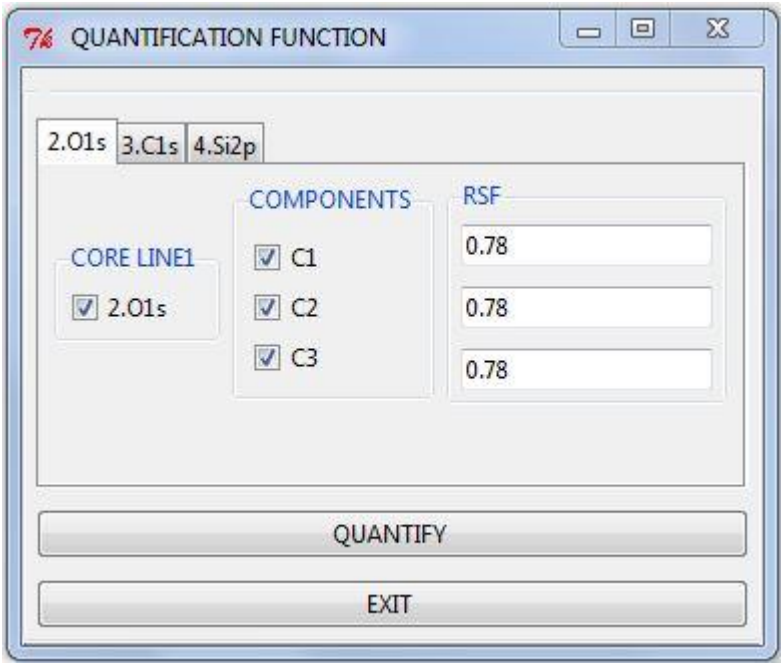
N.B. any time a component is changed, a quantification table will appear in the R console. In this way one can control/adjust the stoichiometry among the fit components.

Once the stoichiometry is OK, press the *Save button* to save changes in the main memory of the software.

- ***Change core line:*** to select another coreline to adjust fitting components;
- ***Fit Lev. Marq.:*** avter moving components, it is possible to run the Levenberg Marquardt algorithm to refit the coreline starting from the new component position;

- ***Fit ModFit:*** after moving components, it is possible to run the ModelFit interface to refit the coreline starting from the new component position;
- ***Expand X scale***: it is possible to expand the abscissa scale to increase the precision when moving the components. For high zooms press this button more times.
- ***Reduce X scale***: to go back in the original situation;
- ***Save***: to save changes in the software main memory;
- ***ReLoad Data***: the *Move Component* can be utilized in parallel with the *Constraints* option. Let us consider the case when the fit performed after moving components is not satisfactory. For example fit convergence brings the components in unwanted positions (no chemical meaning for those binding energies). One solution is to move components in a meaningful position to adjust stoichiometry and then change the fit constraints to obtain a good fit. To do this (1) move components in the desired position and (2) press S*ave* button to save the changes; (3) go in the *Constraints* option, and (4) *reload* data to import the changes made in the *Move Component* into the *Constraints* procedure. (5) set the new constraints accordingly to the changes made and (6) *Save* changes in the main memory. (7) *Re-Load Data* in the *Move Components* procedure to import the new constraints and (8) re-run the fit and check results. If results are not satisfactory you can repeat steps (1) – (8) until optimization.
- ***Exit** button:* to exit the Move Component procedure.

⇨ ***QUANTIFY:*** this option is used to perform elemental quantification. The quantification needs the baseline under a given spectrum to be defined for the estimation of the peak spectral intensity (which is proportional to the concentration of the correspondent element). If peak fitting is performed, the quantification is calculated considering the spectral intensity of all the fit components. The quantification option enables the following window:



- A notebook pages are created for each of the corelines. In each page it is possible to set/unset the checkbox to include/exclude the correspondent element from the elemental quantification.

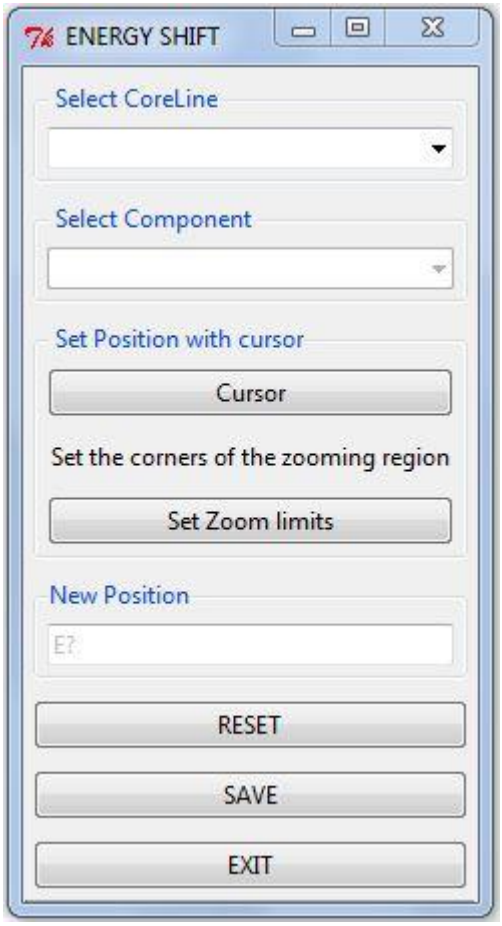
- If fit is performed, it is possible to set/unset each of the fit components to include/exclude it from the elemental quantification.
- The RSF of the element or each component is editable and can be changed ;

- The default is each element with defined baseline/fit is included in the quantification, each of the fit component are included, the Sensitivity Factor is that provided by the manufacturer of the XPS instrument utilized (Kratos/Scienta).

- ***Quantify** button***:** runs the quantification procedure and quantification table shown in the Rstudio console;

- ***Exit** button:* to exit the quantification procedure.

⇨ ***ENERGY SHIFT:*** this option is used to perform a binding energy shift on all the XPS-Sample spectra. When XPS spectra are acquired on insulating samples charge compensation is needed. Charge compensation causes a shift of the energy scale. It is possible to recover this shift using the *Energy Shift* option which enables the following window:



- ***Select core line:*** to recover the binding energy shift caused by the compensation, a spectral reference falling in a well known position is needed. Generally this reference is the carbon C1s from hydrocarbon contaminants CH_x at 285eV. CH_x is a rather frequent contamination and then could be a convenient reference. Also gold 4F at 84eV is frequently used as a reference.

- ***Select Component:*** if a fit was performed on the reference core line, here it is possible to select the component assigned to a known chemical bond and energy position. For example the hydrocarbon contaminations contain also oxidized components. Here you hace to select the C1s component which has to be assigned to CH_x.
- ***Set position with cursor:*** this option has to be used when peak fitting is absent. Press the *Cursor* button and click on the position of the spectral feature having known position (the C1s maximum for hydrocarbon contamination, the Au 4f 7/2 maximum for gold ecc.). A red marker will appear on the spectral feature and the correspondent energy position will be displayed in the panel.
- ***Set Zoom Limits:*** spectral zoom is possible to have higher precision in determining the position of the reference spectral feature. This is useful for example when working on wide spectra (survey). Press the *Set Zoom Limits* button and then clicking with the cursor on the spectrum to identify the opposite corner of the area to be zoomed.
- ***New position:*** you can edit the energy position and give the correct one (i.e. 285eV for CH_x, 84eV for Au 4f 7/2…)
- ***Reset:*** press this button to unzoom.
- ***Save:*** when a correct position for the reference spectral feature is given, press *Save* button to save the energy shift in the software main memory.
- ***Exit:*** to exit the energy shift procedure.

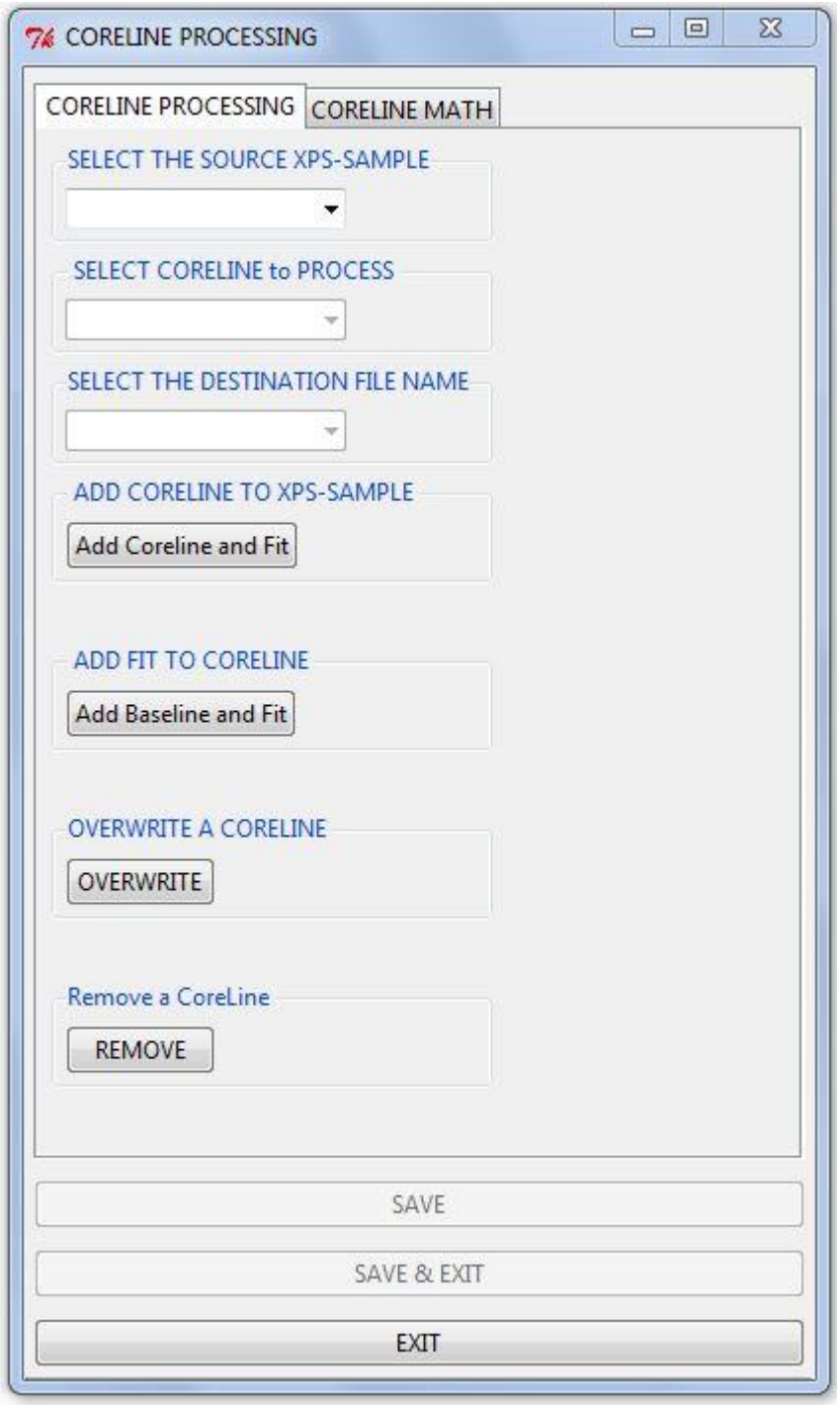
⇨ ***PROCESS CORE LINE:*** this option is used to apply a set of operations on core lines. In the first notebook page the operations include: add a coreline to the current XPS-Spectrum, copy baseline and fit performed previously on another XPS-Sample to the current coreline, overwrite the current coreline, delete a coreline.
In the second notebook page simple math operationcan be applied to the XPS-Sample spectra.
The *Process Coreline* procedure activate the window shown below.

N.B. before processing the core line control if energy shift is needed and possibly perform energy scale calibration!

❖ ***Core Line processing:*** this page offers some options to simplify coreline analysis. In all the cases of repetitive analysis on similar XPS-Sample the *Process Core Line* GUI allows copying a fit on a virgin Coreline.

