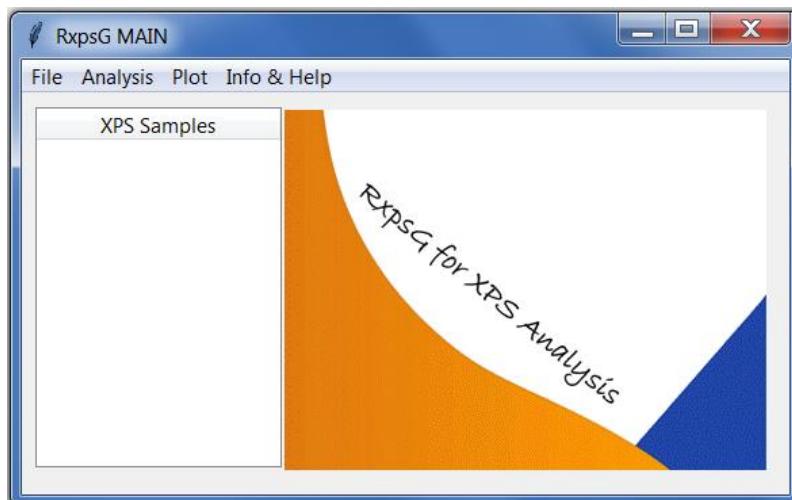


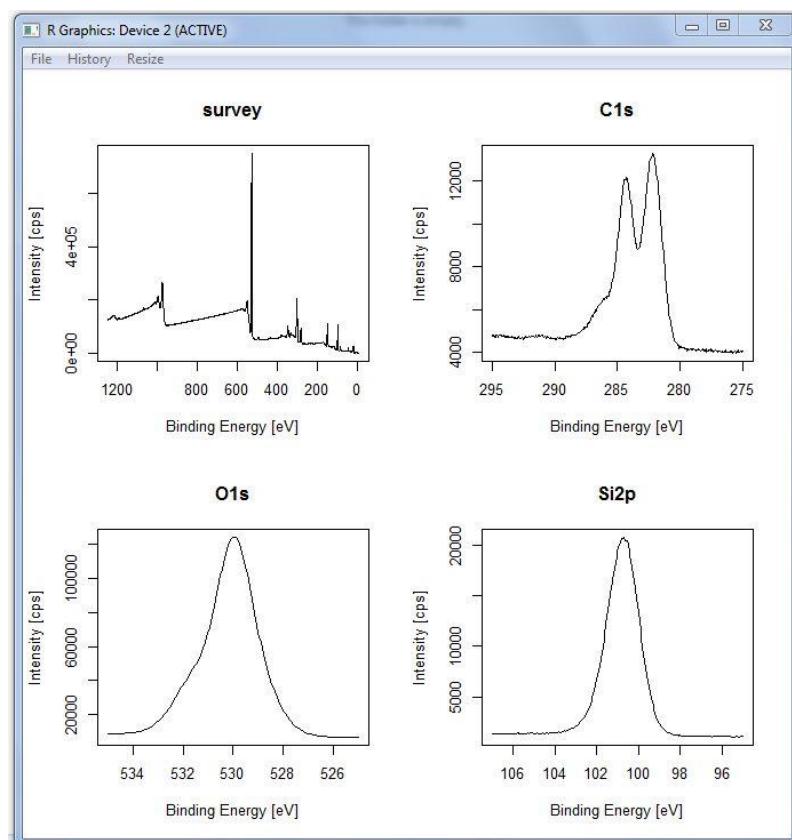
XPS ANALYSIS - the software to analyze XPS spectra

By G. Speranza - 2023

Make sure all libraries *digest*, *gWidgets2*, *gWidgets2tclt*, *import*, *latticeExtra*, *memoise*, *minpack.lm*, *signal* are correctly installed in R. In RStudio select the pakages tab, go through all the installed libraries and select RxpsG.



The **xps()** command will run the XPS-Analysis software, opening the RxpsG main interface.



and its graphical main window

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

RxpsG Software description:

The XPS Main Panel shows four main menus:

- [FILE](#);
- [ANALYSIS](#);
- [PLOT](#);
- [INFO & HELP](#).

The RxpsG interface shows on the left-hand side a list 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.

The *active XPS-Sample* and the *active Core-line* are the data file and the spectrum which are selected for the analysis.

=> Double clicking on one of the names render the correspondent XPS-Sample active. 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 and performs a given operation. This operation affects data ONLY in the local memory. All the operation results (for example peak fitting) are lost when exiting without saving.

Pressing the SAVE button will save the results in the main memory of the software making them available for further processing. The effect of save is seen in the main graphical window where the processed spectrum is drawn and changes visible.

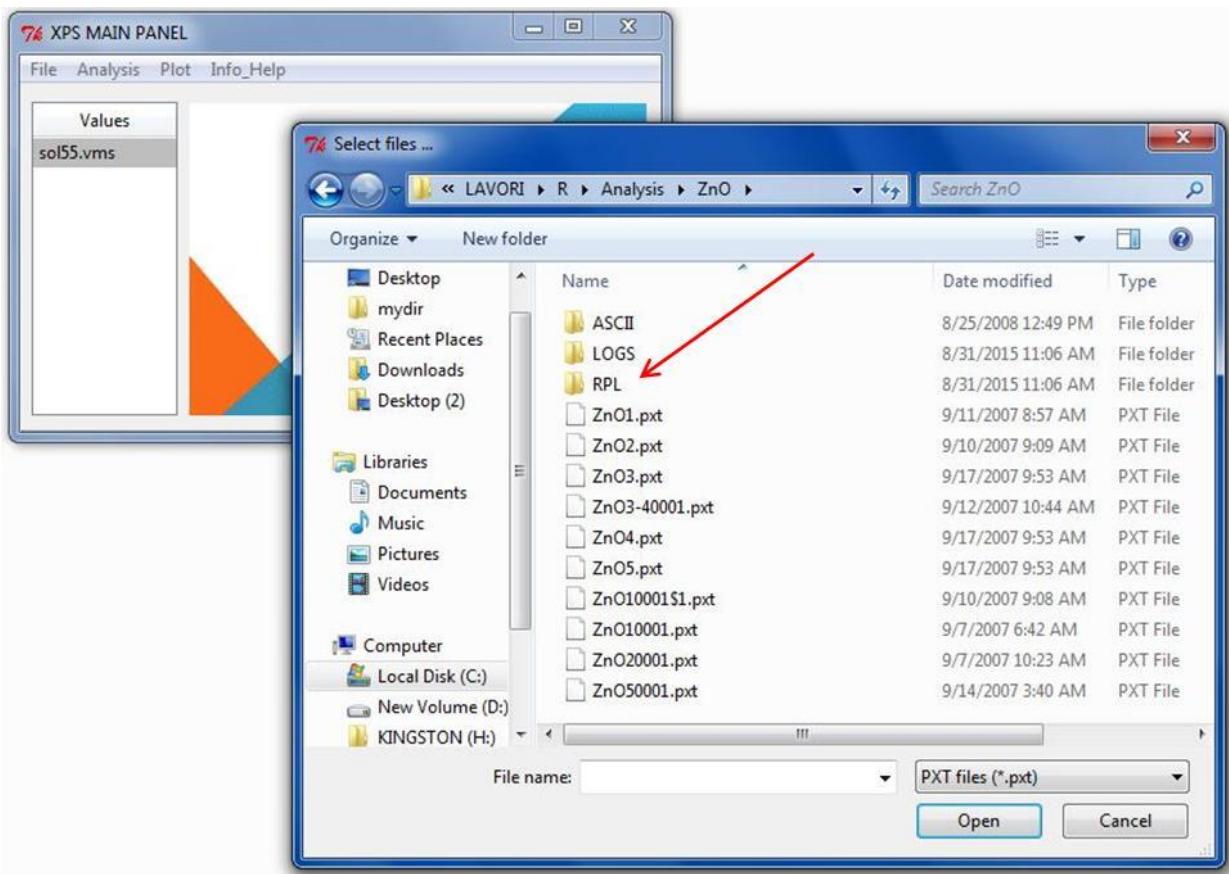
Results of data processing will not affect original raw data and will be stored in separated slots of the memory. Also analyzed data are saved by default in xxx.Rdata files preserving the source data.

List of options

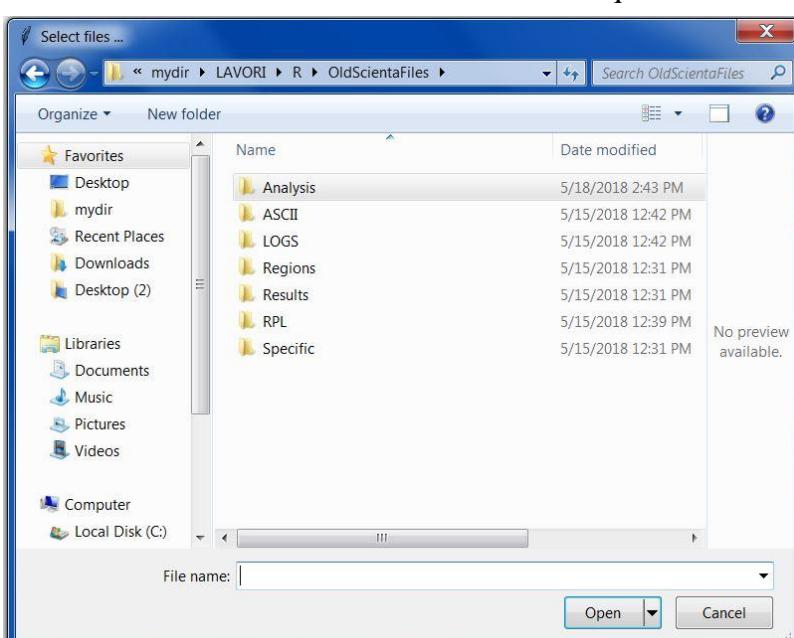
FILE	ANALYSIS	PLOT	INFO & HELP
Load VMS, PXT data	Spectrum selection	Plot	XPS Sample Info
Load PXT+RPL data	Analyze	Spectrum selection	Core Line Fit Info
Load Analyzed data	Fit Constraints	Overlay	Analysis Report
Save Analyzed Data	Fit Lev.Marq.	Compare Spectra	Help
Import Ascii	Fit ModFit	Two Y-scale Plot	
Export Ascii	Move Components	Custom Plot	
Split PXT data	Quantify	Annotate	
Remove Curr. XPS-Sample	Energy Shift	Zoom & Cursor	
Remove All. XPS-Samples	Process Coreline	Graphic Device Options	
Set Working DIR	Extract from survey	Set Analysis Window Size	
	Reset Analysis		
	AdjustBaseline		
	Depth Profile		
	Smoothing		
	Differentiation		
	VBtop Estimation		
	Sprucing Up		
	Change Spectrum Label		
	Element Identification		
	Coreline&AugerTables		
	VMS Transm. Correction		

FILE menu:

- ⇒ **LOAD VMS, PXT DATA:** load vamas and scienta.ptx data-files;
- ⇒ **LOAD PXT+RPL DATA:** load scienta.ptx files analyzed by the Genplot software. This option reads Analyzed Scienta files and the analysis information stored 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 analysis information, differently the program blocks.

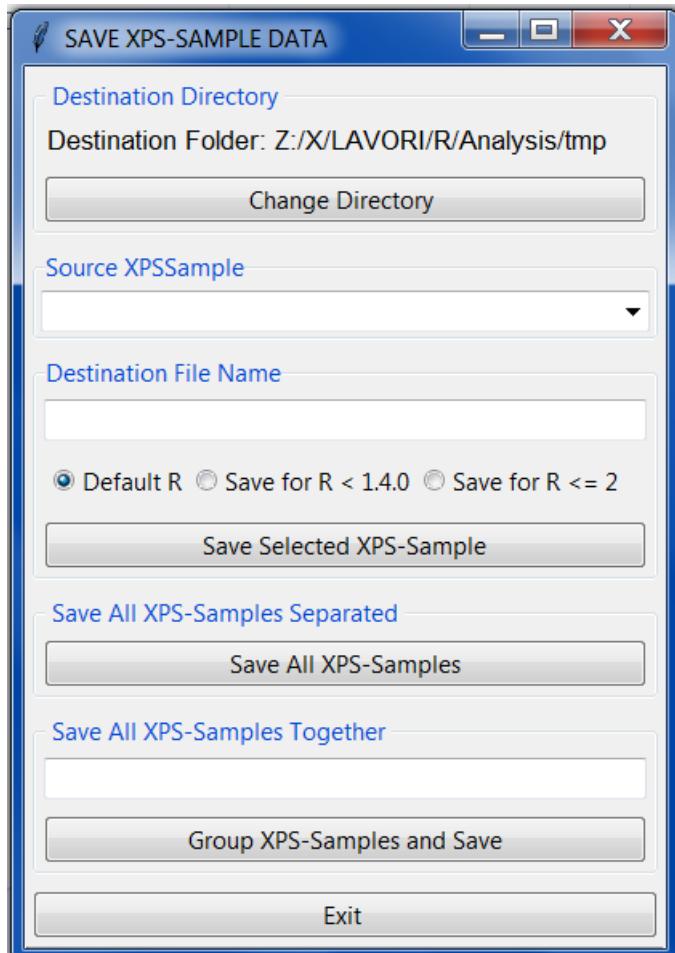


- ⇒ **LOAD OLD SCIENTA DATA:** load files acquired with the Old Scienta Software (not .pxt). Data are saved in multiple folders organized in:
Analysis, Ascii, Logs, Regions, Results, Specific as shown in the figure.



To read old Scienta data:
i) select the .../Analysis folder; ii)
select the desired filename;
The selected spectra should be
visualized.

- ⇒ **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 (see figure):



- **Change directory button** to change the folder where to save the analyzed data;
- **Source File Name:** select the XPS-Sample to save. The relative *Destination Folder* will be visualized
- **Destination XPSSample name:** once the source filename is selected the software suggests a default name for the destination file which will appear in the window. You can change this name. The .RData extension is added by default and cannot be changed.
- **Save Selected XPS-Sample** to save the analyzed spectra in the selected XPS Sample;
- **Default R:** file format compatible with updated R version is used by default. However, file formats compatible with old R versions can be selected
- **Save All XPS-samples** to save all the analyzed XPS-samples (XPS data file loaded). In this case default names and their original folders will be utilized;
- **Group XPS-Samples and Save** all the analyzed XPS-samples will be grouped and saved in just one file instead of separated files.