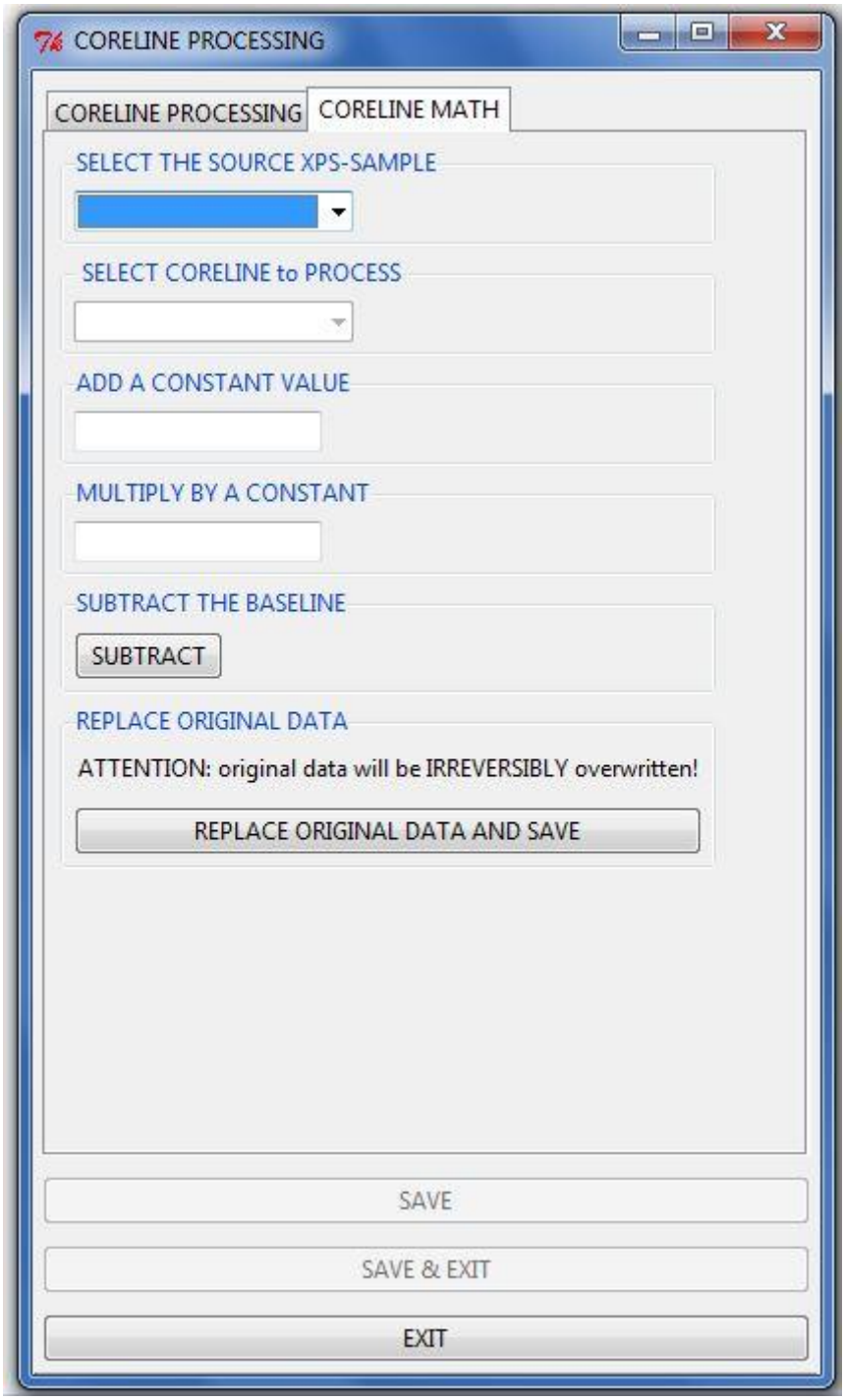
- ***Select the Source FileName:*** select the file name of the source XPS-Sample in the drop down list of XPS-Sample names loaded in the software.
- ***Select the Core Line to process:*** select the coreline which you want to process;

Select the operation you want to apply:
- ***Add Core Line and Fit:*** add the selected coreline from the source XPS-Sample and fit (if present) to the current XPS-Sample;
- ***Add Fit to Core Line:*** fit information are loaded from the source XPS-Sample and copied in the current core-line. This option allows replicating fits when dealing with similar corelines. The fits can be modified using Move Components option and refit.
- ***Overwrite a Coreline:*** overwrites the existent coreline with that coming from the source XPS-Sample.
- ***Remove a Coreline:*** this button removes the selected coreline from the actual XPS-Sample



- ***Save:*** this button saves the new data in the software memory. After pressing this button you can select another coreline to process without exiting the procedure.
- ***Save & Exit:*** to save changes and conclude the *Process Coreline* procedure.
- ***Exit:*** this button to quit the *Process Coreline* procedure without saving any change.

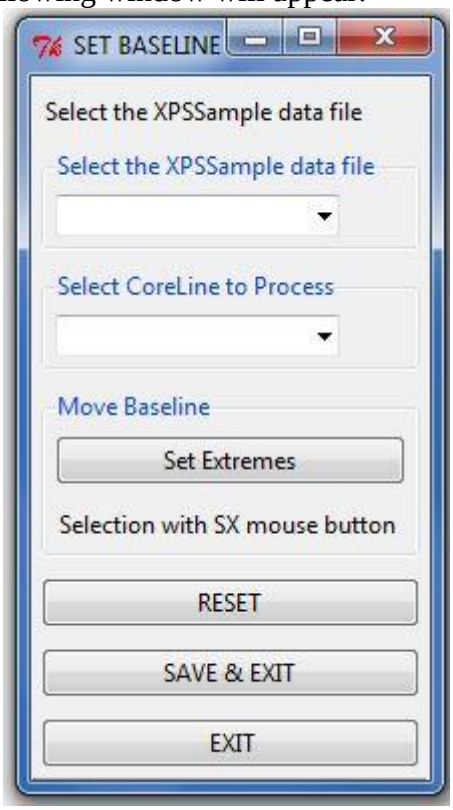
❖ ***Core Line Math:*** simple math operation may be applied to the Core Line.



- ***Select the Source FileName:*** select the file name of the source XPS-Sample in the drop down list of XPS-Sample names loaded in the software.
- ***Select the Core Line to process:*** select the coreline which you want to process;
- ***Add a Constant Value:*** the Core Line may be shifted Up/Down adding a positive/negative constant value;
- ***Multiply by a Constant:*** the Core Line may be amplified/decrease the spectgrum intensity;
- ***Subtract Baseline:*** the baseline will be subtracted from the spectum;
- ***Replace original Data And Save***: original data will be changed coherently with operations described above. ATTENTION: this operation is irreversible. This kind of saving will affect the plot routines such as *Overlay* and *Custom Plot* when simple spectrum are plotted (no baseline, no fit).

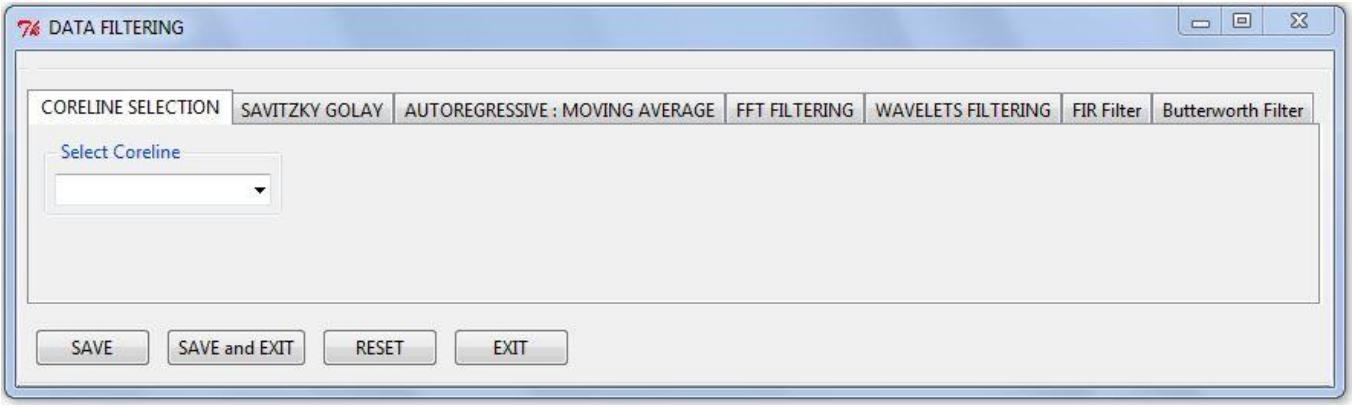
- ***Save** button:* results of the math operations above described will be saved. This kind of saving will not affect original data. *Overlay* and *Custom plot* routines will show processed data only when baseline or fit will be included in the plotting.
- ***Save and Exit:*** the same as *Save* and exit from *Coreline processing* routine.

⇨ ***MOVE BASELINE:*** this option is used IN COMBINATION WITH THE *Process Coreline* option when fit information are loaded from a source XPS-Sample and overlapped to the current coreline. It might be that the background level of the source and the actual corelines does not correspond exactly. This option allows to change the baseline on the background level. Selecting this option the following window will appear:



- ***Select the XPS-Sample:*** in the drop down list select the XPS-Sample containing the coreline to process;
- ***Select the CoreLine to process:*** in the drop down list select the the coreline containing the baseline to optimize;
- ***Move Baseline:*** pressing the button *Set Baseline Ends* you can set the new baseline ends. This allows you to redefine the region where perform peak fitting and the baseline level in agreement with the background;
- ***Reset:*** this button will reset the changes made on the baseline;
- ***Save & Exit:*** to save changes in the software main memory end exit the *Move Baseline* procedure;
- ***Exit:*** to exit the *Move Baseline* procedure without saving.

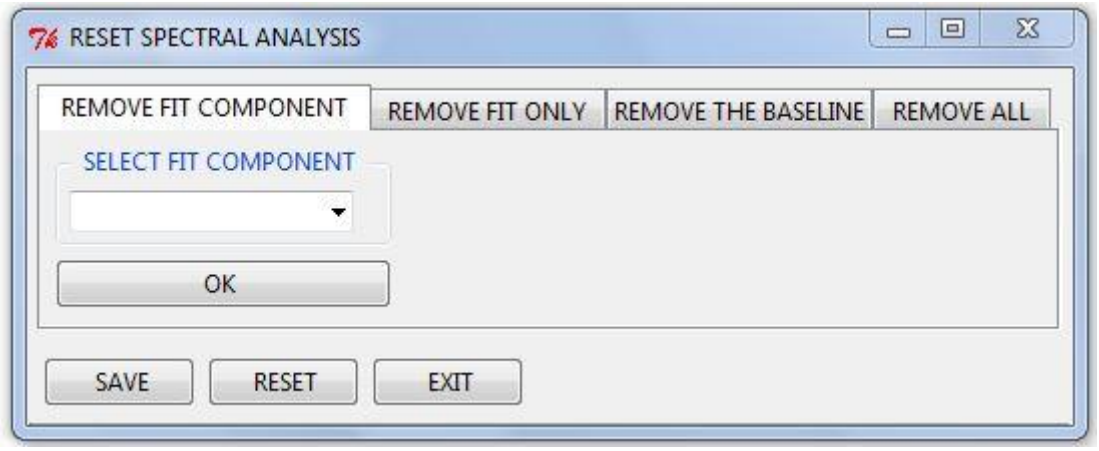
⇨ ***SMOOTHING:*** this option is used to remove Gaussian noise from the spectra. There are a set of different filters which can be applied to remove noise as shown by the *Smoothing* window:



Select the desided filter and the filter parameters, press filter to smooth the spectrum. For any kind of filter it is possible to change the filter parameters and re-filter the spectrum as many times as desired.

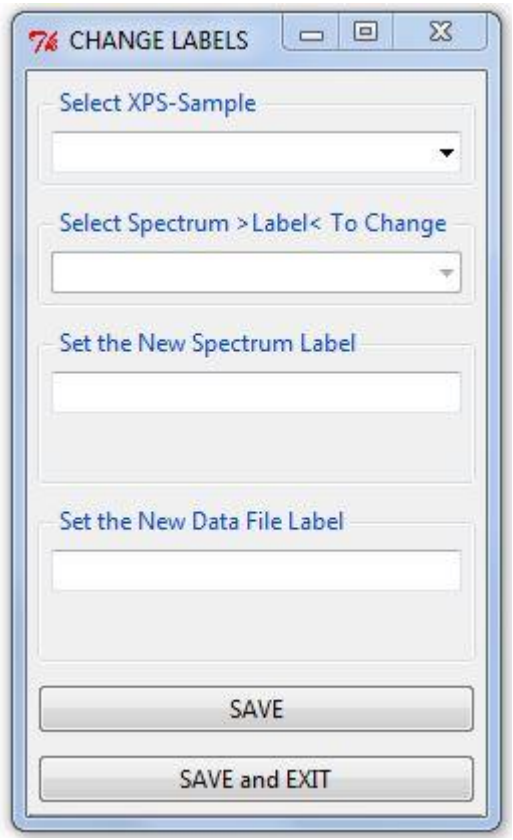
- ***CoreLine Selection:*** here the coreline to smooth is selected;
- ***Sawitzky Golay:*** is one of the most popular filters used to perform smoothing. Select the degree of the filter: the higher the degree the higher the noise rejection. Make sure that you afe not removing also spectral information when removing noise.
  - ***Filter:*** this button activate the filtering, the results is overlapped to the original data.
  - ***Background:*** if *BKG substraction* is cecked the filtering routine is applied subtracting the background. This could generate more precise filtering.
- ***Autoregressive : MovingAverage:*** The *Autoregressive* model specifies that the output variable depends linearly on its own previous values. The *Moving Average* output at point i is the average of data i-n … i … i+n . The higher the filter degree the higeer the rejection of the noise for both the filters. *Filter button* and *BKG substraction* work as described above
- ***FFT filtering:*** apply the FFT transform to perform filtering. Again the higher the filter degree the higher the noise rejection. *Filter button* and *BKG substraction* work as described above.
- ***Wavelets Filtering:*** uses the wavelets to perform filtering. Here the number of wavelets has to be chosen (more wavelets should correspond to higher degree of information rejection). The default is 5. Select the noise rejection level and press *Filter* button***;***
- ***FIR Filter:*** *the Finite Impulse Response* it is a zero distortion filter. The number of coefficient is generally rather high (default =20) to reject only the noise and maintaining the information. Generally higher the number of coeff. higher the filter precision. Select the noise rejection level and press *Filter* button***;***
- ***Butterworth filter:*** it is an *Infinite Impulse Response* filter. Generally these filters leads to high degree of noise rejection with a rather low number off coeff. (the default is 4). Differently from the FIR, the *Butterworth* filters can introduce signal distortions. Select the noise rejection level and press *Filter* button***;***
- ***Save:*** to save the smoothed coreline in the software main memory. Now it is possible to select another coreline and proceed with another smoothing.
- ***Save&Exit:*** to save the smoothed coreline in the software main memory and exit the routine;
- ***Reset:*** to reset the smoothing;
- ***Exit:*** to exit the procedure without saving.