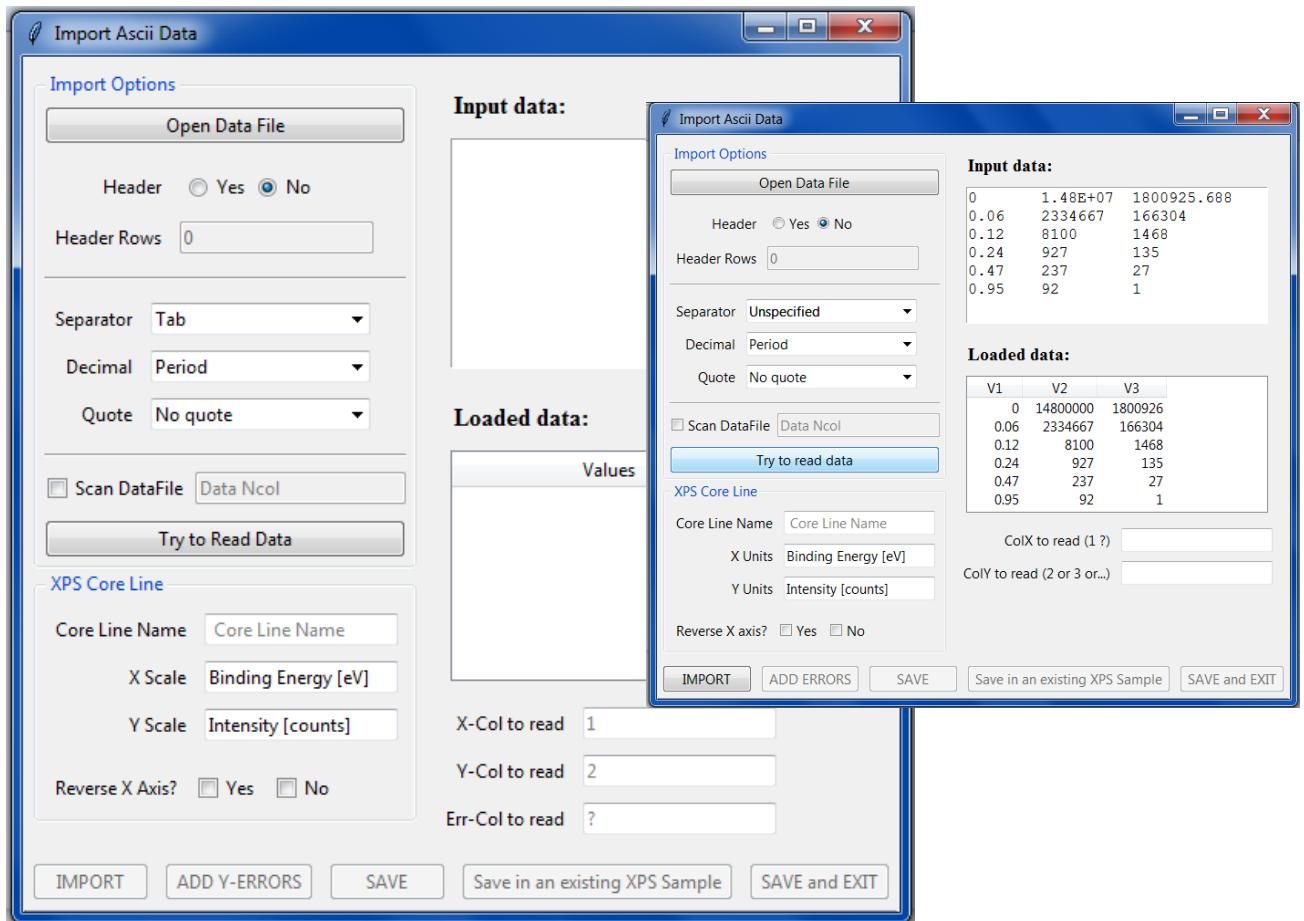
- ⇒ **IMPORT ASCII:** to load ascii (text) data files. This option will open the following window (see figure):

- **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

Import Options: 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.
In the example: No Header, Separator = undefined, Decimal = Period, Quote = No quote. If information is correct, data are visualized in columns in the LOADED DATA window.



Core Line Options: define core line parameters.

- **Core Line name:** define the name of the column of data to be read. This name will be used by the software to identify these data;
- **X Units:** define the units for the X-axis;
- **Y Units:** define the units for the Y-axis;
- **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);
- **Err-Col to read:** if Y data are provided by standard errors, you can select the ERR-COL column to read. *Custom Plot* must be utilized to plot the data and errors.

Command Buttons:

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

- **Add Errors** button: add standard errors associated to the previously imported data;
 - **Save** button: use this button to save data: a new XPSSample will be created. The XPSSample name will be the same as the input ascii data file;
 - **Save in an existing XPSSample** button: use this button to add imported data to the new XPSSample previously created with the SAVE button;
 - **Save & Exit** button: to save read data in the selected XPSSample for further processing and terminate the loading operation.
- ⇒ **EXPORT ASCII:** to export spectra and analyzed spectra in an ascii data file. The data are organized in a set of columns: x, raw data, baseline, components, fit.

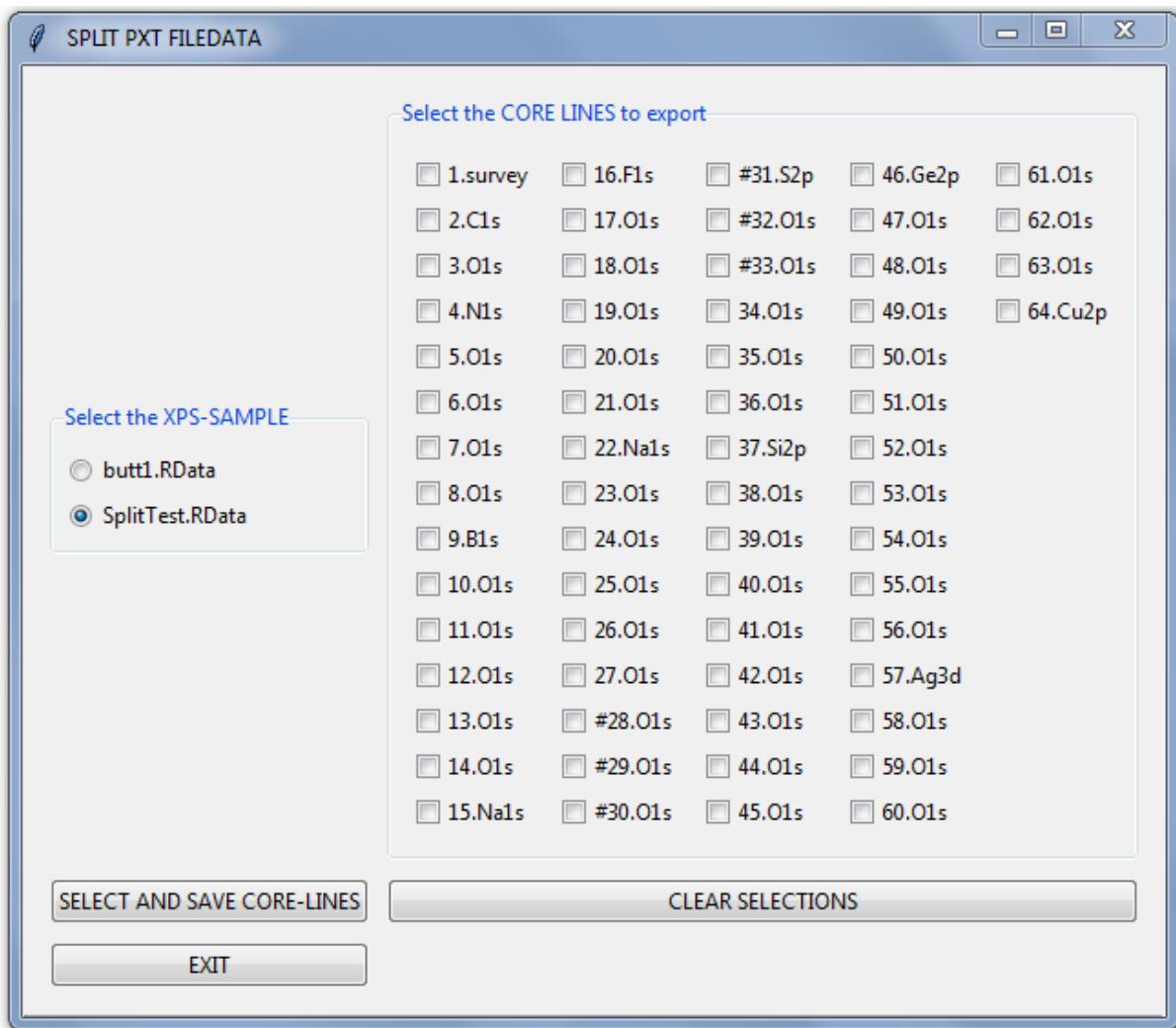


- **Select CoreLine:** select the Core-Line you want to export in ascii. Original spectrum and fit components (if present) will be exported.
- **Select output format:** here you select the kind of data separator and if Period or Comma will be used as separator for decimals;
- **Export Data** button: 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.

After loading the .PXT file to split, select *Split .PXT Data* a window similar to that in figure below will appear:

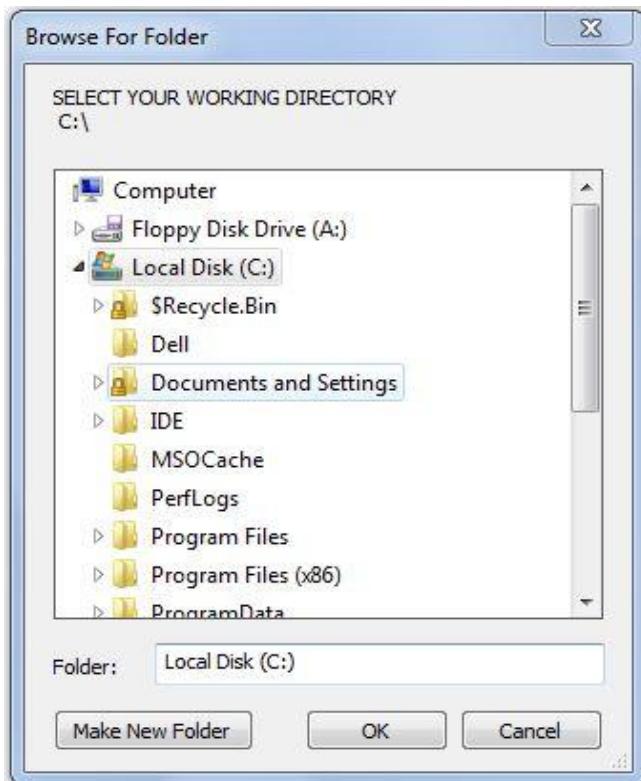
- **Select the Data file to split:** on the left side will appear the list loaded in the memory of the XPS-Analysis software. Select the one you want to split with the radio-button;
- **Select the group of corelines:** the checkbox allows you to select individual corelines you want to separate from the others. In the example a group of six coreline are selected.
- **Select and Save Core-Line** 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. The previously selected core-lines are marked with “#”
- **Exit** button: to terminate the splitting operation.



This example shows a typical Scienta datafile containing 64 different spectra.
Each of these spectra can be selected individually.

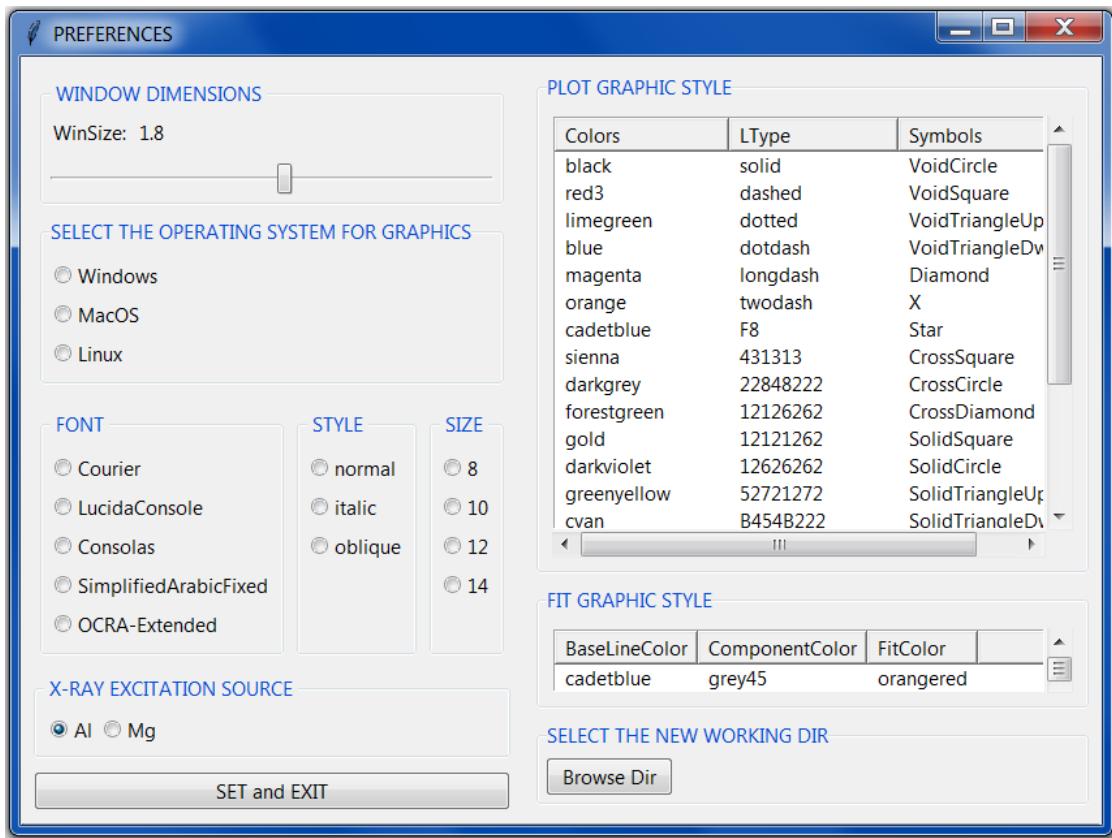
- ⇒ **REMOVE CURRENT XPS-SAMPLE:** you can remove the current XPS data from the list of loaded XPS-sample data (i.e. from the software memory);
- ⇒ **REMOVE ALL XPS-SAMPLES:** you can remove all the XPS data from the list of loaded XPS-sample data (i.e. from the software memory) at once;
- ⇒ **SET THE 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.

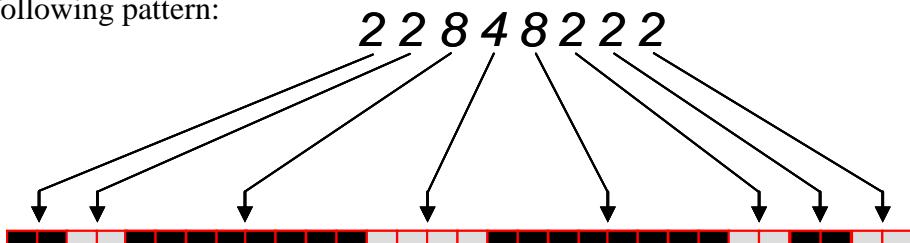


- ⇒ **PREFERENCES:** here one can select the screen size and the fonts used in tables.
In Preferences it is possible to set the Analysis Window size and Font Styles, colors, linestyle and symbols for plot and the default X-ray source:
- *Window dimensions*: sets the dimension for the *Analysis*, *Extract from Survey* and *Sprucing Up* windows:
 - A *slider* allows the selection of the optimal window dimension for the analysis graphic window.
 - *Window device*: select the device used by R to open a graphic window. The appropriate device is dependent of the computer operating system:
 - **MicroSoft device**: device for MS-windows systems;
 - **MacOS device**: for Apple operating systems;
 - **Linux device**: for linux operating systems.
 - *Font, Style Size*: Available Fonts and Styles to print Quantification Table or XPS-Sample Report:
 - **Fonts**: *Courier New*, *Lucida Console*, *Consolas*, *Simplified Arabic Fixed*, *OCR A Extended*;
 - **Styles**: *Normal*, *Italic*, *Oblique*
 - **Font Size**: 8, 10, 12, 14 pix. fonts are available for outputs such as the quantification

These preferences do not affect the R-console Font and Style



- *Window Dimensions*: defines the maximum dimension of the interactive window utilized in Analysis
- *Set the Operating System for Graphics*: the RStudio graphic window is a device which depends on the operating system utilized by your computer. To correctly open the graphic window select your operating system.
- *Font*: this is the font utilized in widgets, for example in the quantification widget. You can select among the list of fonts and styles the preferred ones.
- *X-ray excitation*: the anode used to generate the X-rays i.e. the energy of the X-ray source. By default is Al, Al K α radiation 1486.6eV.
- *Plot Graphic Style*: list Colors, Line Type and Symbols used in the graphic options Overlay. The list of parameters is editable. It is possible to customize the set of personal graphic parameters changing the Colors, the LineTypes and symbols.
For colors please refer to the Table of Colors at the end of this document.
For line type you may change the order of the line patterns or define your personal pattern using a string of digits. Each digit corresponds alternatively to black and white segments which indicate the segment length. For example the number 22848222 will then correspond to the following pattern:



where grey parts are white gaps.

Concerning symbols only 25 different shapes are defined in R. In *RxpsG* the default symbol order of R was changed to select the more suitable void/solid symbols. When data are plotted, RxpsG starts using the symbols in the order set in the *XPSPreferences*.

You can freely personalize the symbol order acting on the list of symbol names. Pay attention to use exactly the same symbol names as those listed in the *XPSPreferences* for making the program to work correctly.

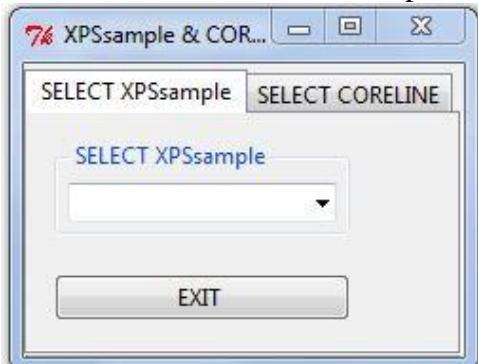
The R symbols with the correspondent R index are plotted following the RxpsG order. Symbols are also listed in the table the displayed in the following figure

R symbols with the correspondent index						R index	RxpG index	Symbol Name
○	□	△	▽	◇		1	0	VoidCircle
1	0	2	6	5		0	1	VoidSquare
						2	2	VoidTriangleUp
						6	3	VoidTriangleDwn
						5	4	Diamond
●	■	▲	▼	◆		16	5	SolidCircle
16	15	17	25	18		15	6	SolidSquare
						17	7	SolidTriangleUp
						25	8	SolidTriangleDwn
×	*	⊗	⊕	◇		18	9	SolidDiamond
4	8	7	10	9		4	10	X
						8	11	Star
						7	12	CrossSquare
⊗⊗	田	□	⊗	+		10	13	CrossCircle
11	12	14	13	3		9	14	CrossDiamond
						11	15	DavidStar
						12	16	SquareCross
●	○	□	◆	▲		14	17	SquareTriang
20	21	22	23	24		13	18	CircleCross
						3	19	Cross
						20	20	Bullet
						21	21	FilledCircle
						22	22	FilledSquare
						23	23	FilledDiamond
						24	24	FilledTriangleUp

- *Select new working Dir:* select your personal working directory. This will be the location where RxpsG will look for new XPSSamples to load.

ANALYSIS menu:

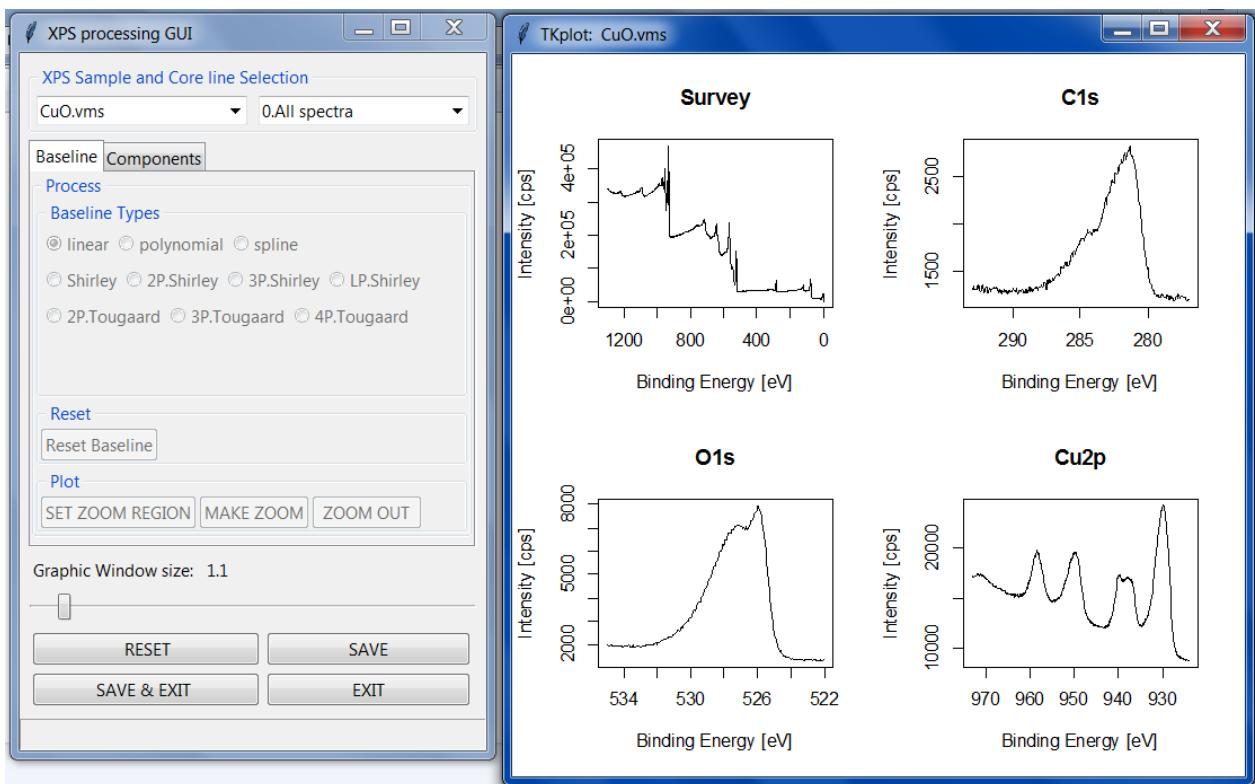
- ⇒ **SPECTRUM SELECTION:** option to select the actual XPS-sample/core line to analyze;



- **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 Core-Line

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



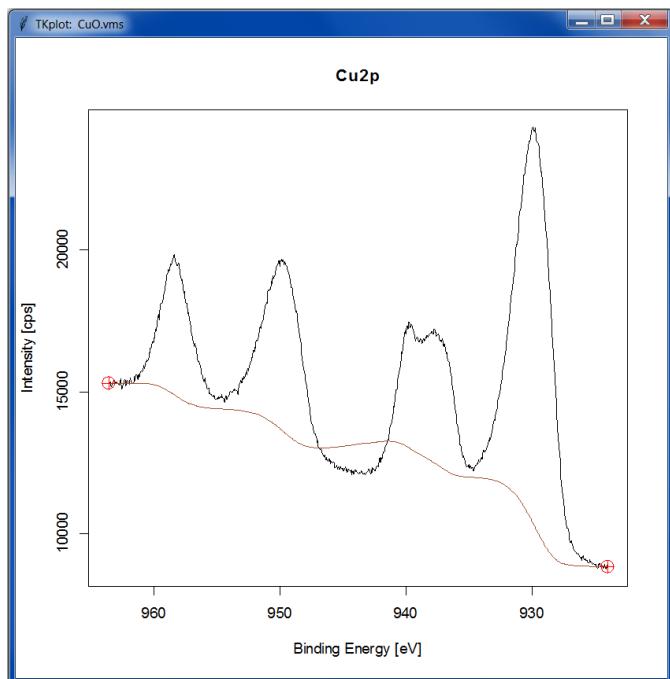
The GUI on the left is rather easy to use. On top, drop-down menu lists enable the selection of the XPS Sample and of the coreline. At beginning options are disabled until a coreline is selected. Upon selection, selection of the desired baseline is possible



The *Analysis* window is organized with a dropdown list to select the coreline, a 2page notebook to manipulate the Core-Line and some button to save or exit this option.

❖ **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.
- **Linear:** Select the desired baseline and define the edges of the fitting regions moving the red_cross cursor at the ends of the spectral region to be fitted. Immediately the baseline will be shown under the defined region.
- **Polynomial:** after defining the region boundaries, select the polynomial degree. The correspondent background will be shown;



- **Spline:** sometimes the Shirley algorithm does not provide useful background for Core-Line acquired on metals as shown in the next figure for the Cu 2p Core-Line

In these cases you can use the spline function to define a more appropriate background. Define the Region-to-Fit boundaries using the left mouse button. Then the right mouse button, select points (generally at the Regio-To-Fit edges and in the middle) where you want to constraint the spline: they will appear in green. Finally press the *Make Baseline* button to define the *spline* baseline.

- **Shirley:** applies the Shirley algorithm to compute the background for Core-Line acquired on metals:

$$F_n(i) = J(i) - k_n * \sum_{j=i+1} F_{n-1}(j) \Delta E$$

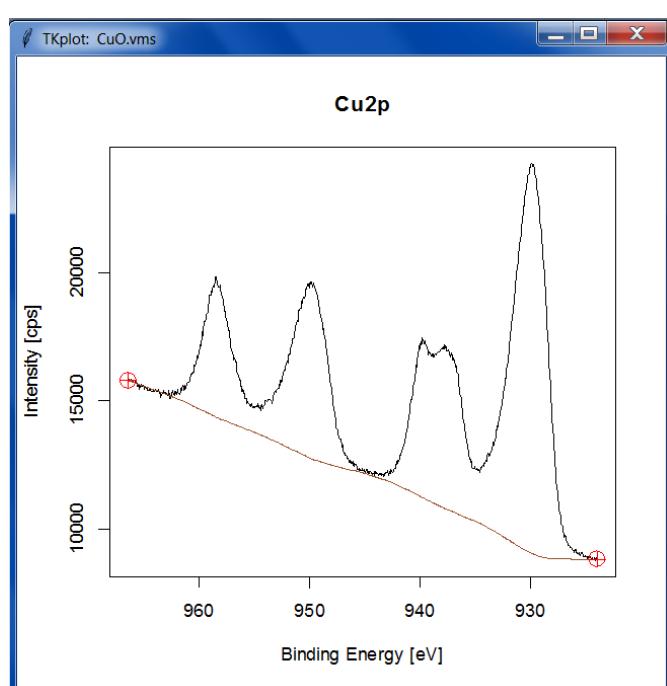
Where $F(i)$ is the corrected spectrum at point i , $J(i)$ is the acquired spectrum, ΔE is the energy step, k_n is a constant found by requiring $F_n(i)=0$. The Shirley background is generally computed with the Proctor and Sherwood algorithm [A. Proctor, P.M.A. Sherwood, Anal. Chem. 54 (1982) 13] The algorithm of Proctor and Sherwood is based on the assumption that for every point of the spectrum, the background intensity generated by a photoelectron line is proportional to the number of all photoelectrons with higher kinetic energy. The background is then computed by iteration.

- **2P. Shirley:** it can be demonstrated that the Shirley background may be described through a *Shirley cross section* function K_S [J. Vegh, Surf. Sci. (2004), 563, 183.]

$$K_S(T) = B_S * T / [C_S + T^2] \quad T=E'-E \text{ describes the energy loss.}$$

K_S describes the probability that an electron of energy E propagating in the material can lose energy $E'-E$ per unit path length. B_S coefficient is the “scattering intensity” and is automatically computed to make the background to assume the spectral intensity at high BE (low KE) edge of the region where the background has to be defined. C_S describes the “distribution width” $C_S = 2500$ was evaluated for a class of elements with core lines at different BE. The Shirley background can be described as:

$$S(E) = \int K_S(E'-E) (J(E') - S_0(E')) dE'$$



where $J(E)$ is the measure spectrum at energy E , $S_0(E')$ describes an initial estimate of the background (a simple base-level). This method simplifies the computation of the Shirley and avoids divergences when the background crosses the acquired spectrum.

- **3P. Shirley:** it may happen that also the 2P. Shirley algorithm crosses the spectrum. Even if it does not diverge, it gives a non appropriate background description. The 3P. Shirley algorithm uses a modified expression of the Shirley

cross section function. Now the Shirley cross section is multiplied by the factor $1 - \exp(-Ds^*(E'-E))$ which concurs to lower the background intensity below the spectral features. The modified Shirley background now is described by:

$$S(E) = \int [Bs T (1 - e^{-Ds^*T}) / (Cs + T^2)] * J(E) dT$$

where $T = E' - E$ is the energy loss

In the example shown in the figure a 3p Shirley was applied with Distortion parameter = 0.3.