⇨ ***RESET ANALYSIS:*** this option allows to reset partially or totally the results of a coreline analysis. This option activate the following window:



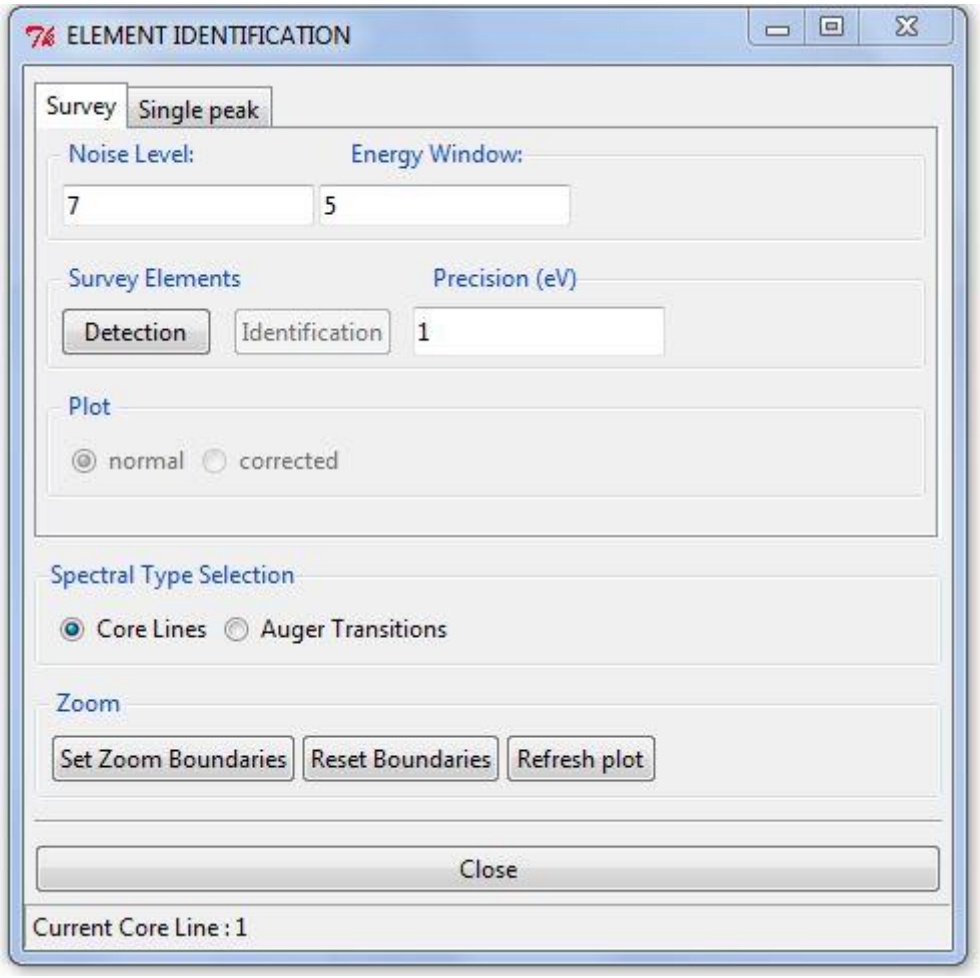
- ***Remove fit component:*** it is possible to remove the a single fit component among the other of the coreline peak fitting. Doing this operation causes the loss of the fit constraints;
- ***Remove fit only:*** removes the best fit only;
- ***Remove the baseline:*** this causes the region to fit to be reset. Elimination of the baseline causes the whole fit to be deleted.
- ***Remove all:*** reset completely the fit and baseline data.
- ***Save:*** this button saves the changes in the program main memory;
- ***Reset:*** undo the changes done;
- ***Exit:*** exit the *Reset Analysis* procedure without saving changes.

⇨ ***CHANGE SPECTRUM LABEL:*** sometimes it happens that the name given to one (or more) of the corelines is inappropriate. This option allows changing the coreline name.



- ***Select the XPS-Sample:*** slect the XPS-Sample using the drop-down list. After selection the XPS-Sample name will appear in the bottom-text-box;
- ***Select the Spectrum Label to change:*** for the selected XPS-Sample the list of CoreLines is give in this drop-down list. Names are written between >…< symbols (for example >survey< to correctly identify all the characters of the coreline name)
- ***Set the new Spectrum label:*** write in this text-box the new coreline name;
- ***Set the new XPS-Sample Name:*** in this text-box appears the selected XPS-Sample name. You can give a new name if desired (make a copy of an existing analysis: this option changes the XPS-Sample-Name info inside the Rdata file).
- ***Save&Exit:*** to save the smoothed coreline in the software main memory and exit the routine;
- ***Exit:*** to exit the procedure without saving.

⇨ ***ELEMENT IDENTIFICATION:*** in wide spectra (survey) it is possible to perform an automatic identification of peaks.

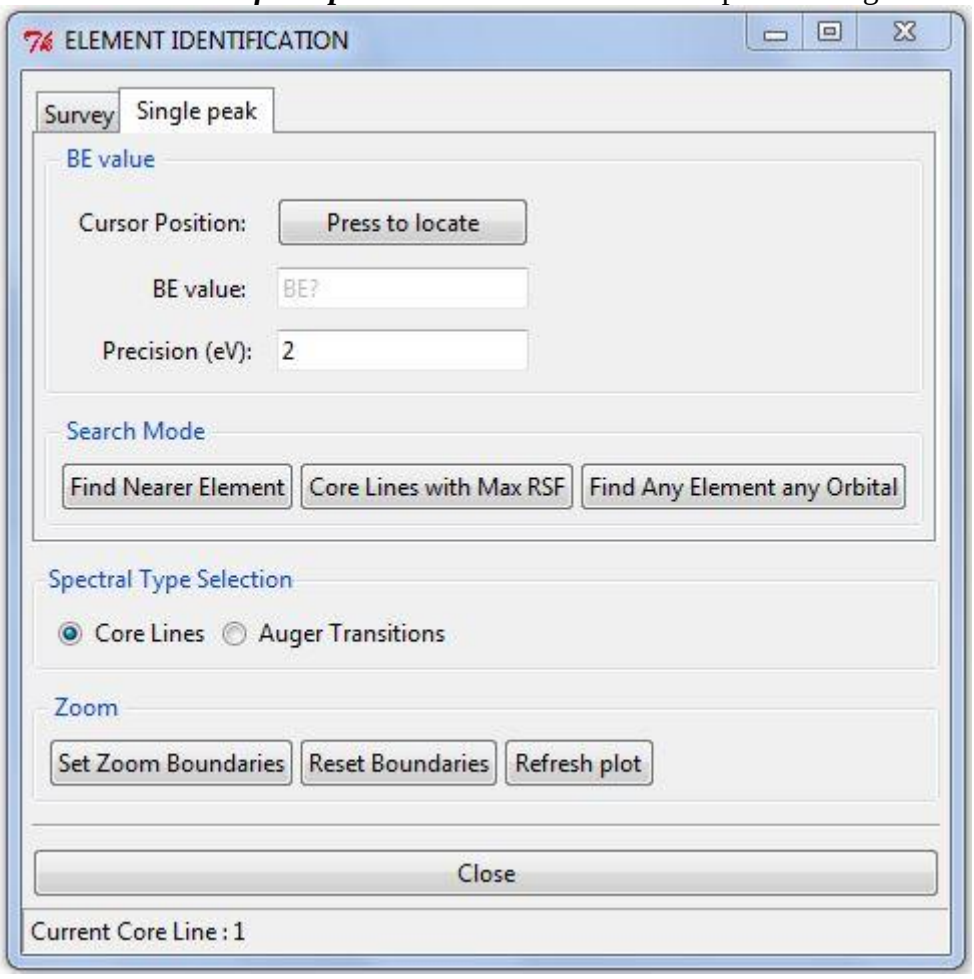


❖ ***Survey*** *page*:

- ***Noise level:*** the default is 7 but it is possible to increase the noise level in case of high spectral noise.
- ***Eenergy range:*** 5eV is the default. The energy window is used to increase/decrease the data smoothing for the identification of peaks. The smaller the energy window, the higher the precision the smoothed signal follows the original data.

- ***Detection:*** activate the detection of peaks. A green marker shows all the identified peaks;
- ***Identification:*** runs the identification routine. The elements falling within the energy window around an identified peak will be written on the spectrum and on the consolle;
- ***Precision:*** the interval (in eV) centered around the identified peak, where to look for elements.
- ***Spectral Type selection:*** it is possible to identify core lines or Auger features (which sometimes are rather sharp!).

- ***Zoom:*** it is possible to perform a zoom:
  - ***Set Zoom Boundaries:*** to set the corners of the zooming area;
  - ***Reset Boundaries:*** to reset the boundaries
  - ***Refresh plot:*** to clean detection and re-plot the original data.



❖ ***Single peak*** *page:* it is possible that the number of survey peaks which are automatically identified is rather long. For this reason many times it is convenient to identify a single peak at a time.

- ***Cursor position*** *button:* *press to locate* to identify the position of the peak to be identified just locating it with the mouse SX button.
- ***BE value:*** the binding energy value of the peak to be identified. It will appear when the peak is located with the mouse or the BE value can be directly input in this window.
- ***Precision(eV):*** the energy range around the located peak to look for elements. The smaller the value the smaller the number of elements which fall inside the energy range.

- ***Search mode:*** method to search for the elements matching the defined energy range:
    - ***Find Nearest Element:*** a list of elements will be produced starting from the nearest element to the peak to be identified and encompassing all the elements falling inside the "precision" energy range.
    - ***Core Lines with max RSF:*** a list of elements falling inside the "precision" energy range will be produced, following a higher to lower RSF ordering.
    - ***Find eny Element any Orbital:*** a list of elements falling inside the "precision" energy range will be produced without any particular ordering rule.

- ***Spectral Type selection:*** the detection may be applied to identify corelines or Auger transition selecting the correspondent radio-button.

- ***Zoom:*** to increase the precision to define the peak position, a zoom can be performed:

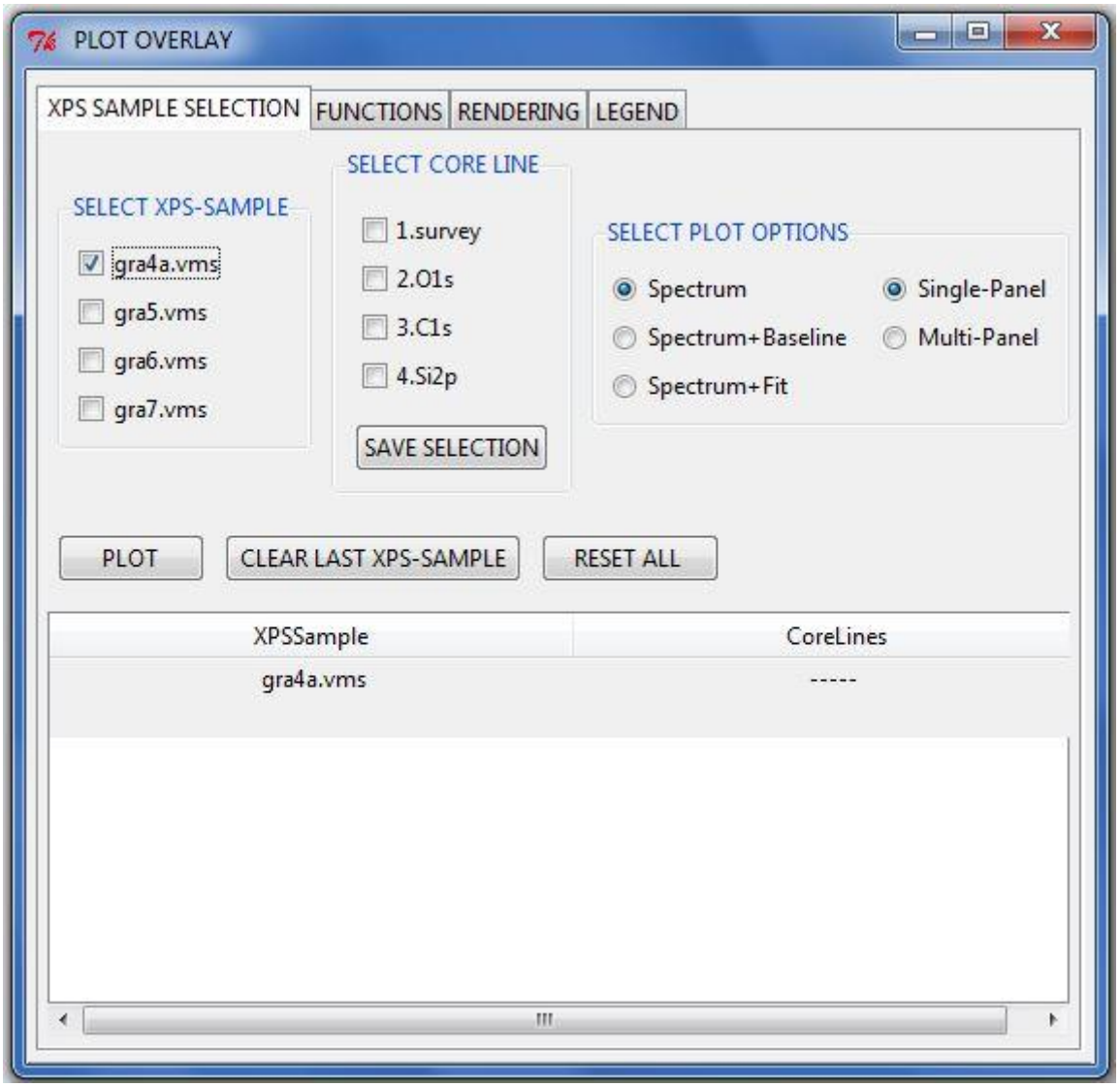
    - ***Zoom boundaries:*** to define the corners of the area to be zoomed through SX mouse button;
    - ***Reset Boundaries:*** to reset/re-define the zoom boundaries;
    - ***Refresh plot:*** to reset the plot to its original view.