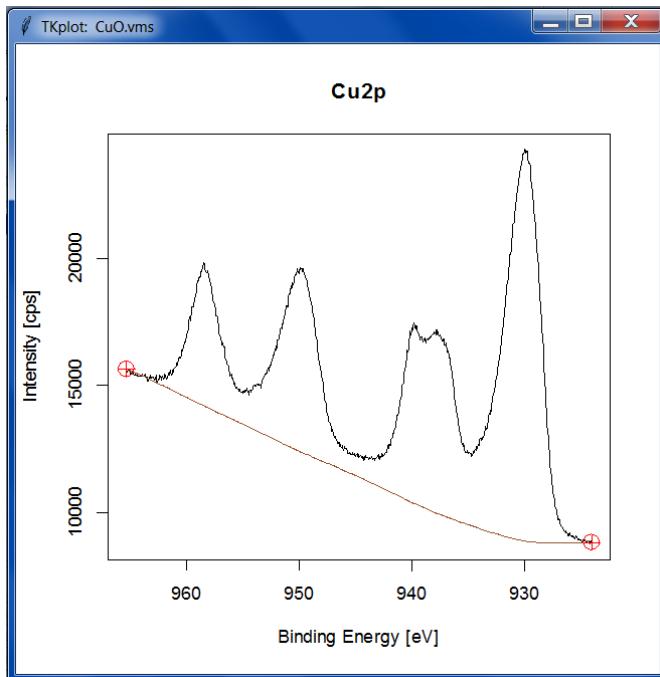
- **LP.Shirley:** combines the *Shirley cross section* function with a linear weakening polynomial introduced by Bishop [D.Briggs and M.P. Seah “Practical Surface Analysis”, vol. 1, J. Wiley ed.]

$$K_S(T) = B_S T * (1 - m T) / (C_S + T^2) \quad T = E' - E \text{ is the energy loss}$$

The Bishop polynomial weakens the background contribution as the energy loss increases. The program requires the user to define the m parameter ranging between 0 and 1.

- **2P.Tougaard:** for metallic elements S. Tougaard [S. Tougaard, Sol. Stat. Comm. (1987), 61(9), 547] was able to define a *universal cross section* K_T defined by

$$K_T(T) = B_T T / [C_T + T^2]^2$$



K_T describes the probability that an electron of energy E through scattering processes will lose energy $E' - E$ per unit path length traveled in the solid. Then the background subtracted spectrum $F(E)$ at energy E may be expressed as [S. Tougaard, Surf. Sci. (1989), 216, 343]:

$$F(E) = J(E) - B_T \int K_T(E' - E) J(E') dE'$$

where $J(E)$ is the measured spectrum. The parameter B_T is automatically computed to make the background 1 intensity as high as that of the core line at the high BE (low KE) edge. $C_T = 1643\text{eV}$ was estimated by Tougaard for a class of metallic elements.

In this example the classic 2P Tougaard background was calculated

- **3P.Tougaard:** for non-metallic elements S. Tougaard [S. Tougaard, J. Vac. Sci. Technol. (2003), A 21(4), 1081, S. Hajati, Surf. Sci. (2006), 600, 3015] proposed a modified universal cross section K_{TM} defined by

$$K_{TM}(T) = B_T T / [(C_T + T^2)^2 + D T^2]$$

where C_T and D_T are constants characteristic of the solid. They were evaluated by Tougaard for a class of elements and are fixed to $C_T = 551\text{eV}$ and $D_T = 436\text{eV}$. Again B_1 is computed automatically in order to make the background intensity equal to that of the core line at the high BE (low KE) edge. Then the background subtracted spectrum $F(E)$ at energy E may be expressed as :

$$F(E) = J(E) - B_T \int K_{TM}(E' - E) J(E') dE'$$

where $J(E)$ is the measured spectrum.

- **4P.Tougaard:** for general use R. Hesse and R. Denecke [R. Hesse et al. Surf. Interface Anal. (2011), 43, 1514] added a further modification to the previous version of the universal cross section K_{TM} introducing the parameter C' so that now the cross section becomes a four parameter cross section K_{T4} :

$$K_{T4}(T) = B_T T / [(C_T + C'T^2)^2 + D T^2]$$

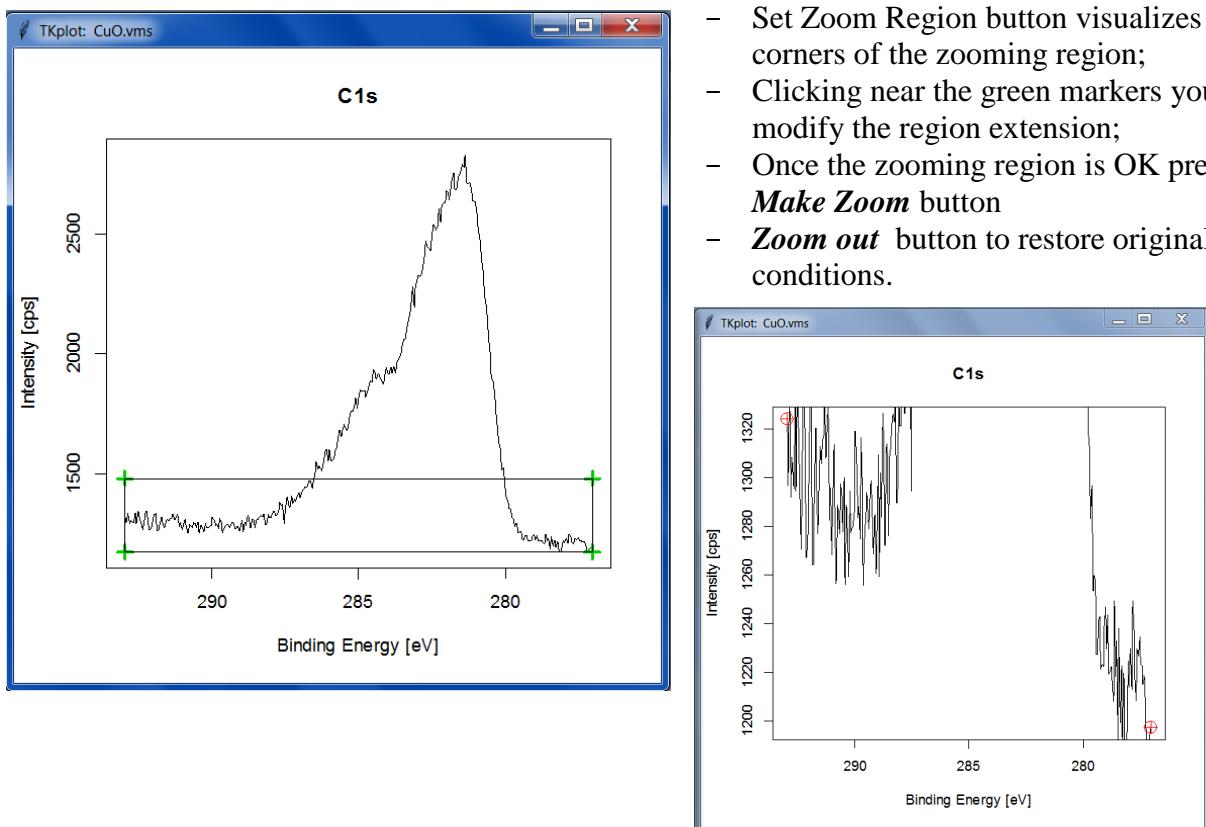
where C_T and D_T are fixed constants assuming same values $C_T = 551\text{eV}$ and $D_T = 436\text{eV}$ as in the 3P.Tougaard K_{TM} cross section function. Then the background subtracted spectrum $F(E)$ at energy E may be expressed as :

$$F(E) = J(E) - B_T \int K_{T4}(E' - E) J(E') dE'$$

where $J(E)$ is the measured spectrum at energy E . The parameter C' is manually adjusted to obtain the best background below the spectral data.

N.B. please refer to XPS surface analysis texts for the selection of the appropriate background

- **Zooming** sometimes it is useful to zoom spectral regions to better define the baseline edges.

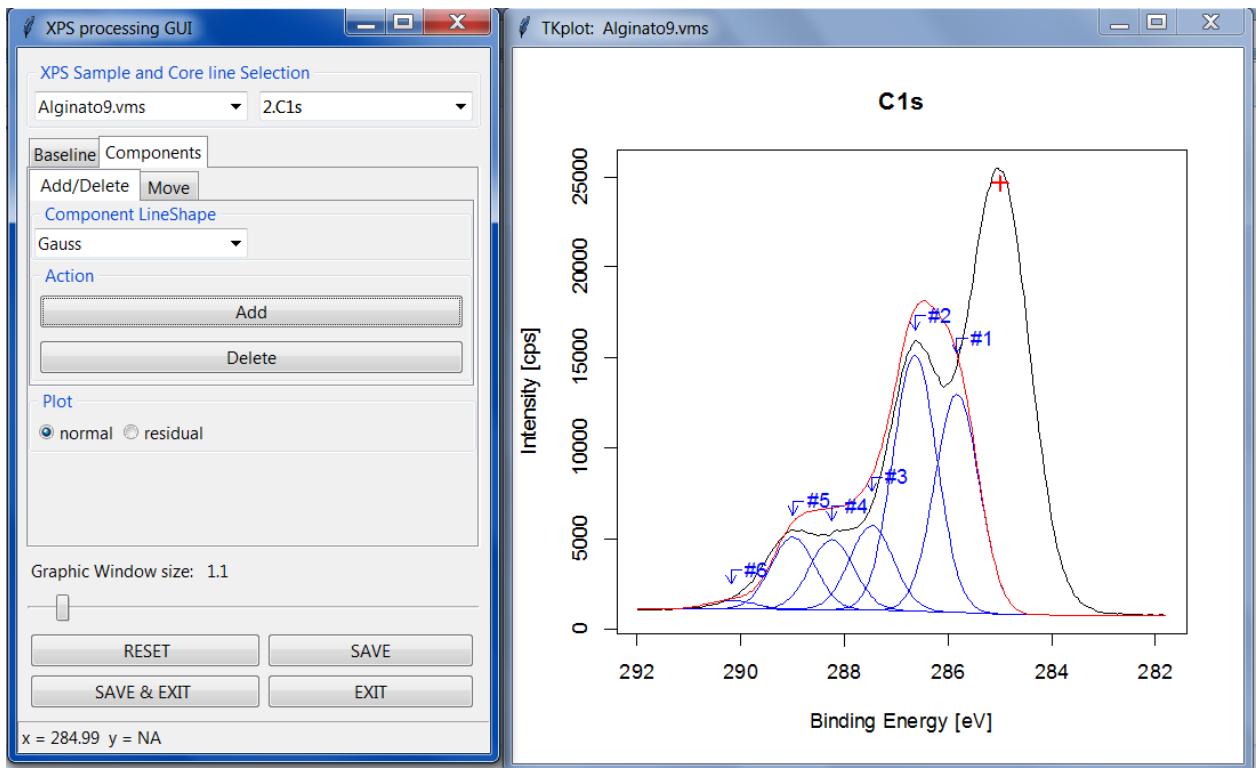


- Set Zoom Region button visualizes 4 corners of the zooming region;
- Clicking near the green markers you can modify the region extension;
- Once the zooming region is OK press the **Make Zoom** button
- **Zoom out** button to restore original plotting conditions.

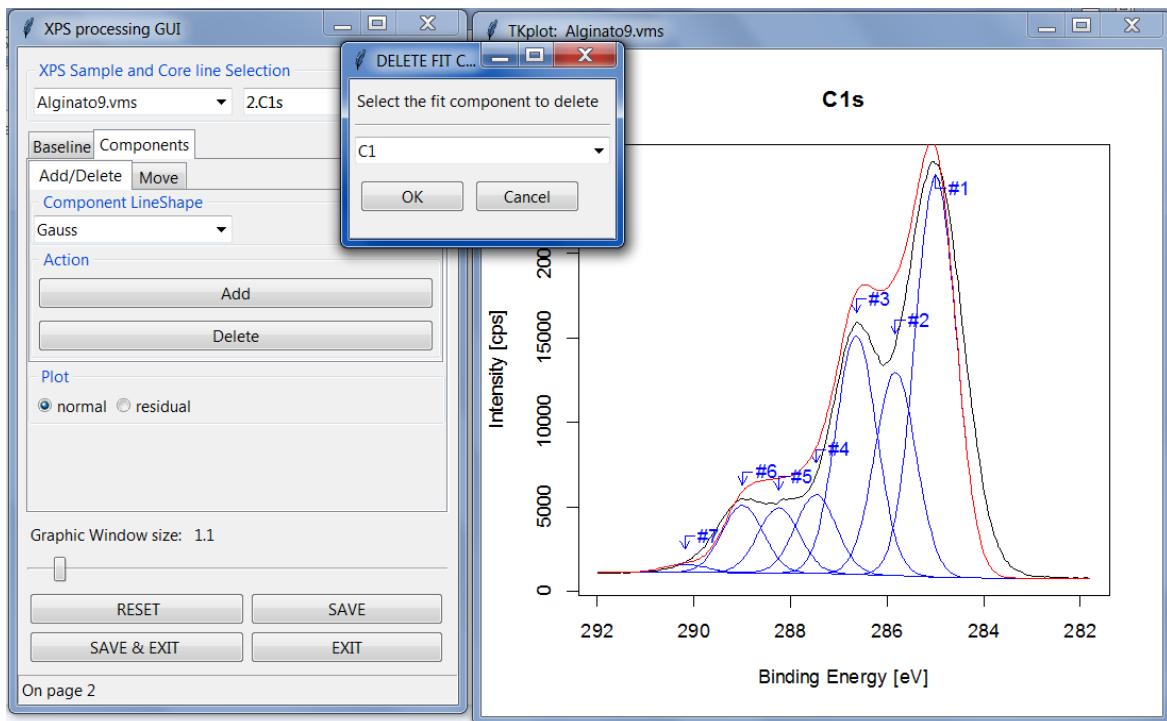
- ❖ **Components:** the *components* notebook page contains the **Add/Delete** option