***PLOT menu*:**

⇨ ***PLOT:*** plots the active XPS-Sample including wide spectra, corelines and peak fittings when present. Due to limited extension of the graphic window, only the first 12 spectra are plotted. Next corelines may be visualized right-clicking on the XPS-Sample name and selecting the desired coreline to plot.

⇨ ***SPECTRUM SELECTION:*** description of this option is given above. This option is replaced by right/left clicking on the XPS-Sample list of names appearing in the main panel.

⇨ ***OVERLAY:*** this option allows an overlaying of spectra. This option activate a notebook window with pages: *XPS-Sample selection, Functions, Rendering, Legend.*



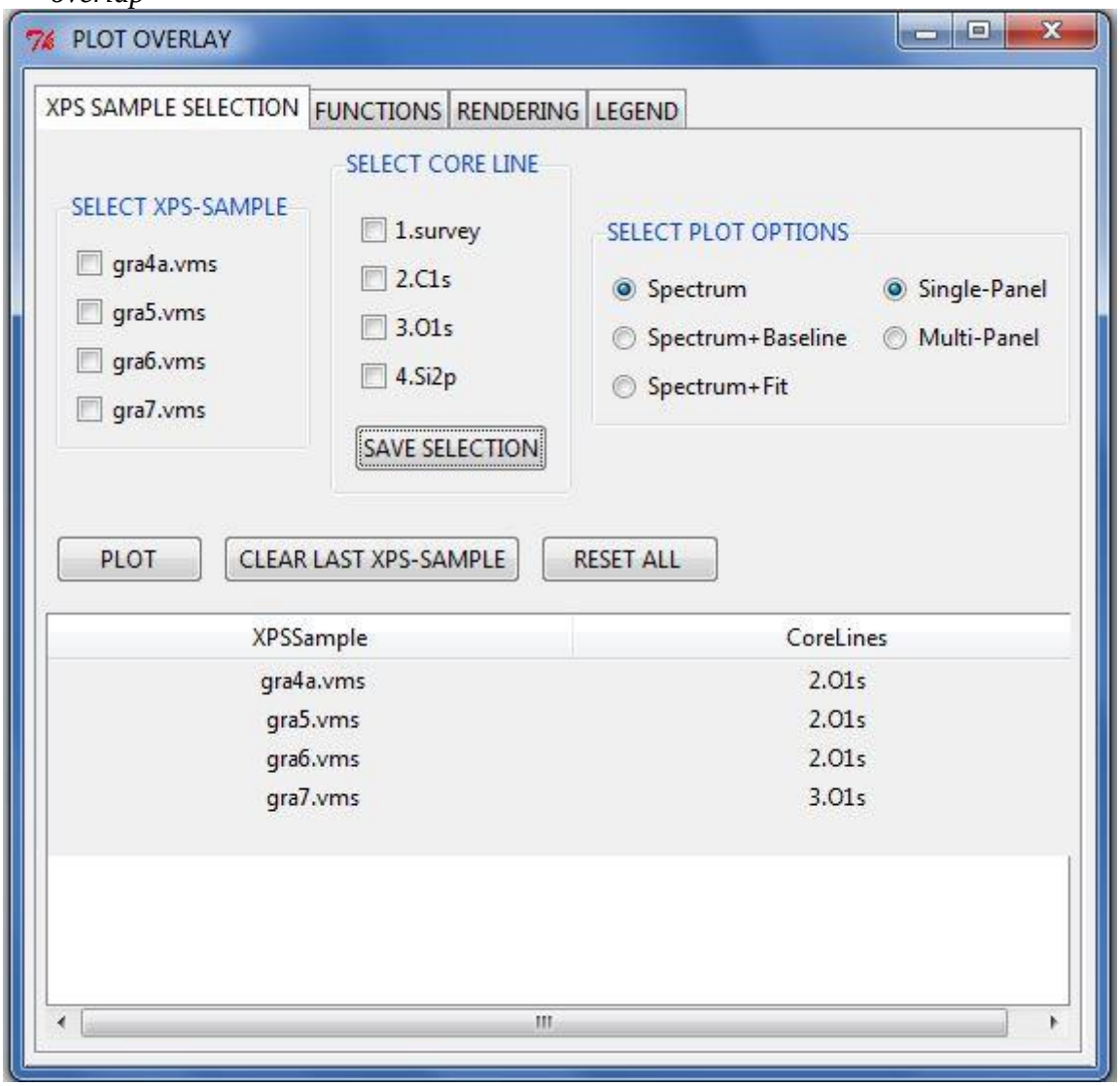
❖ ***XPS-Sample Selection:*** in this page are the options relative to XPS-Sample and core line selection.

- ***Select XPS-Sample:*** On the left-hand side in the *Select XPS-Sample* frame, is presented a checkbox list of the XPS-Samples loaded in the software. On selection of one of these XPS-Samples a checkbox-list of the correspondent corelines is shown in the *Select Coreline* frame.

At the same time the chosen XPS-Sample name will appear in the XPS-Sample/Corelines list window on the bottom.

- ***Select Coreline:*** a check-box list of the corelines of the chosen XPS-Sample is displayed. Select the desired coreline and press the button *Save Selection* each time.

- *=>Repeat same steps for the XPS-Samples, Corelines to define the list of spectra you want to overlap*



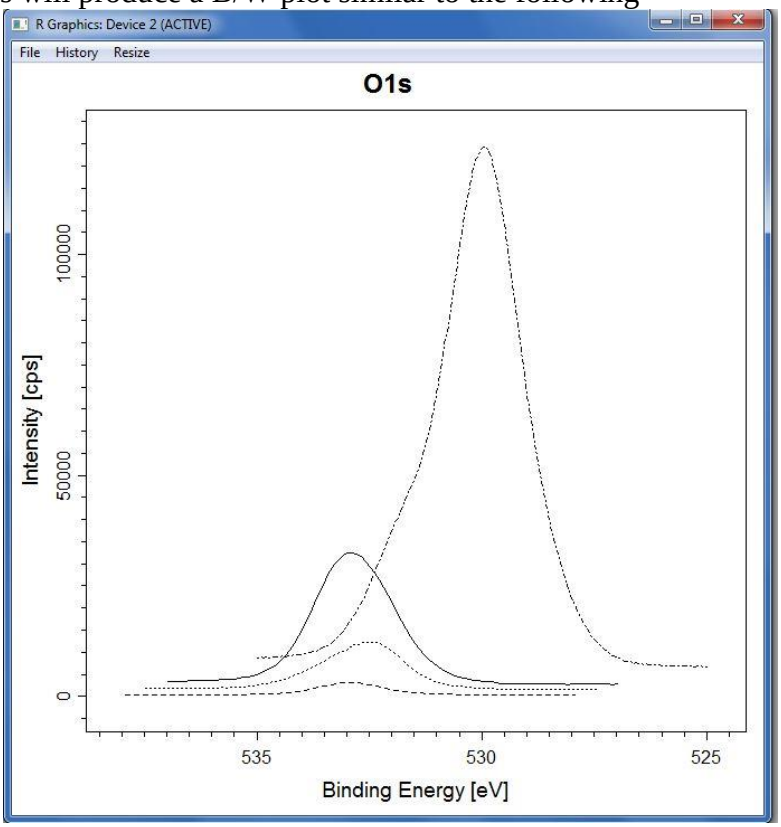
- ***Select the plot options:*** list of different options regarding spectral details to be plotted and plot mode:
  - ***Spectrum:*** just the original data will be plotted;
  - ***Spectrum + Baseline:*** spectrum + baseline will be plotted;
  - ***Spectrum + Fit:*** spectrum + complete fit will be plotted;

  These spectral details will be plotted either in
  - ***Single panel:*** all the spectra overlapped in a single graphic panel;
  - ***Multi-panel****:* the different corelines corredated with the selected details will be plotted in separated panels.
- ***Plot*** *button:* this will enable plotting the selected corelines following the selected plotting mode.

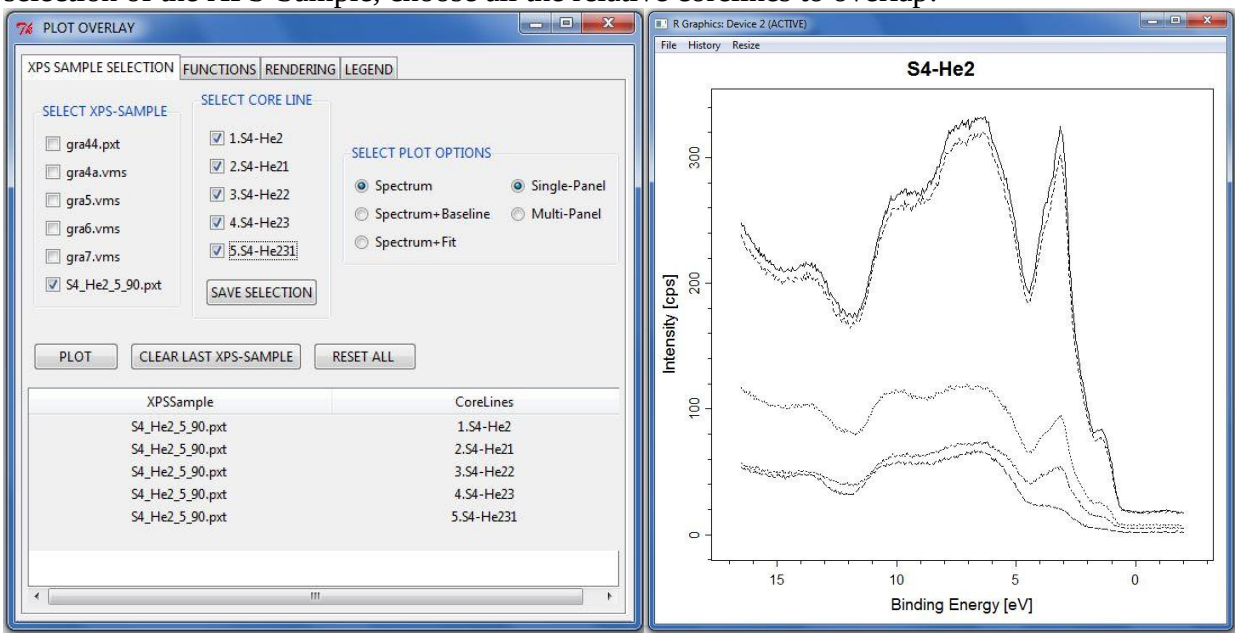
- ***Clear Last XPS-Sample:*** remove the last XPS-Sample from the list of the spectra to be plotted;

- ***Reset All:*** resets the whole list of the spectra to be plotted.

This will produce a B/W plot similar to the following

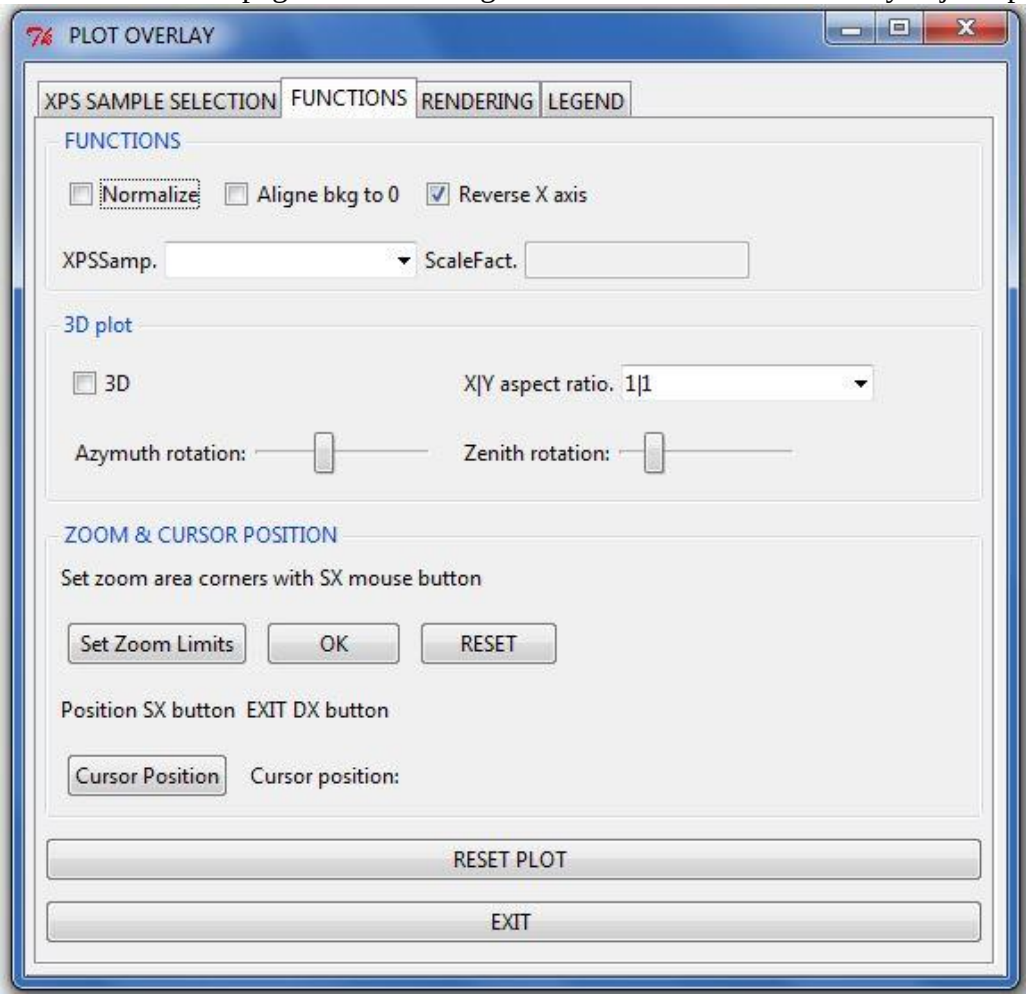


It could happen that a single XPS-Sample file contains more than one coreline you want to overlap (for example a depth profile or same coreline acquired at different tilt angles etc…). In this case after selection of the XPS-Sample, choose all the relative corelines to overlap:



In this example the XPS-Sample S4_He2_5_90.pxt contains a series of five VBs which are selected and overlapped in a unique figure.

❖ ***Functions:*** in this page are the some general functions used to modify/adjust spectra.

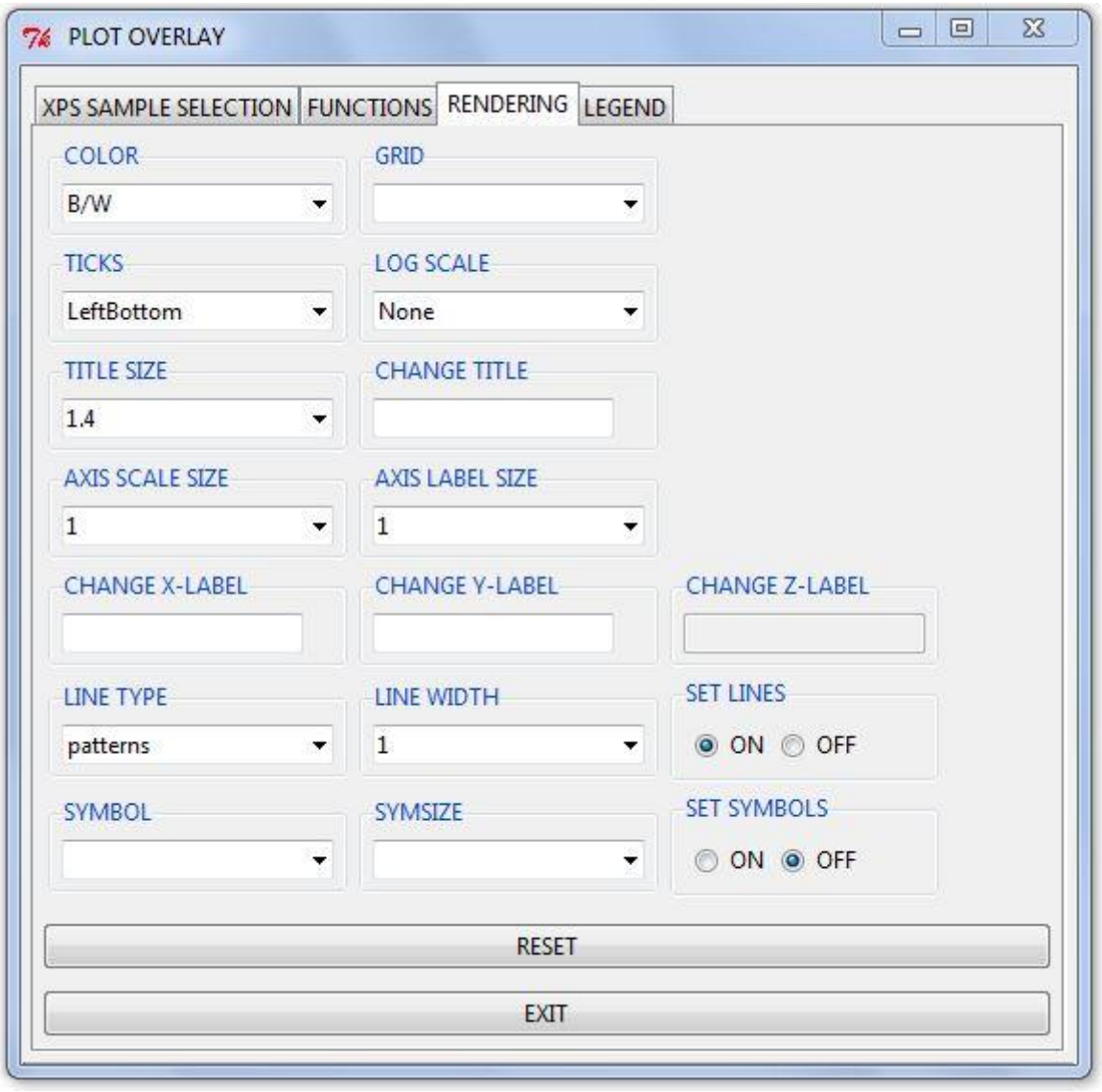


- ***Normalize:*** to normalize all the spectra to intensity = 1.
- ***Aligne bkg to 0:*** for each of the spectra this option puts the background minimum = 0;
- ***Revers X-axis:*** reverse the X axis (this to plot in binding energy);
- *Rescaling the single spectrum:* ***XPSSamp:*** select the XPS-Sample of the coreline to rescale with the drop-down list; input the ***Scale-Factor*** to amplify/reduce the intensity of the selected spectrum;
- ***3D:*** checking this box will visualize the spectra in a 3D fashion;
- ***X/Y aspect ratio:*** will modify the proportion of the X, Y axes fro an optimal rendering;
- ***Azymuth rotation, Zenith rotation:*** this sliders allow for modifying the orientation of the 3D representation for an optima rendering.
- ***Zoom and Cursor position:*** it is possible to perform zooming of a spectra overlap (not working in 3D!). => *Set zoom limits*: to define the corners of the area to be zoomed with SX mouse button; Exit_Zoom_Limits and Zoom using the DX mouse-button

- ***Reset plot*** *button:* to reset the changes done and replot spectra as initially done.

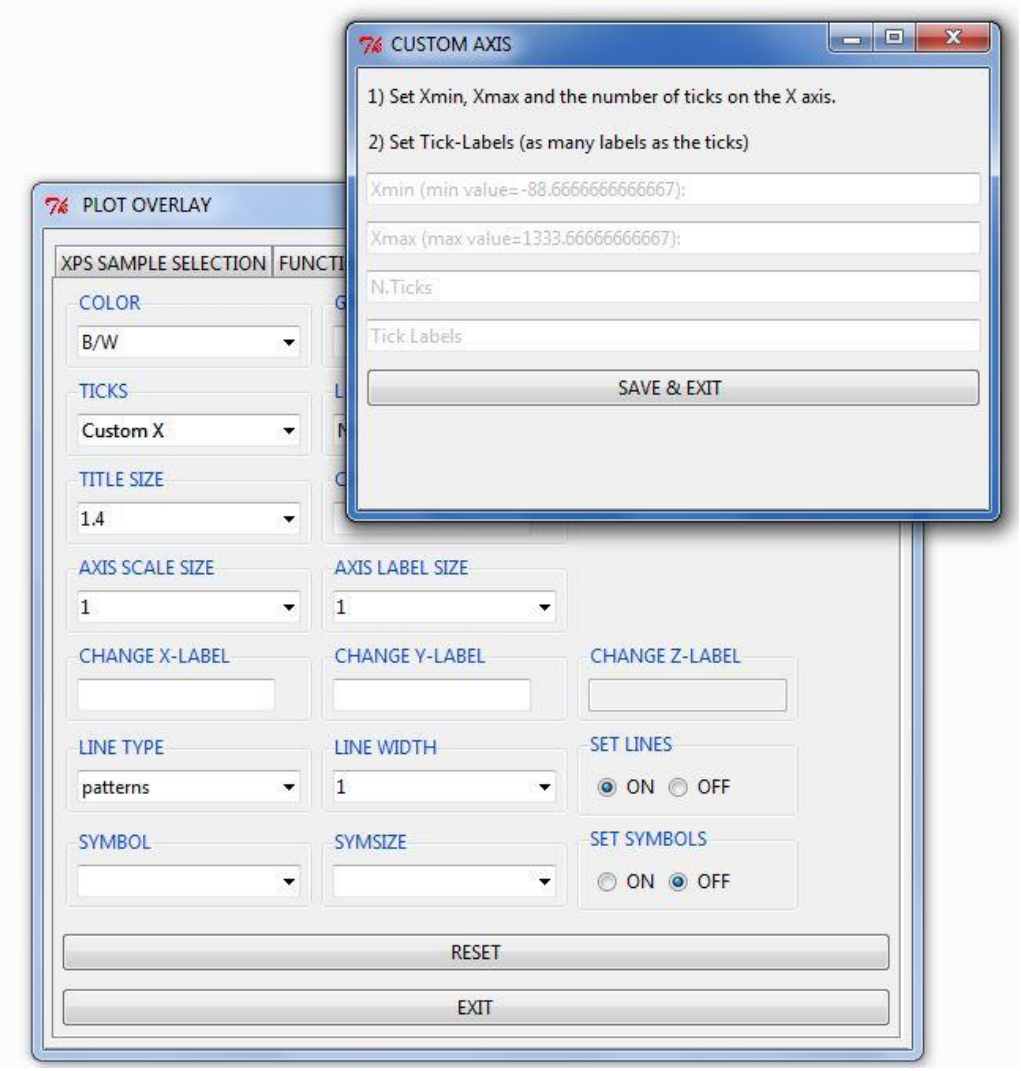
- ***Exit:*** to exit the overlay procedure.

❖ ***Rendering:*** in this page are the some general options used to optimize the figure rendering:



This page contains self explaining options acting on the figure:

- ***B/W color:*** to use black/white or color lines
- ***Grid:*** to set a grid on/off;
- ***Ticks:*** to set which axis should have ticks. This option allows for a custom design of the X and Y axis