Under the

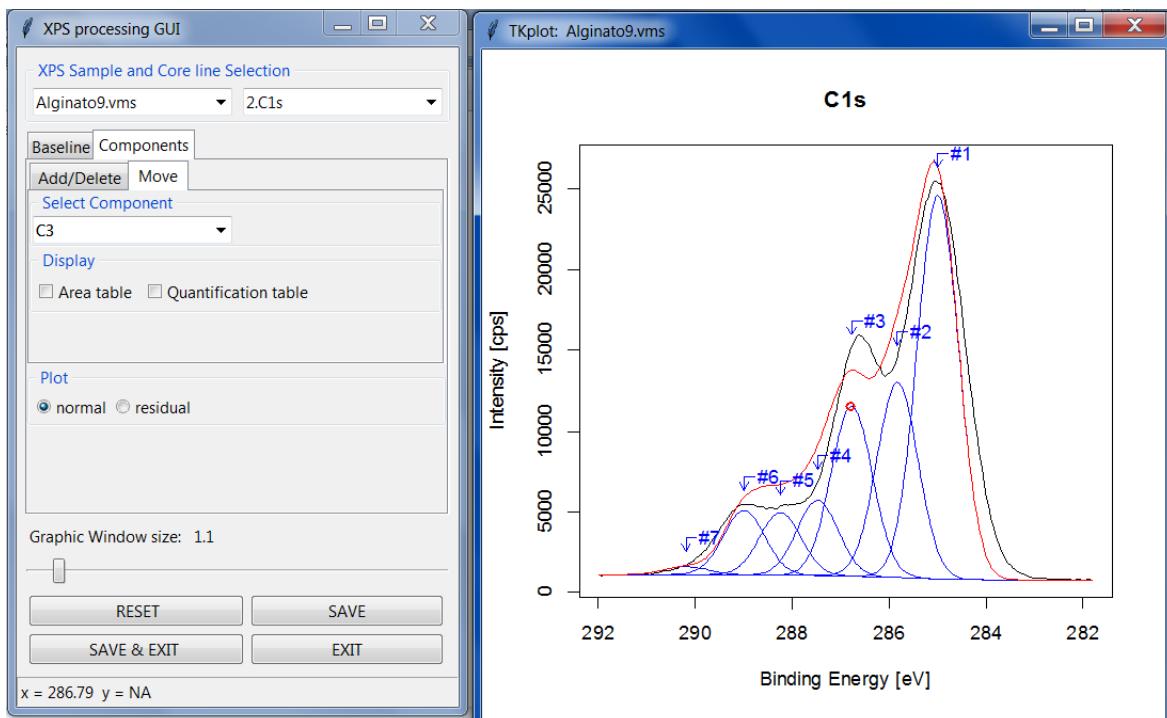
- **Add/Delete** : option to add/delete fit components once the baseline is defined. Now the cursor changes in a red cross  . Sequence of operations:
 - **Component Lineshapes:** option to select the function for the best fit procedure. Gaussian component are selected by default a complete list of functions are listed in the drop-down menu. The list includes the following functions: Gauss, Lorentz, Voigt, Sech2, GaussLorentzProd, GaussLorentzSum, AsymmGauss, AsymmVoigt, AsymmGaussLorentz, AsymmGaussVoigt, AsymmGaussLorentzProd, DoniachSunjic, DoniachSunjicTail, DoniachSunjicGauss, DoniachSunjicGaussTail, SimplfiedDoniachSunjic, ExpDecay, PowerDecay and Sigmoid. Suitable lineshapes can be freely selected and added to the spectrum. Different lineshapes can be added to fit a given core line.
 - **Component position:** in the graphical window just click with the mouse on the desired position. A red cross will appear indicating position and intensity of the fitting component ;
 - **Add:** pressing this button the fitting function will be added to the spectrum in the chosen position (see figure). Add as many components as you need and then SAVE the spectrum.



- **Delete:** pressing this button fitting components can be removed. A Dropdown list will be available to select the component to remove. Removing fitting components will cause the loss of constraints on the fitting parameters.



- **Move:** it is possible to adjust component positions/intensity to the spectrum to make the fitting procedure easy and faster.
 - **Select Component:** select the fitting component you want to adjust. A ● marker will appear in correspondence of the selected component (the C3 is shown in the example in the next figure);
 - **New component position:** just click with the left mouse button in the place where to move the marker of the selected component. The Core-Line with the selected component in the new position ad the correspondent sum of components will be shown.



- **Area Table, Quantification Table:** if checked moving the fit component you can control the area of the fit components or the quantification table.

Plot dimensions

- **Graphic Window size:** a slider allows adapting the TKgraphic window to the screen dimensions of the computer.

Button options

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

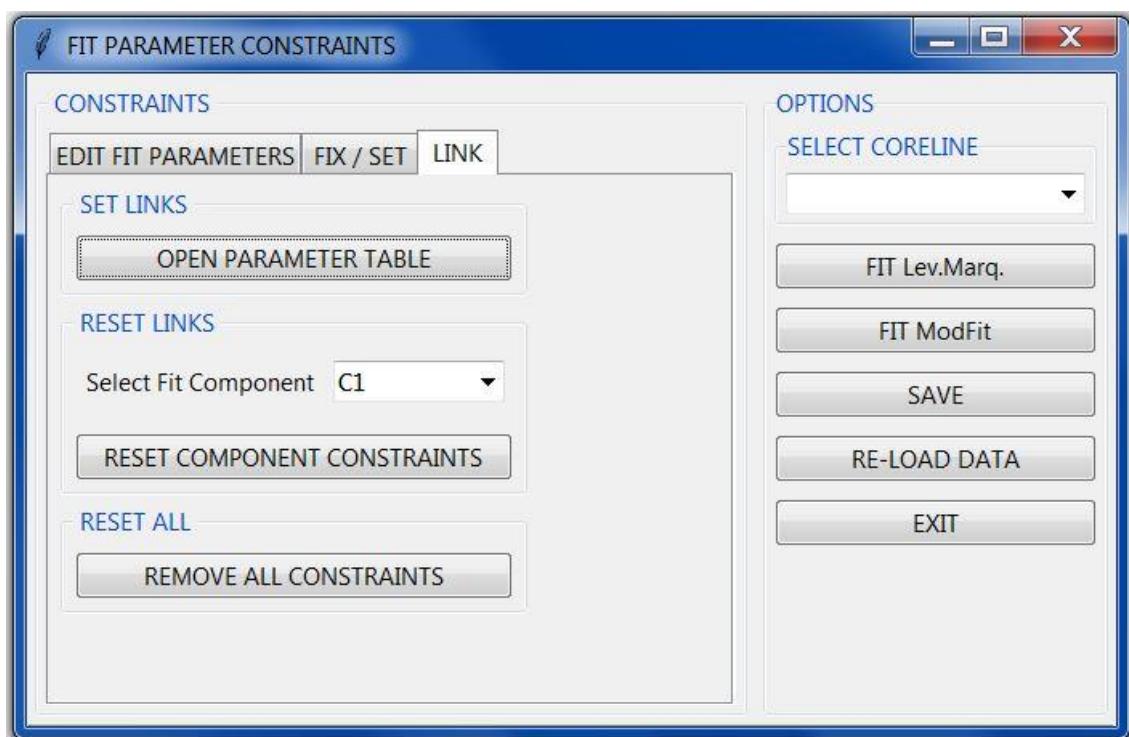
N.B. in *linux* operating system the control of the mouse buttons and cursor positions is different and the The *Analysis* GUI and the selection of positions on the graphical window with mouse cannot be active at the same time as in PC with *windows* operating system. When the cursor position is active for reading positions, the *Analysis* GUI is OFF and the user cannot select any option.

In *linux* when the *Analysis* option is run the user must select the Core-Line and then the kind of Baseline to apply. This last choice activates reading the mouse positions on the graphical window.

=> Cursor positions are assigned by pressing the left mouse button;

=> To proceed this process must be always stopped by pressing the right button. This enables the GUI option to become active and be selected.

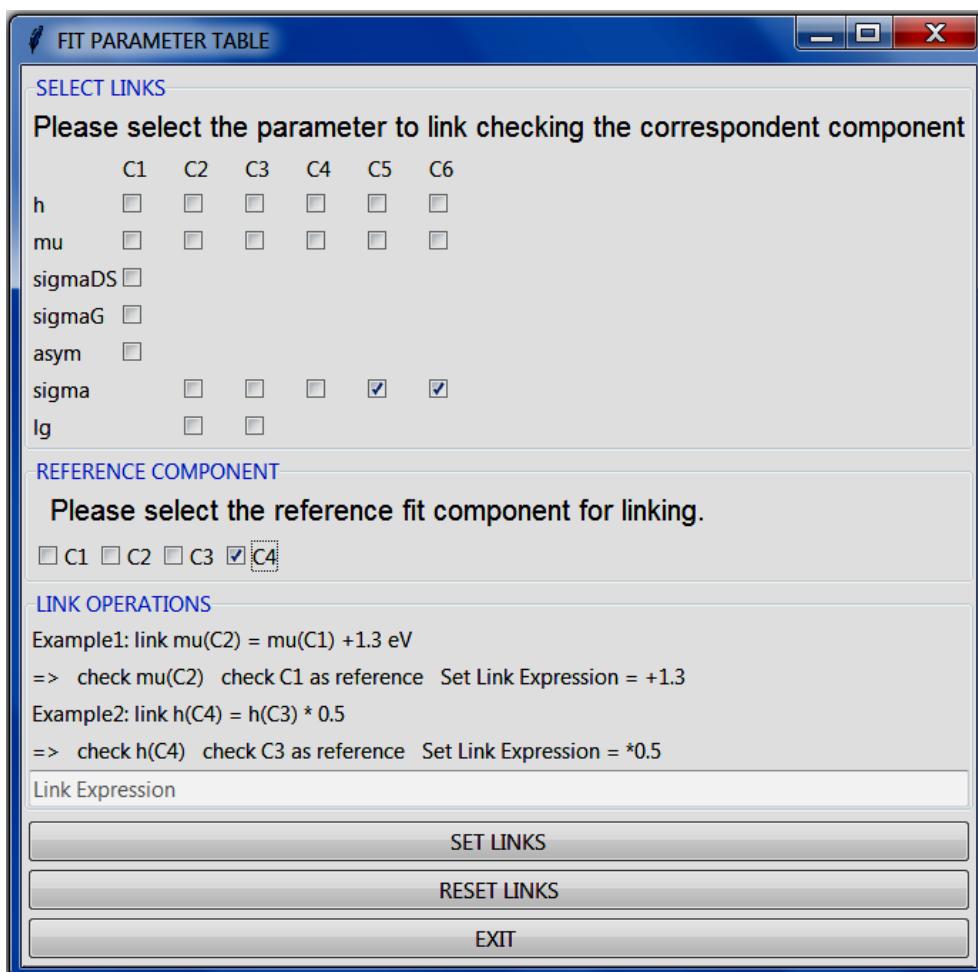
⇒ **FIT CONSTRAINTS:** option to set constraints among the fitting components set for a given coreline. This option opens the following window:



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 fit component to that of another component. Three buttons can be pressed to activate different options:
 - ***Open Parameter Table***: open the Parameter Table to set links;
 - ***Reset 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;

N.B. when ***Open Parameter Table*** is pressed the following panel showing the fit parameters of the curves utilized to fit the selected Core-Line is activated.



The first column of the Table indicates the parameter name. The first table row, *C1 ...Cx* indicates the name of the components utilized to fit the actual Core-Line. Checkboxes are generated only if the correspondent parameter is contained in the parent component function. In the example is shown the Parameter Table of a fit performed using different lineshape functions (*). The Component **C1** is a Doniach-Sunjic-Gauss function described by the five parameters **h**, **mu**, **sigmaDS**, **sigmaG**, and **asym**. The Component **C2** and **C3** are Voigt function described by 4 parameters **h**, **mu**, **sigma**, and the Lorentzian/Gaussian mix **lg**. The parameters **h**, **mu**, **sigma** appear also in **C4**, **C5** and **C6**.

In the *Reference Component* frame initially all the fit components appear because all of them can be potentially selected as reference for the link. However, upon parameter/component selection in this area will be shown only the possible reference components which can be selected. Observe that the *sigma* act differently in the *Voigt* or *Gaussian* lineshapes. For this reason it is recommended to not link together parameters belonging to different fitting functions.

In the example the parameter **sigma** of components C5, C6 are linked to the sigma of the remaining components C4.

In the *Link Operation* frame it is possible to set a constraint on the link.

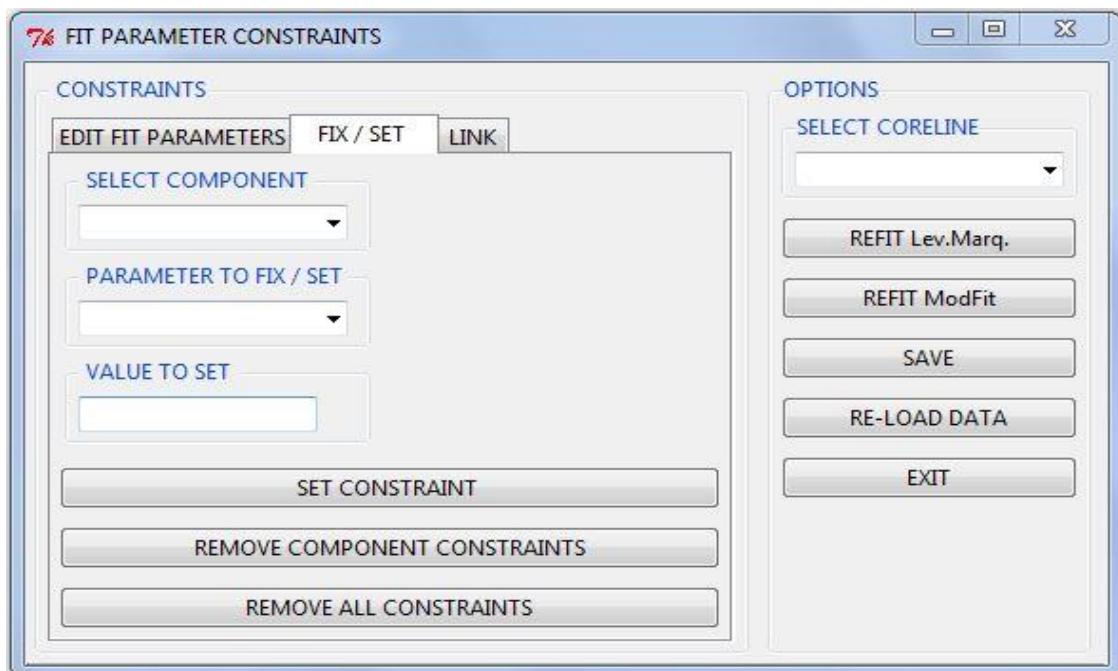
Example 1: if we want to link the intensity of component C2 be 0.5 that of component C1 we will check the *h* parameter of component C2, select C1 as a reference component and write ***0.5** in the *Link Operations*.

Example 2: if we want the energy position of component C4 is that of component C3 + **1.3eV** we will select the parameter *mu* of component C4, select C3 as reference component and write **+1.3** in the *Link Operations*.

(*) **NB:** here different lineshapes are selected to fit a Core-Line just to show how to set links among fitting components. Generally fits are performed using the same function for each of the fitting components. Physical reasons should justify the use of different lineshapes.

❖ **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;

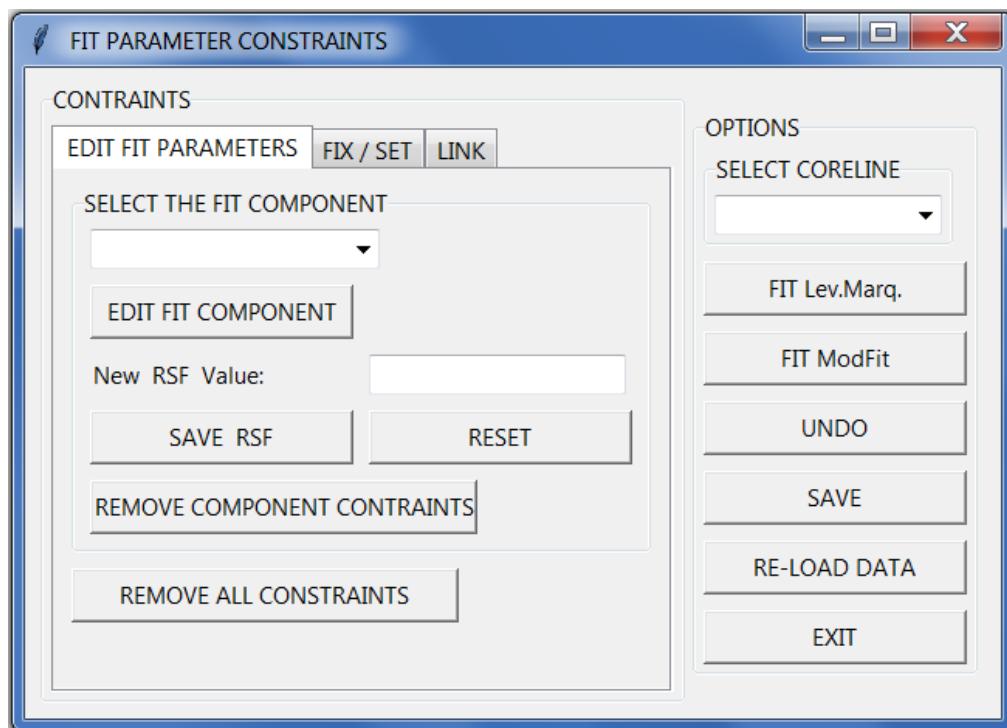


- ❖ **Edit Fit Parameters:** this page is used edit the table of fitting parameter for each of the fitting components.

After selection of the Fit Component:

- the *Edit Fit Component* button opens a window summarizing all the fitting parameters of the correspondent core line and it is editable. Just clicking on the desired parameter you can change the value or its limits (min, max values). Press enter to input the parameter Then press the button *Save Parameters* to save the changes the core-line fit will be replotted following the new parameter values.

VarNames	start	min	max
h	7858.94599892418	0	47595.
mu	284.900899213254	283.499860582119	286.49
sigma	1.42474429647447	0.1	10

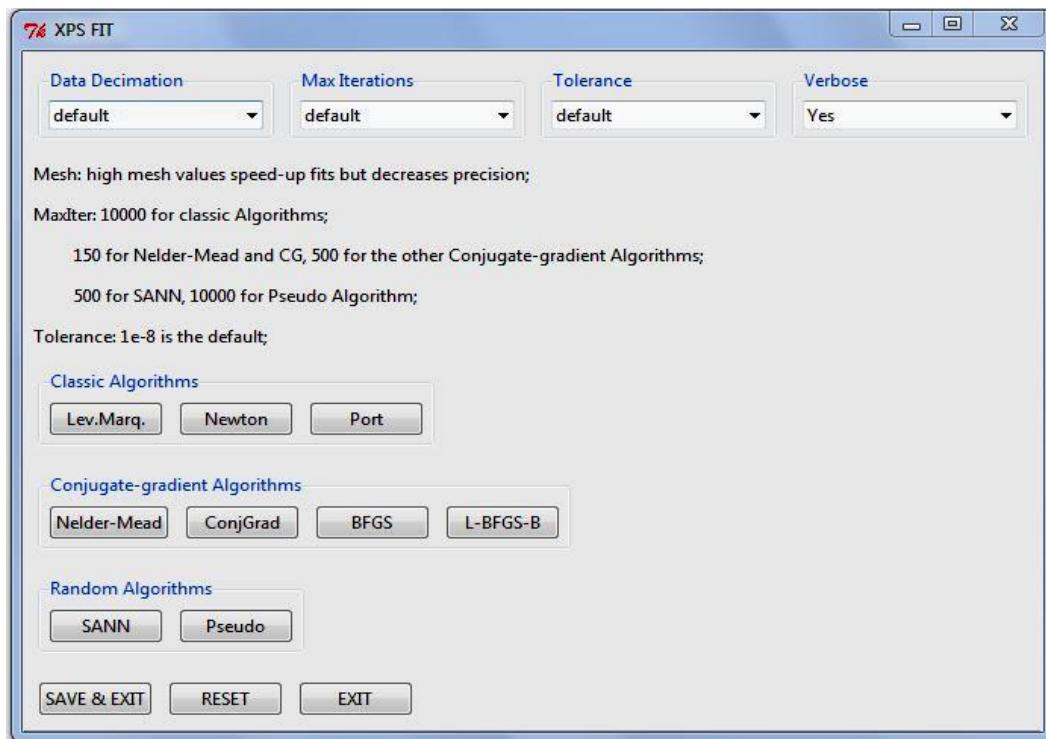


- It is possible to change the fit component RSF which is then saved pressing the *SAVE RSF* button
- Remove constraints related to the selected Fit Component

The *Remove All Constraints* button removes all the constraints from all the fit components

Common to all the three pages are the following options:

- **Refit Lev.Marq.:** this button runs the fit using the Levenberg Marquardt algorithm;
- **Refit ModFit:** this button opens a fitting option window (see below);
- **Save** button: the fit constraints MUST be saved before running the best fit algorithms;
- **Reload** button: loads the actual Core-Line and fit information from main memory. This allows a use in combination with *Move Component* to optimize fits and bond stoichiometries. See *Move Component* option for more details.
- **Refit ModFit:** this button opens the following window:



It could happen there are local minima preventing the convergence of the Levenberg-Marquardt algorithm. In this case it is possible to refit the same spectrum 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 it could be reasonable to *decimate* the set of data due to the time required for fitting (Conjugate-gradient, Random algorithms). Select the decimation level (i.e. 3 means 1 data over three), the number of iteration and the tolerance. (indications are shown in the window).

=> *Classic algorithms*: Levenberg-Marquardt 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.

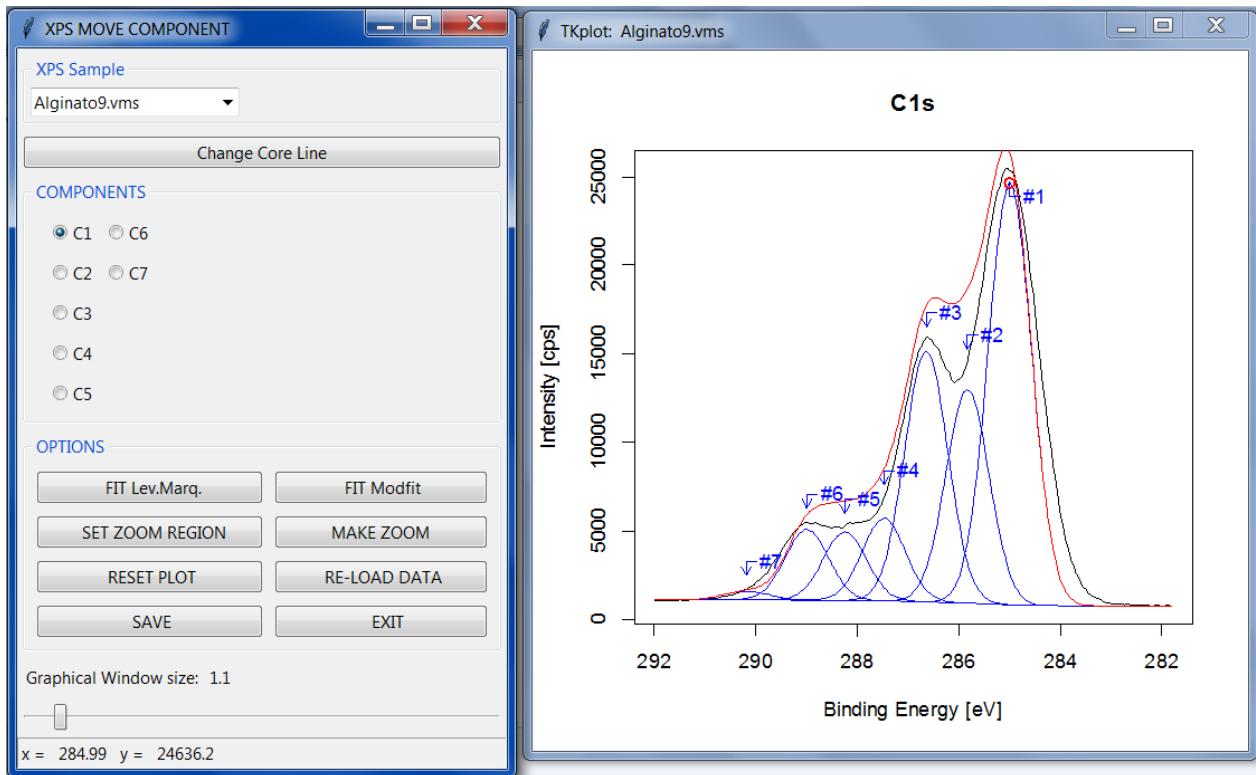
Decimation=Yes in case of consistent number of data to fit, *MaxIteration=500(Sann)* *10000(Pseudo)*, *Tolerance=1e-8*.

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 options are available also directly from the Analysis menu

- ⇒ **FIT LEV.MARQ.:** option to run the Levenberg Marquardt algorithm to fit spectral data from main panel. See the *Analysis* option for more details.
- ⇒ **FIT MODFIT:** option to run the ModelFit interface to fit spectral data from main panel. 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 options on the left side.

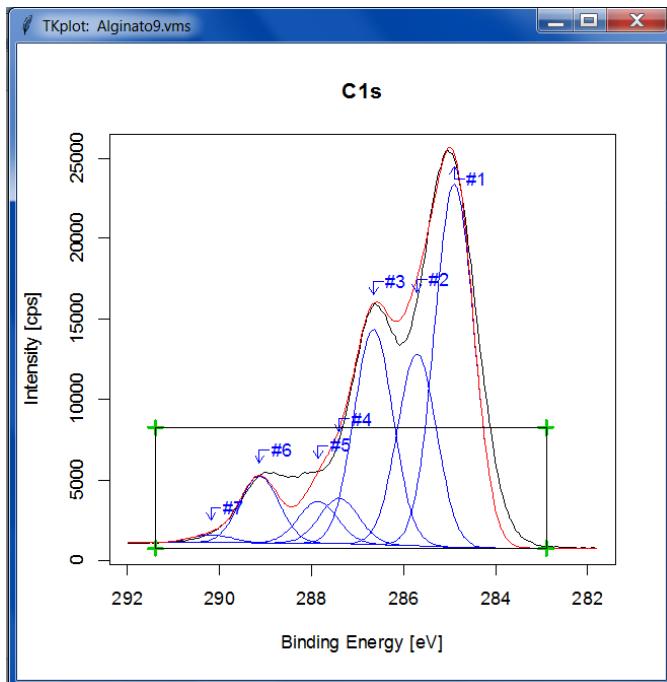
- **XPS sample:** when opening the *Move Component GUI* the active CoreLine of the current XPS Sample is shown. A drop-down list of the loaded XPS Samples allows selection of a different XPS Sample.

- **Change Coreline:** enable selection of the desired coreline. The selected component will be indicated on the plot by the ● marker;
- **Select Component:** radio buttons enable the choice of the fit component for changing its position and intensity.
- **Mouse pointer:** just going with the mouse on the graphic window the mouse pointer changes from the classical mouse  arrow to cross . The cross indicates the new position for the selected component identified by the red circle in the graphic window. Clicking with the  pointer will make the component to be placed in the new position and the fit 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 Core-Line to adjust fitting components;
- **Fit Lev. Marq.:** after moving components, it is possible to run the Levenberg Marquardt algorithm to refit from the *Move Component* panel the Core-Line starting from the new component position;
- **Fit ModFit:** after moving components, it is possible to run the ModelFit interface from the *Move Component* panel, to refit the Core-Line starting from the new component position;



- **Set Zoom Region:** select the region to zoom defining the two opposite corners by using the RIGHT mouse button. Green crosses will appear and a square will show the selected area. By clicking near each individual green cross it is possible to modify the extension of the region.
- **Make Zoom:** when correctly defined the zooming area press the *Make Zoom* button to expand the selected area;

- **Reset Plot:** to go back to the original plot dimensions.
- **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 and intensity 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 *Save* 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.