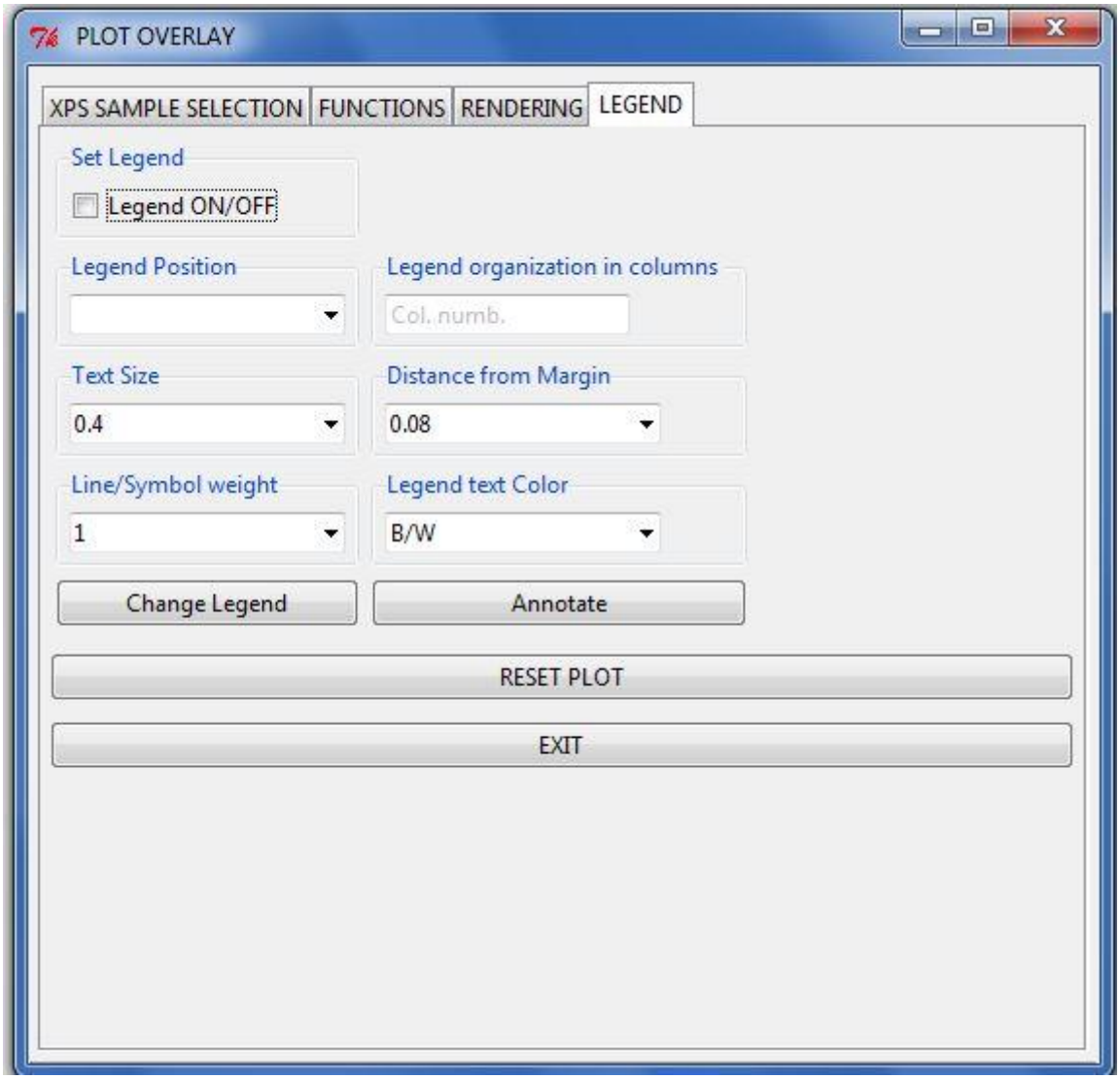
Selection of *Custom X* (*Custom Y*) will open a new window where to set the X minimum, X maximum, the number of ticks and as many tick-labels as the ticks. Number, letters and also white spaces can be used for the tick-labels.
Es: Xmin=0, Xmax=10, NTicks = 5, TickLabels = A, ,B, y ,3

- ***Log. Scale:*** to set logarithmic scale on X axis, Y axis, both;
- ***Title size:*** to set the size of the title characters;
- ***Change title:*** to change the title;
- ***Axis scale size:*** to set the size of the characters of the X, Yaxes;
- ***Axis label size:*** to change the size of the characters of the axis names;
- ***Change X, Y label:*** to change the name of the X, Y axis;
- ***Line Type:*** when colors are selected lines can be solid or different patters can be chosen;
- ***Line Width:*** to select the weight of the lines
- ***Set Lines:*** the default is ON: lines will be used for the plot;
- ***Symbol:*** to use symbols instead of lines for plotting;
- ***Set Symbol:*** the default is OFF. When set ON symbols will be used for the plot.
- ***Symsize:*** to select the symbol size.

N.B. :*Lines* and *Symbols* are used for plotting when both are set ON.

- ***Reset plot** button:* to reset the changes done and replot spectra as initially done.
- ***Exit:*** to exit the overlay procedure.

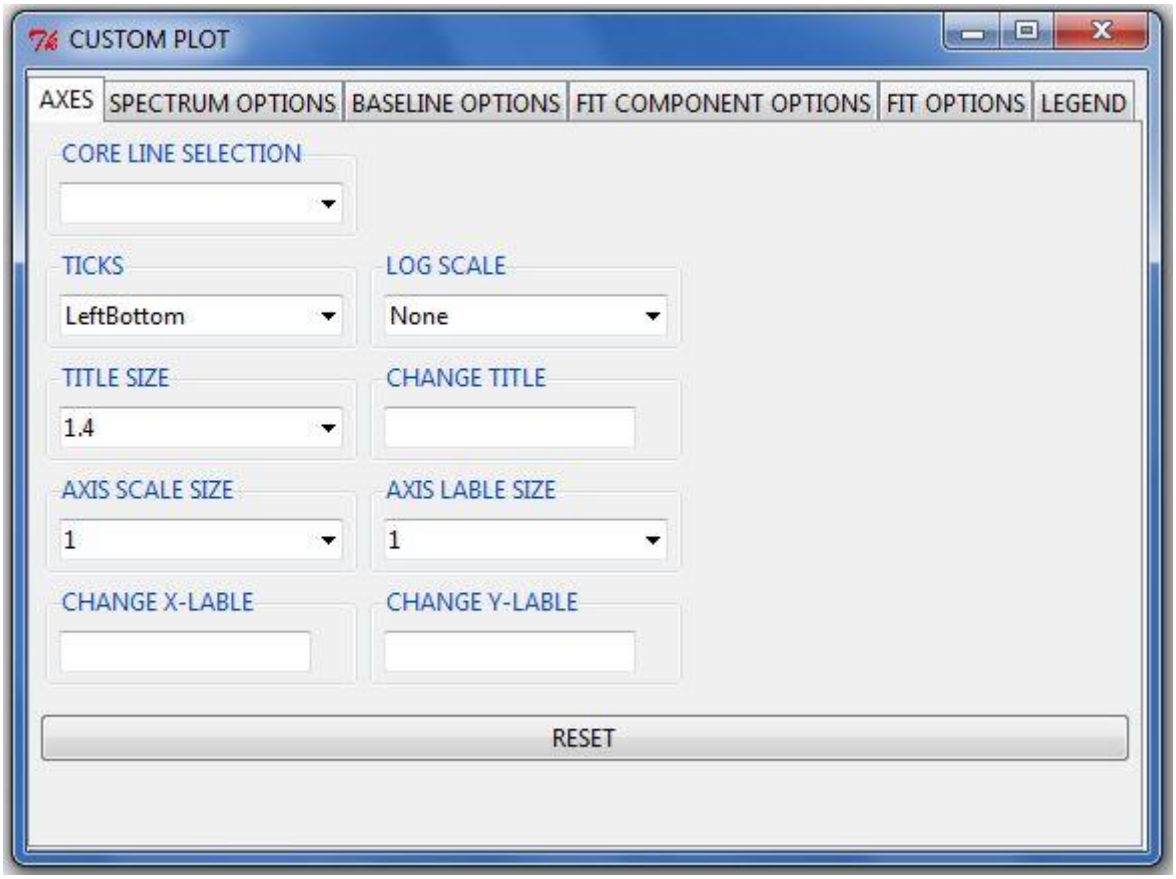
❖ ***Legend :*** to add text to the figure:



- ***Set legend:*** to set plot legends on/off;
- ***Legent position:*** there are 8 different positions available for the legend corresponding to the four corners in inner and outside position;
- ***Legend orientation:*** in presence of more than one names, these can be organized in a table having the number of columns you input;
- ***Text size:*** to set the size of the legend characters;
- ***Distance from margin:*** to increase/decrease the distance of the legend position from the box containing the figure;
- ***Line/Symbol weight:*** to increase decrease the weight of lines/symbol used to identify spectra in the legend;
- ***Legend text Color:*** to write legend labels in B/W or color style.
- ***Change legend:*** this button allows changing the legend names;
- ***Annotate:*** to add text to the figure.

- ***Reset*** *button:* to reset the changes done and replot spectrum as initially done.***:***
- ***Exit:*** to exit the *Custom Plot* routine.

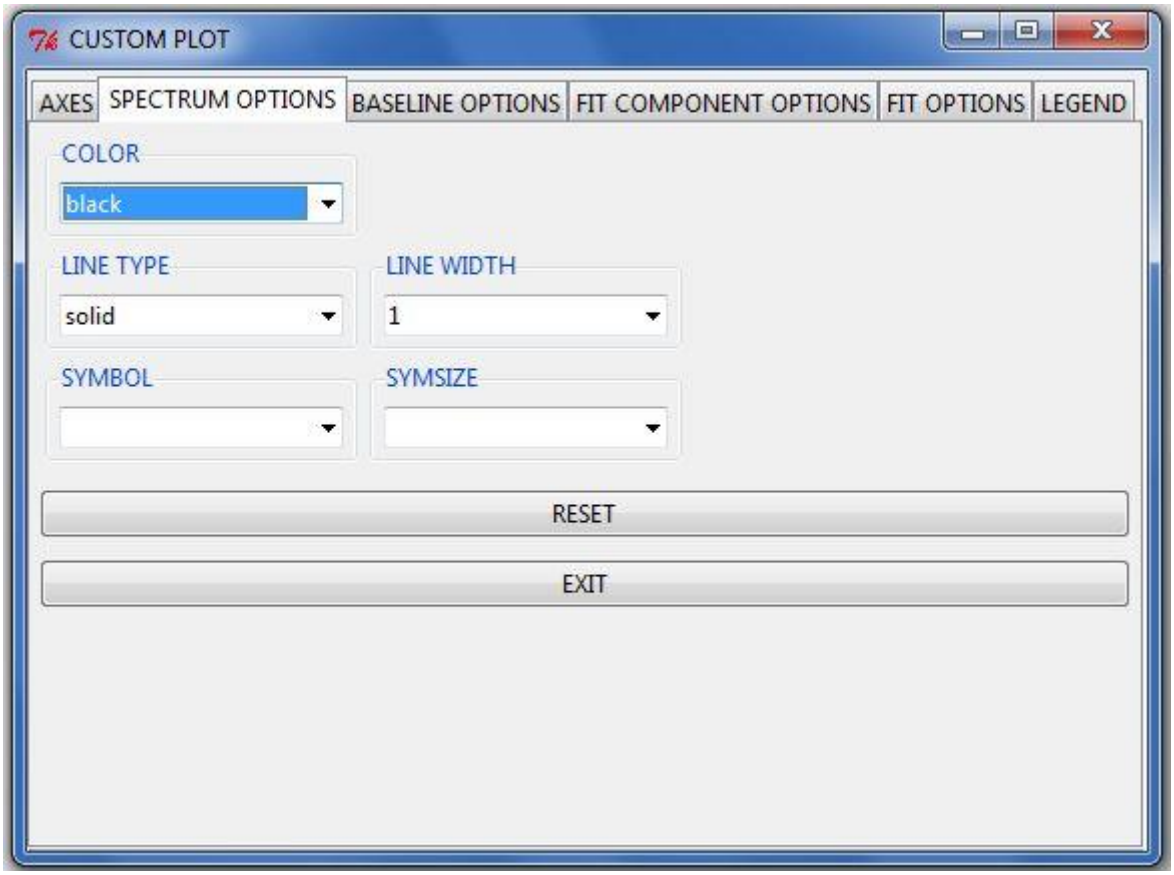
⇨ ***CUSTOM PLOT:*** this options allows potting a spectrum in a personalized and easy way. This function is organized in notebook pages containing several options.



❖ ***Axes:*** this page contains the options regarding the axes format:

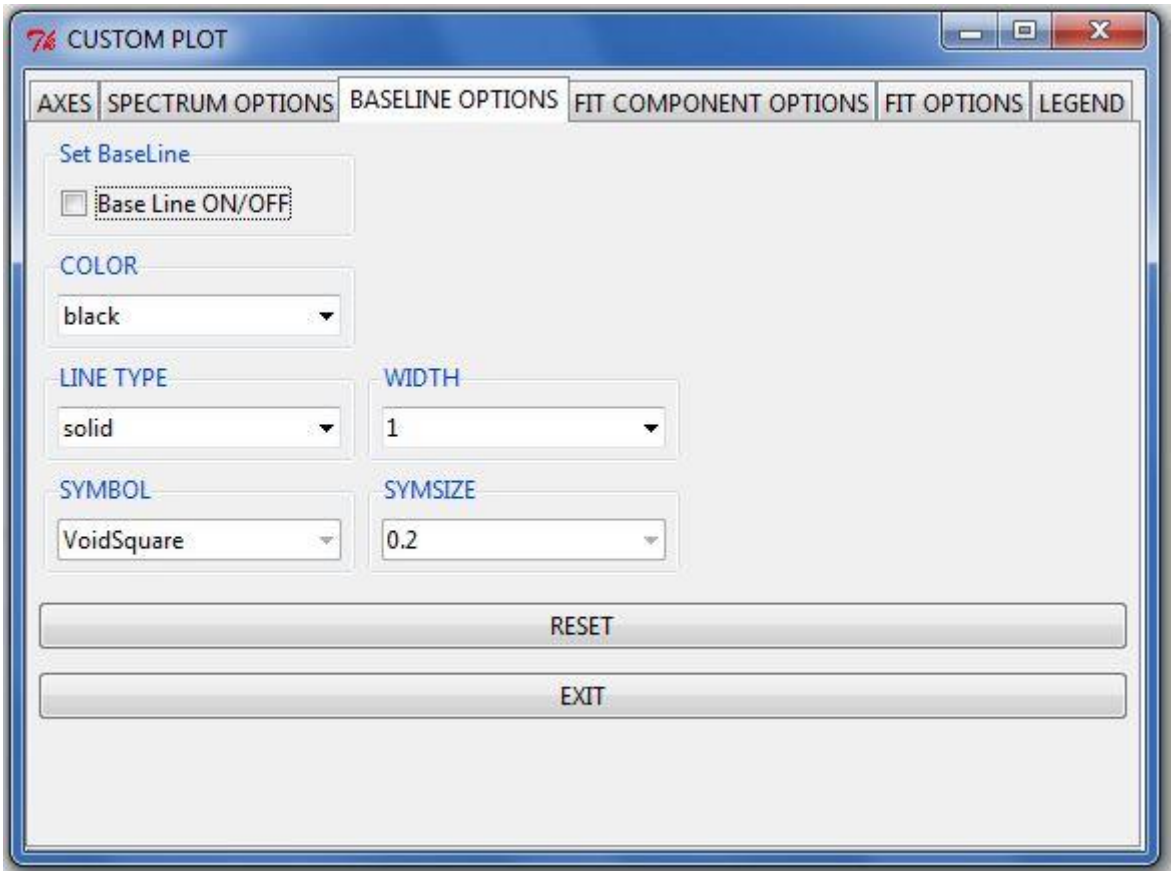
- ***Coreline selection:*** to select the coreline of the active XPS-Sample to plot;
- ***Ticks:*** to set which axis should have ticks;
- ***Log. Scale:*** to set logarithmic scale on X axis, Y axis, both;
- ***Title size:*** to set the size of the title characters;
- ***Change title:*** to change the title;
- ***Axis scale size:*** to set the size of the characters of the X, Yaxes;
- ***Axis label size:*** to change the size of the characters of the axis names;
- ***Change X, Y label:*** to change the name of the X, Y axis;
- ***Reset*** *button:* to reset the changes done and replot spectra as initially done.***:***