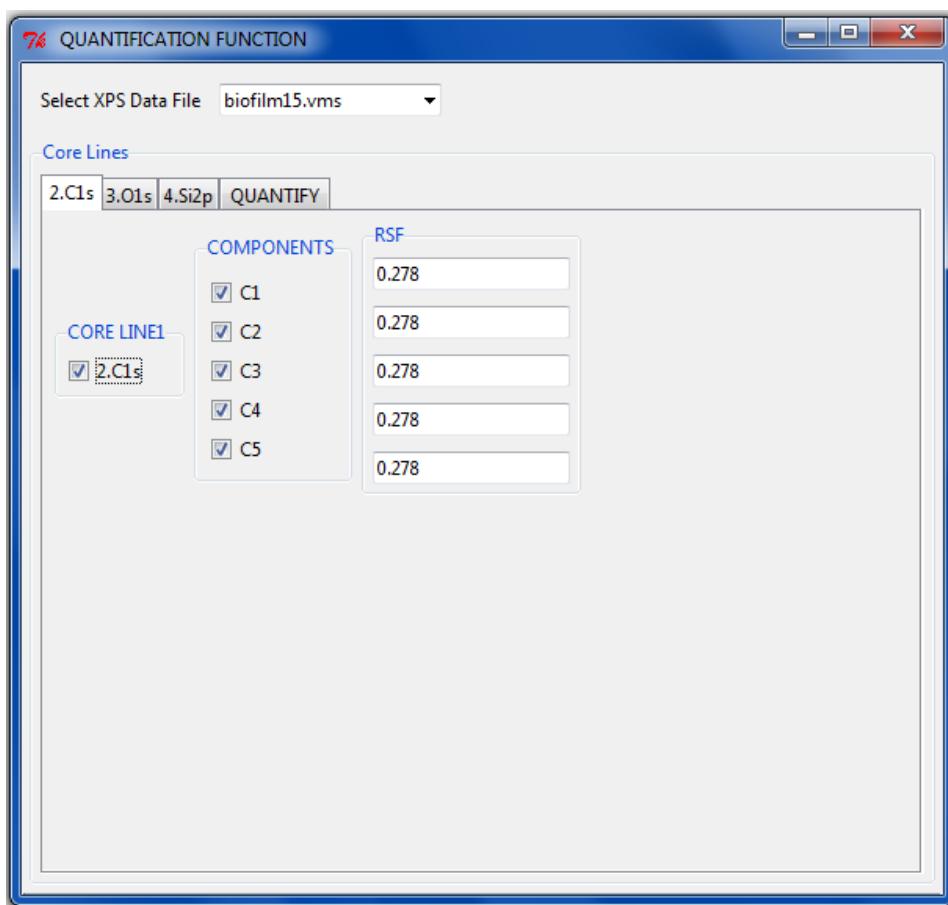
- ***Exit*** button: to exit the Move Component procedure.

N.B. in *linux* operating system the control of the mouse buttons and cursor positions is different and the The *Analysis* GUI and the selection of positions on the graphical window with mouse cannot be active at the same time as in PC with *windows* operating system. When the cursor position is active for reading positions, the *MoveComponent* GUI is OFF and the user cannot select any option. In *linux* when the *MoveComponent* option is run the user must select the Core-Line and then the kind of Baseline to apply. This last choice activates reading the mouse positions on the graphical window.

=> Cursor positions are assigned by pressing the left mouse button;

=> To proceed this process must be always stopped by pressing the right button. This enables the GUI option to become active and be selected.

⇒ **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 page is 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 that of

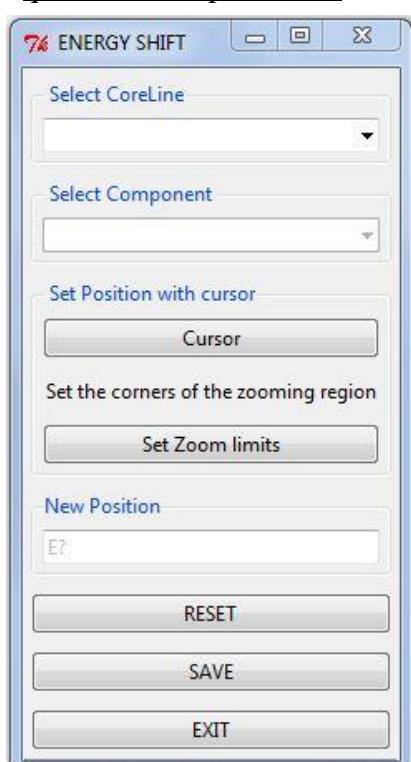
- each component can be changed if needed;
- By default for each element with defined baseline/fit all the fit components are included and the Sensitivity Factors are those provided by the manufacturer of the XPS instrument utilized (Kratos/Scienta RSF automatically set by the program).

- **XPS-Sample:** whenever a list of XPS Samples is analyzed, it is possible to select one them and perform the quantification;
- **Checkboxes:** select the Core-Line and the fit components needed for the quantification. By default all the fitted corelines and all the fit components are selected;
- **RSF:** it is possible to selectively modify the sensitivity factor of the Core-Line or of the desired fit components. By default the RSF is that defined by the Instrument Manufacturer(Scientia or Kratos);
- **Quantify page – quantify button:** runs the quantification procedure and quantification table shown in the Rstudio console;
- **Exit button:** to exit the quantification procedure.

NB1: Quantification Table appears in the text-window ready for cut-and-paste in a word document.. It is possible to select font/style preferences to adapt the quantification table to the word doc format.

NB2: The quantification table is also reported in the R-console using Tabs instead of spaces. This allows to cut-and-paste in a word doc and the text is ready to be converted in a table (in word: insert→ table → convert text to table → separate text at tab).

IMPORTANT: it is possible to quantify elements derived from the survey using the *Extract from survey* function. Because the different PE used for the acquisition, the software automatically computes a *Normalization Coefficient* by comparing a high-resolution coreline with the parent spectrum extracted from the survey. The *Normalization Coefficient* renders the two spectra comparable in intensity: a plot is provided to check if the normalization operation is correctly performed. The *Normalization Coefficient* is applied to the extracted spectra and the quantification performed.



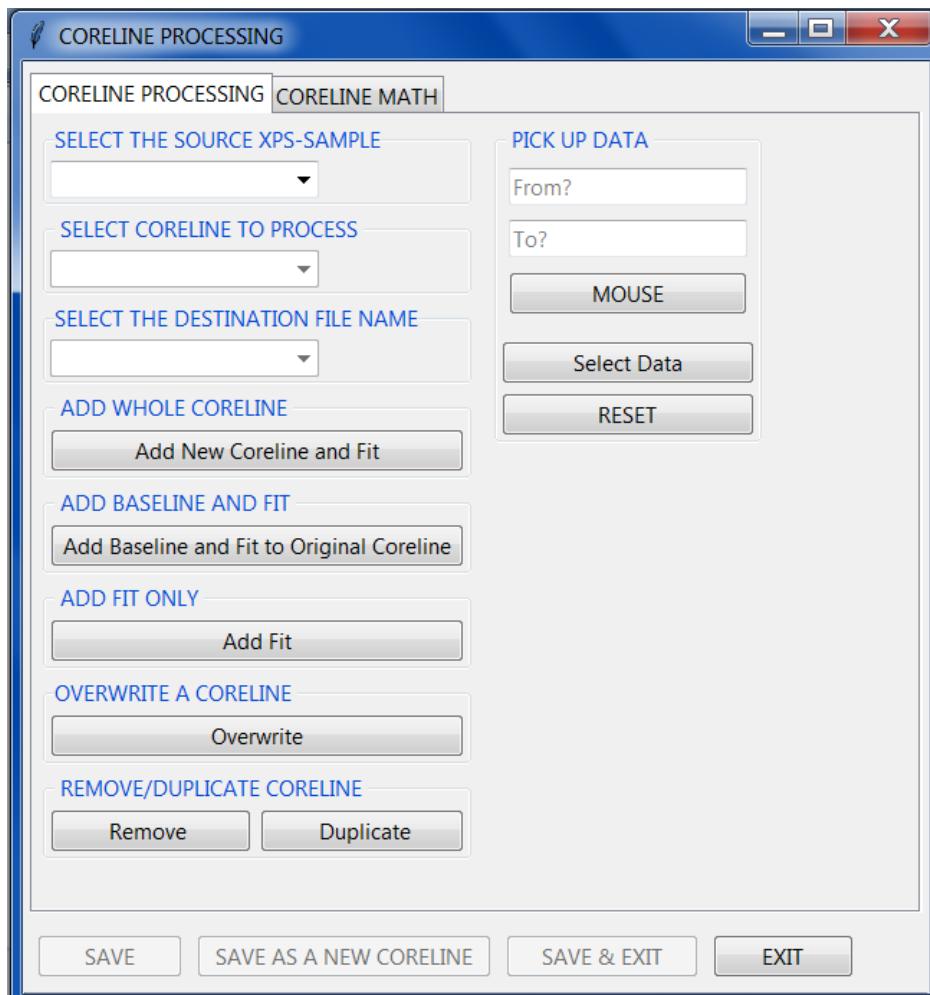
⇒ **ENERGY SHIFT:** this option is used to perform a binding energy shift on all the XPS-Sample spectra. When XPS spectra are acquired on insulating samples charge compensation is needed. Charge compensation causes a shift of the energy scale. It is possible to correct the shift using the *Energy Shift*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

- **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 contains CH_x and also oxidized components. Here a selection of the C1s component which has to be assigned to CH_x can be made.
- **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 in the graphical window having a 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:** 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 Core-Line 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 operation can be applied to the XPS-Sample spectra. The *Process Core-Line* 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!

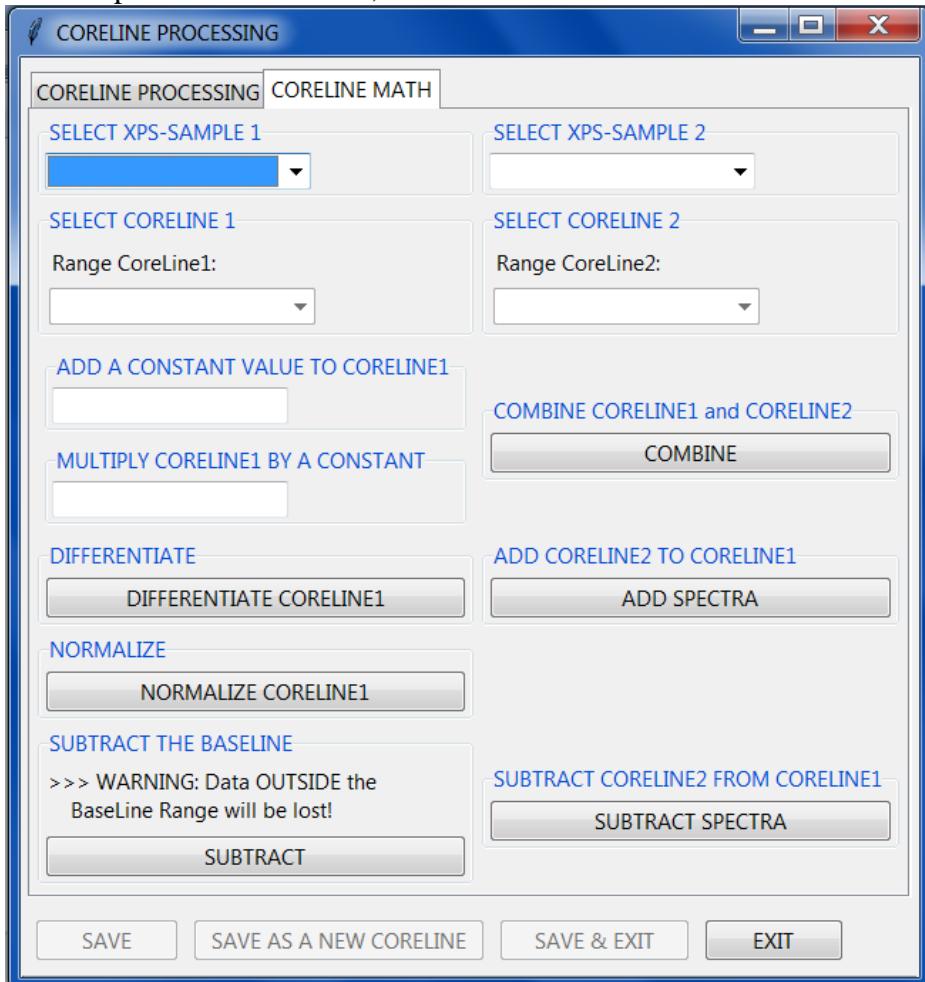
❖ **Core Line processing:** this page offers some options to simplify Core-Line analysis. In all the cases of repetitive analysis on similar XPS-Sample the *Process Core Line* GUI allows copying a fit on a virgin Coreline.

- **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 Core-Line which you want to process; *Select the operation you want to apply:*
- **Select the Destination FileName:** select the file name of the destination XPS-Sample in the drop down list of XPS-Sample names loaded in the software.
- **Add Core Line and Fit:** add the selected Core-Line from the source XPS-Sample and fit (if present) to the current XPS-Sample;
- **Add Fit to Original 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. Then the fit can be modified using Move Components option and refit.
- **Replace a Coreline:** replaces the existent Core-Line with that coming from the source XPS-Sample.
- **Remove a Coreline:** this button removes the selected Core-Line from the actual XPS-Sample
- **Duplicate a Coreline:** this button duplicates the selected Core-Line of the actual XPS-Sample. This option can be useful when different operations can be applied to the same coreline. For example: use different filters, the estimation of the VB top using different algorithms etc. These operations may be applied to the different copies of the Core-Line without losing the original data.
- **Save:** this button saves the new data in the software memory. After pressing this button you can select another Core-Line to process without exiting the procedure.
- **Save & Exit:** to save changes and conclude the *Process Core-Line* procedure.
- **Exit:** this button to quit the *Process Core-Line* procedure without saving any change.