❖ ***Spectrum options:*** this page contains options regarding the axes format:



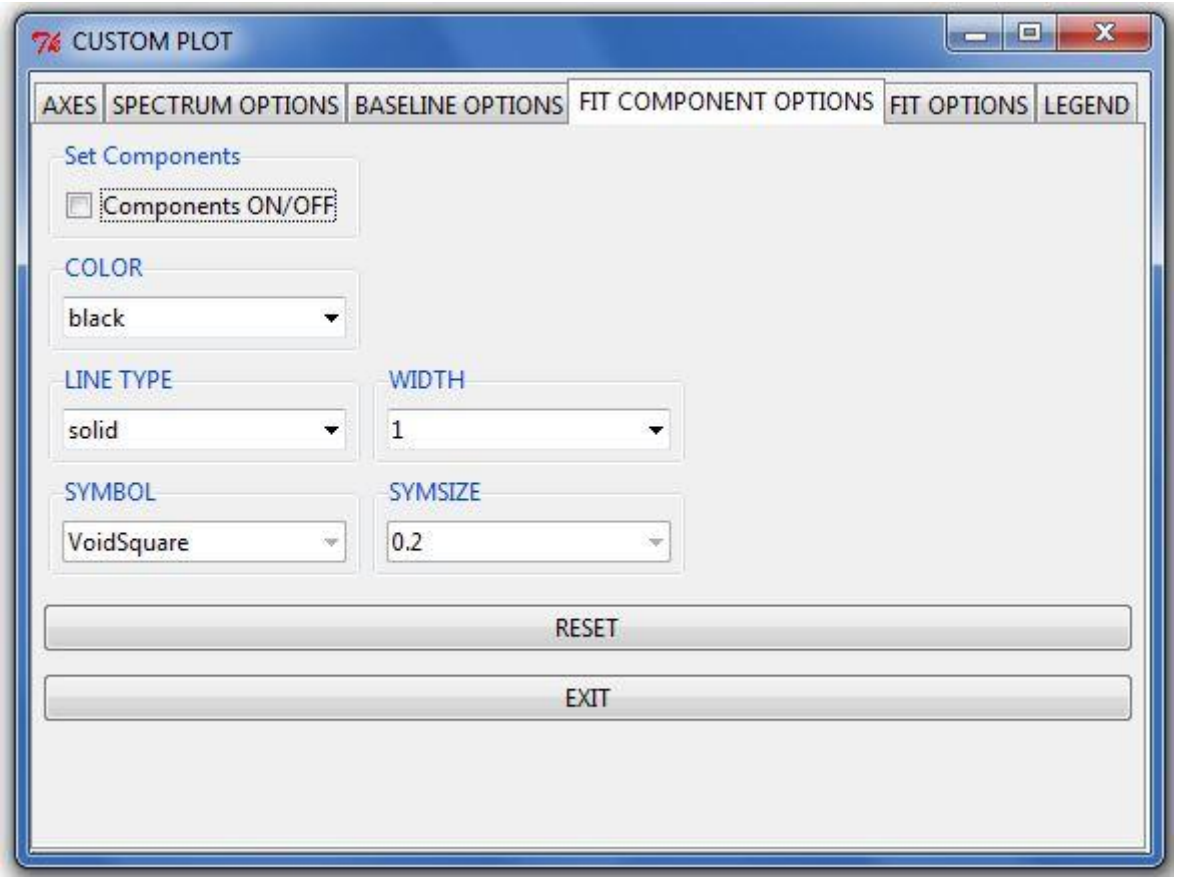
- ***Color:*** to select B/W or color representation;
- ***Line Type:*** when colors are selected lines can be solid or different patters can be chosen;
- ***Linewidth:*** to select the weight of the lines
- ***Symbol:*** to use symbols instead of lines fro replotting;
- ***Symsize:*** to select the symbol size.
- ***Reset*** *button:* to reset the changes done and replot spectrum as initially done.***:***
- ***Exit:*** to exit the *Custom Plot* routine.

❖ ***Baseline:*** this page contains options for plotting the spectrum Baseline:



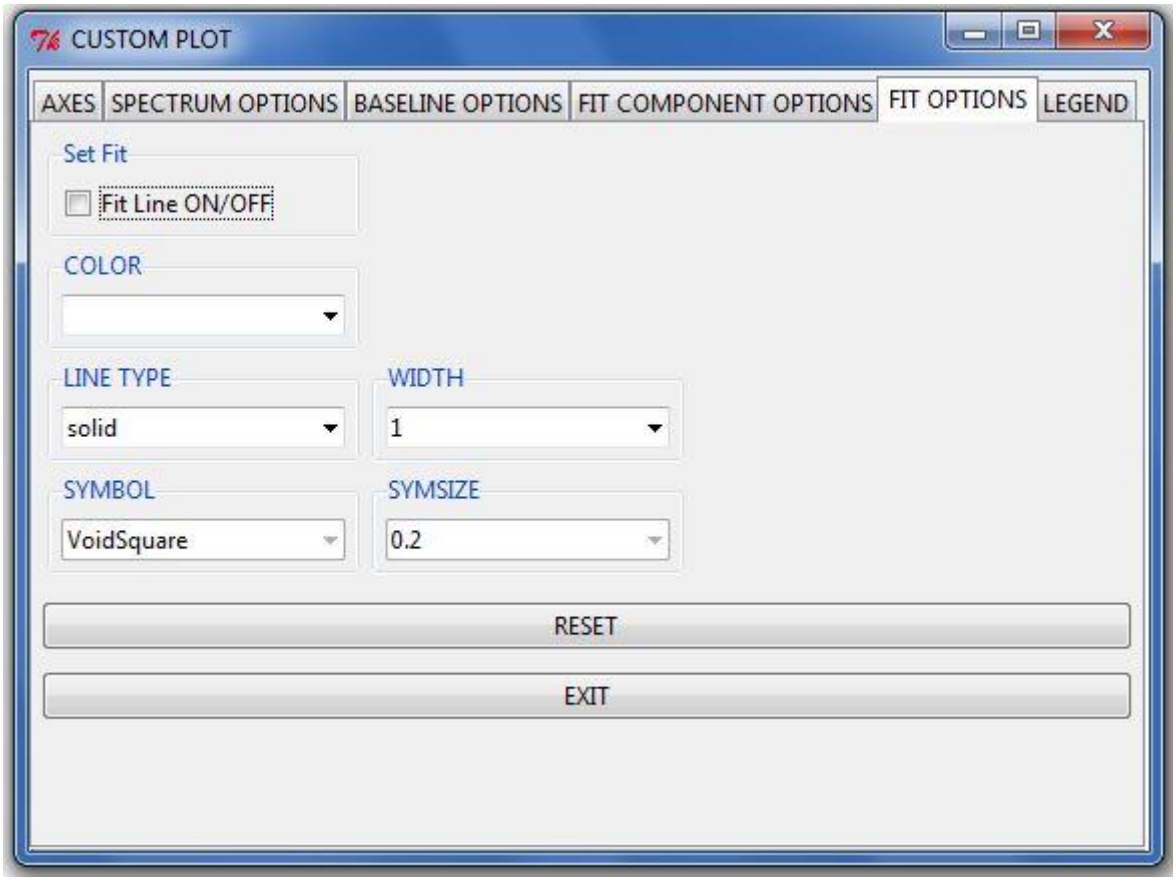
- ***Set Baseline:*** to set Baseline visualization ON/OFF;
- ***Color:*** to select B/W or color representation;
- ***Line Type:*** when colors are selected lines can be solid or different patters can be chosen;
- ***Linewidth:*** to select the weight of the lines
- ***Symbol:*** to use symbols instead of lines fro replotting;
- ***Symsize:*** to select the symbol size.
- ***Reset*** *button:* to reset the changes done and replot spectrum as initially done.***:***
- ***Exit:*** to exit the *Custom Plot* routine.

❖ ***Fit Component Options:*** this page contains options for plotting the spectrum Fit Components:



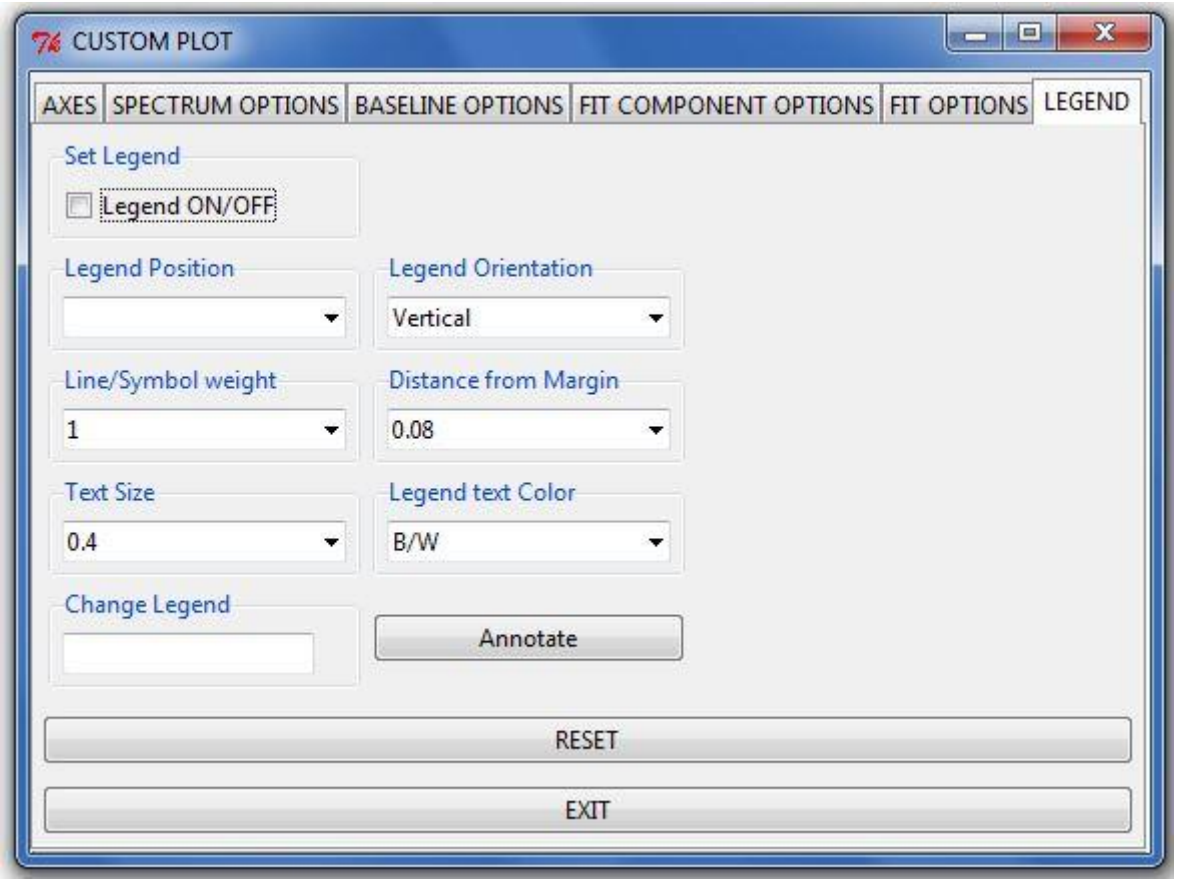
- ***Set Fit Components:*** to set Fit Components visualization ON/OFF;
- ***Color:*** to select B/W or color representation;
- ***Line Type:*** when colors are selected lines can be solid or different patters can be chosen;
- ***Linewidth:*** to select the weight of the lines
- ***Symbol:*** to use symbols instead of lines fro replotting;
- ***Symsize:*** to select the symbol size.
- ***Reset*** *button:* to reset the changes done and replot spectrum as initially done.***:***
- ***Exit:*** to exit the *Custom Plot* routine.

❖ ***Fit Option:*** this page contains options for plotting the spectrum Best Fit:



- ***Set Fit:*** to set the Best Fit visualization ON/OFF;
- ***Color:*** to select B/W or color representation;
- ***Line Type:*** when colors are selected lines can be solid or different patters can be chosen;
- ***Linewidth:*** to select the weight of the lines
- ***Symbol:*** to use symbols instead of lines fro replotting;
- ***Symsize:*** to select the symbol size.
- ***Reset*** *button:* to reset the changes done and replot spectrum as initially done.***:***
- ***Exit:*** to exit the *Custom Plot* routine.

❖ ***Legend:*** this page contains options for drawing the legends:



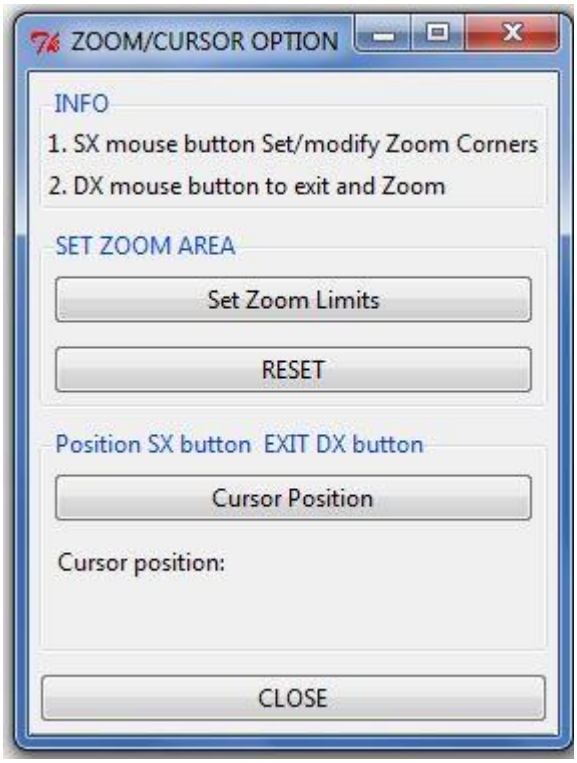
- ***Set legend:*** to set plot legends on/off;
- ***Legend position:*** there are 8 different positions available for the legend corresponding to the four corners in inner and outside position;
- ***Legend orientation:*** vertical or horizontal organization of the legend names;
- ***Distance from margin:*** to increase/decrease the distance of the legend position from the box containing the figure;
- ***Line/Symbol weight:*** to increase decrease the weight of lines/symbol used to identify spectra in the legend;
- ***Text size:*** to set the size of the legend characters;
- ***Legend text Color:*** to write legend labels in B/W or color style.
- ***Change legend:*** this button allows changing the legend names;
- ***Annotate:*** to add text to the figure.
- ***Reset*** *button:* to reset the changes done and replot spectrum as initially done.***:***
- ***Exit:*** to exit the *Custom Plot* routine.

⇨ ***ANNOTATE:*** this options allows for adding text to a figure.

NB: It might happen that an error occurs if the previous plots were done using the *Lattice* Package. In this case the graphic window must be reset opening the ***Graphic device Options*** selecting the proper operative system and pressing OK.

- ***Text:*** the text to add to the figure;
- ***Locate text*** *button:* to locate the text position using the cursor. Click with mouse in the position you want to add the text.
- ***Text size:*** to set the character size of the text to add;
- ***Text color:*** to set the color of the text to add;
- ***ACCEPT*** *button:* if the text is correctly added to the figure press *Accept* to store the figure. After accepting the plot you cannot *Undo* the annotation.
- ***UNDO Annotation:*** it is possible to *Undo* the annotation as many time as required until the *Accept* button is not pressed.
- ***Exit:*** to exit the *Annotate* routine.

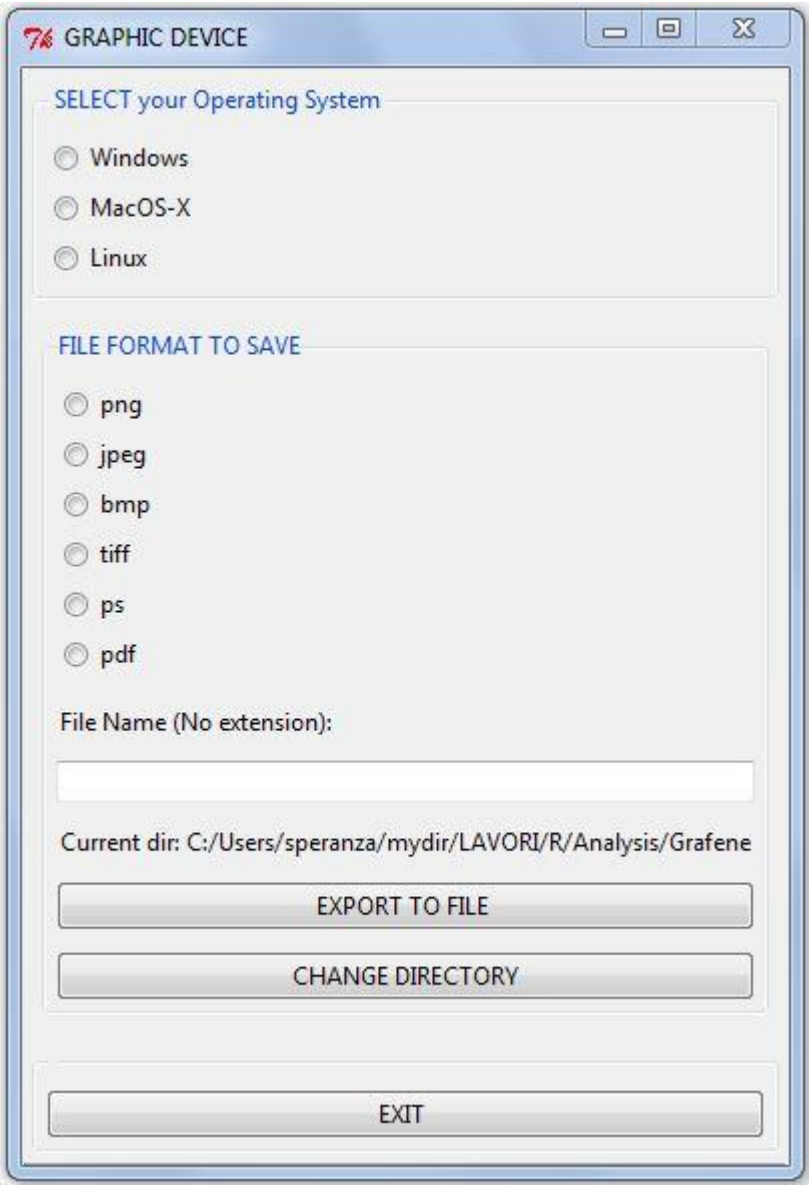
⇨ ***ZOOM AND CURSOR:*** allows zooming the active spectrum.



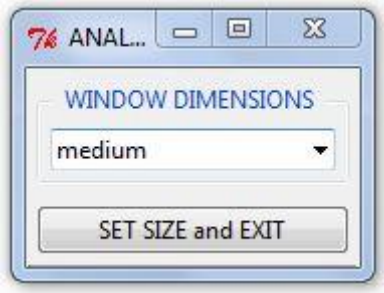
- ***Set zoom area:*** with SX mouse button click on the spectrum to define the corners of the area to be zoomed. DX button exit the definition of the corners;
- ***Reset*** *button*: to reset the zoom to the original visualization;
- ***Cursor Possition*** *button:* click on the spectrum with the SX button to read the mouse position (i.e. binding energy, initensity). The DX button exit reading the mouse position;
- ***Close:*** to exit the *Zoom & Cursor* option.

⇨ ***GRAPHIC DEVICE OPTIONS:*** to select a graphic window in agreement with the operative system (Windows by default), reset the graphic window and save figure in files using different formats.

- ***Select your operating system:*** set/reset the proper graphic window by selecting the proper operating system.
- ***File Format to Save:*** the content of the actual graphic window will be saved in a file following the chosen file format;
- ***File name:*** the file name to save the figure;
- ***Current dir:*** shows the directory where the file will be saved;
- ***Change Directory*** *button:* to change the directory where to save the file;
- ***Export to file*** *button:* to export the image in the file;
- ***Exit:*** to exit the routine.



⇨ ***ANALYSIS WINDOW SIZE:*** to select the dimensions of the *Analysis* graphic window in agreement with the kind of screen used.

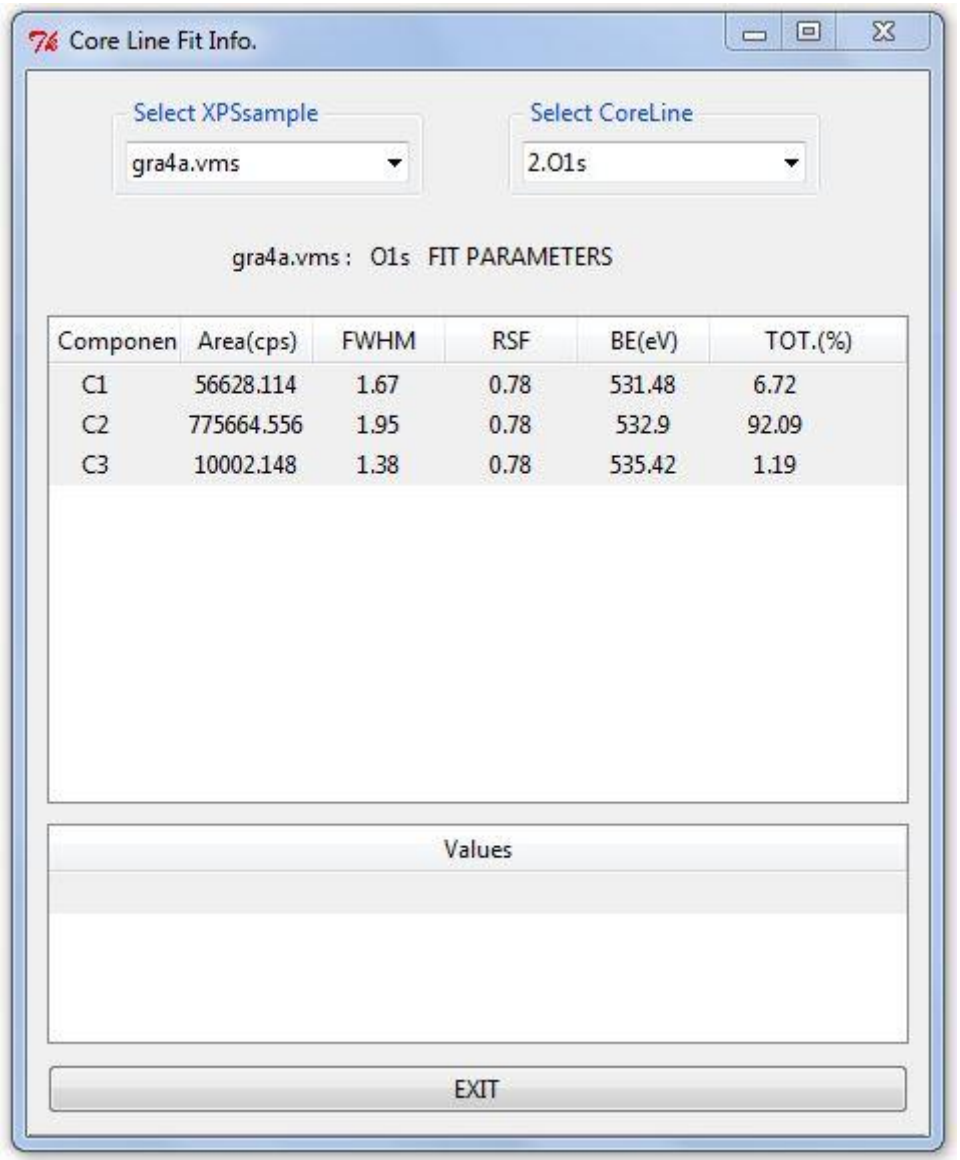


- ***Window dimensions:*** select the window dimension using the drop down list:
  - ***Small*** for laptop computers
  - ***Medium*** for normal sized screens (default);
  - ***Large*** for large dimension screens.

INFO & HELP menu.

⇨ ***XPS-SAMPLE INFO:*** shows a list of information regarding the active XPS-Sample;

⇨ ***CORELINE INFO:*** displays a list of parameters regarding the core line fitting components:



- ***Select the XPS-Sample:*** to select the XPS-Sample containing the desired coreline;
- ***Select the CoreLine:*** to select the desired coreline

The list parameters relative to wach of the fitting components relative to the chosen coreline are displayed in the first parameter table.
Double clicking on one of the components will display all the fitting parameters used for the selected component with their varability ranges.

⇨ ***HELP:*** to open the PDF manual of the software.