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

- **Source XPS-Sample of Core-Line 1:** select the file name of the source XPS-Sample of Core Line 1 in the drop down list of XPS-Sample names loaded in the software.
- **Select Core Line1:** select the Core-Line which you want to process;
- **Add a Constant Value:** the Core Line 1 may be shifted Up/Down adding a positive/negative constant value;
- **Multiply by a Constant:** the Core Line1 may be amplified/decrease the spectrum intensity;
- **Differentiate:** makes the first derivative of the selected coreline. Generally the first derivative of XPS spectra is rather noisy. It is suggested (1) to make a copy of the Core-Line you want to differentiate (see duplicate option in the first notebook page); (2) apply a smoothing; (3) proceed with the differentiation on the smoothed coreline. The first derivative will be saved as a separated component of the Core-Line which can be exported in ascii.
- **Subtract Baseline:** the baseline will be subtracted from the Core Line 1;

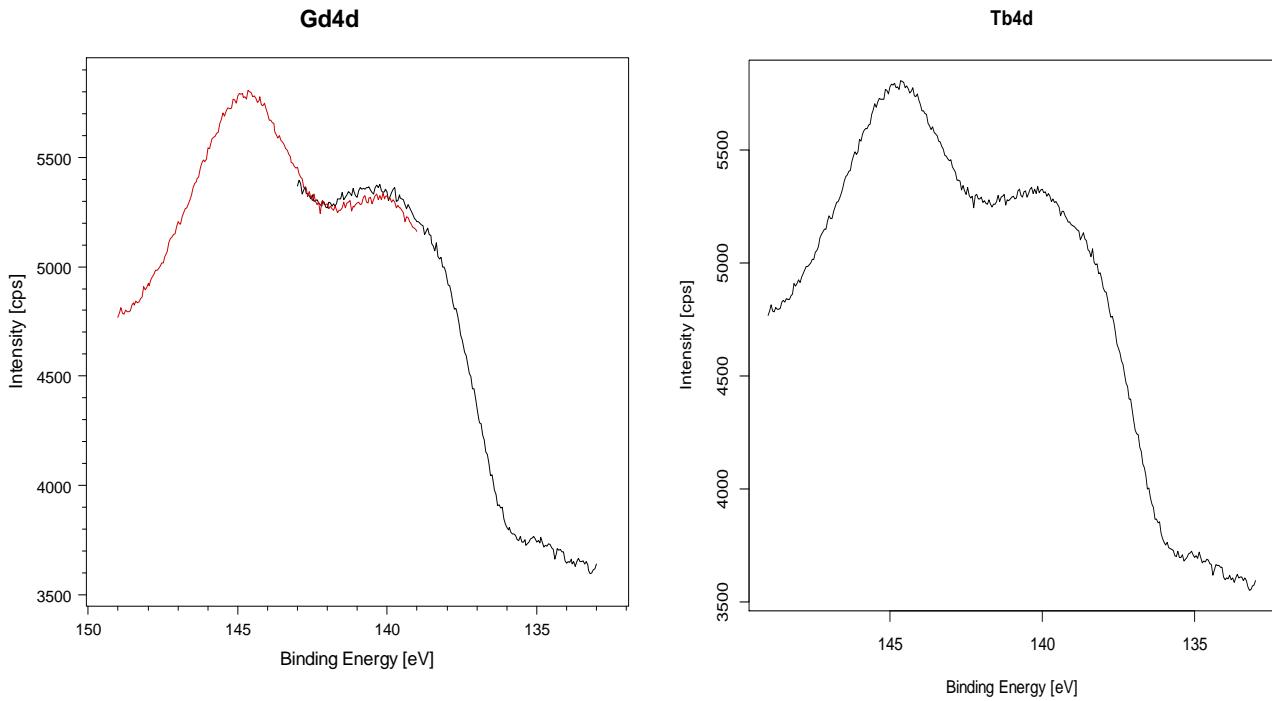
It is possible to combine, add two selected Core Lines or subtract one from the other. In this case, proceed as follow:



subtract to the previous;

- **Combine Core Line 1 and Core Line 2:** it may happen two elements have the main Core-Line overlapped. Initially these Core-lines are acquired separately but it could happen it is needed to combine (join) these features. In this case select the source XPS-Samples for Core-Line 1 and the correspondent Core-Line 1. Select the XPS-Samples for Core-Line 2 and the correspondent Core-Line 2. As shown in the following example, Core-Line 1 is Tb4d and Core-Line 2 is Gd 4d. The figure shows the two overlapped core-lines

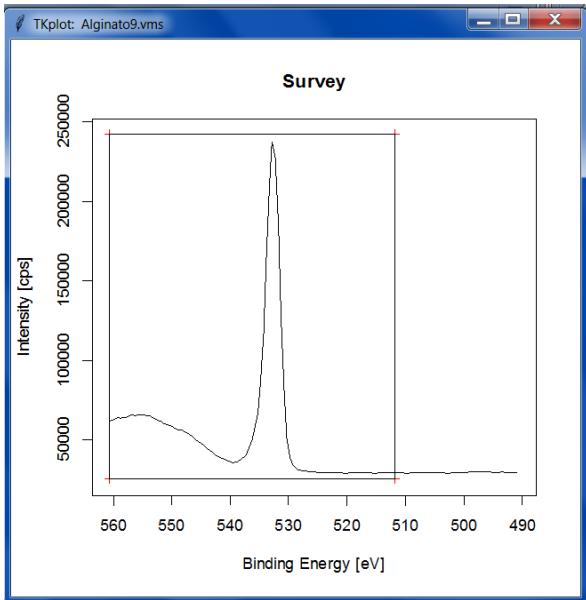
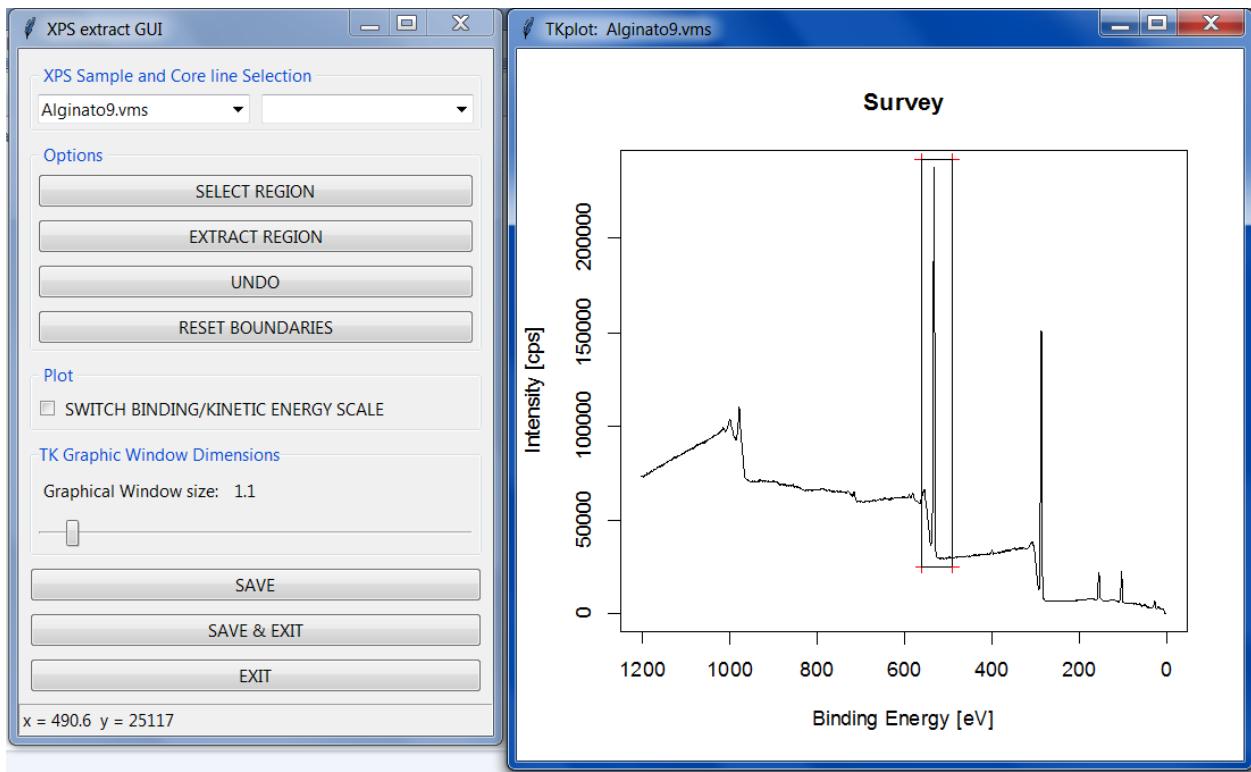
Combining means creating a unique spectrum which will be stored in Core-Line 1, cutting the overlapped region in Core-Line 2. After selection of the two Core-Lines the relative original ranges and the limits for the Core-Line 2 to be joined to Core-Line 1 are shown above the respective core-line names.



- **Combine button:** pressing the button Combine automatically the program adjust the spectral intensities of the two parts, eliminates the overlapped data and shows the spectral combination as in the following figure.
- **Add spectra:** will add the Core Line 1 to Core Line 2. Note that the number of sweeps will be modified as well as the intensity of the spectrum which will be normalized for the total number of sweeps;
- **Subtract spectra:** will subtract the Core Line 2 from Core Line 1. Also here the number of sweeps will be modified as well as the intensity of the spectrum which will be normalized for the total number of sweeps now equal to N1-N2. This operation is allowed only if N1 > N2;
- **Save button:** using this option results of the math operations above described will be overwritten to Core-Line 1 of the original XPS-Sample1.
- **Save as a New Core-Line button:** let the original core-lines unmodified and save the data in a new slot of the XPS-Sample 1.
- **Save and Exit button:** the same as Save and exit from *Core-Line processing* routine.

⇒ **EXTRACT FORM SURVEY:** option to extract spectral features from the survey when not acquired separately as high resolution coreline. Selection of this option will open the window shown in the next figure:

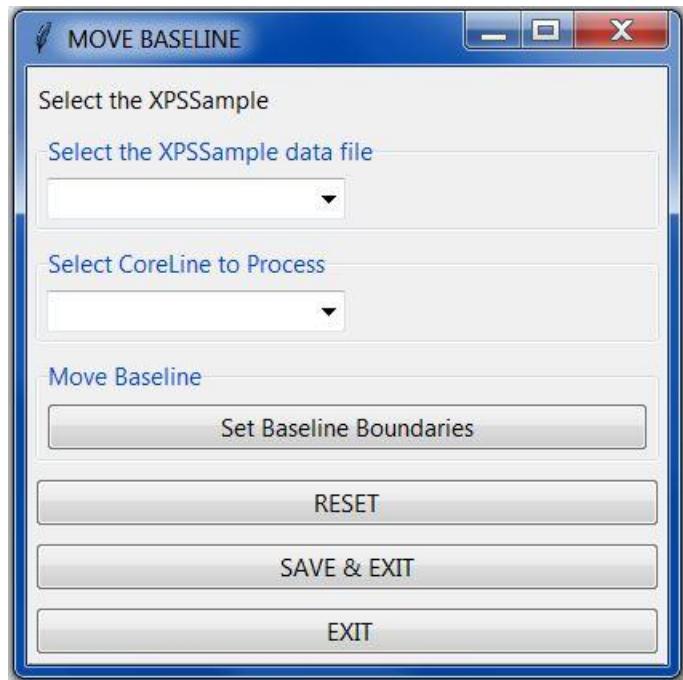
- Click with the left mouse button define the bottom-left and top-right corners of the region containing the peak you want to extract. This is shown below in the figure where the region around the O1s peak at ~530eV is selected in the wide spectrum.
- N.B.** you can modify the frame extension by clicking in proximity of the red crosses in the place you want to extend.



- **Select button:** enable the selection of the chosen region defined by the frame. Adjust the extension of the frame clicking in proximity of the red crosses in the position where you want to place it.
- **Extract button:** when the area is defined press extract button to extract the peak. A pop-up window will open requiring the name of the spectral feature to be saved;
- **Save&Exit button:** press this button to add the new region in the current XPS-Sample and exit the *Extract from Survey* procedure;

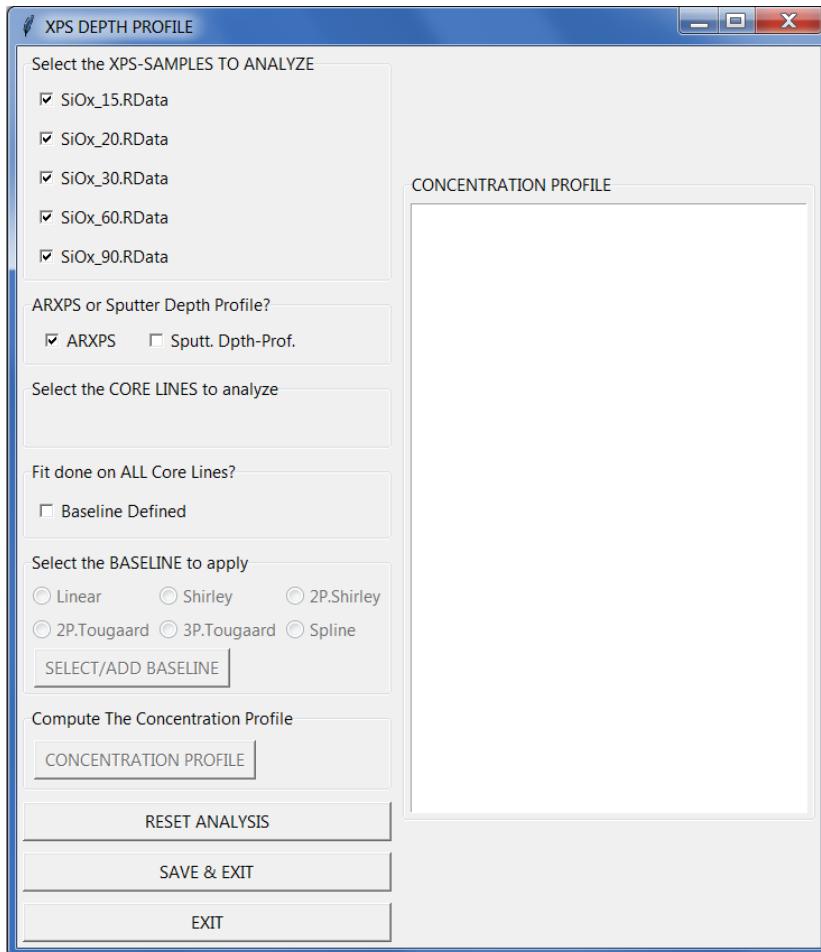
NB: this function works also on corelines is needed.

- ⇒ **MOVE BASELINE:** this option is used IN COMBINATION WITH THE *Process Core-Line* 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 changing the baseline on the background level. Selecting this option the following window will appear:

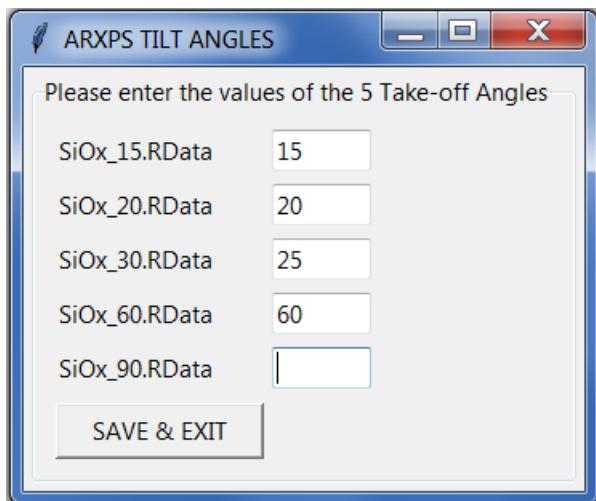


- **Select the XPS-Sample:** in the drop down list select the XPS-Sample containing the Core-Line to process;
- **Select the Core-Line to process:** in the drop down list select the the Core-Line containing the baseline to optimize;
- **Set Baseline Boundaries:** pressing the button *Set Baseline Boundaries* you can set the new baseline ends using the Left mouse button. 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;

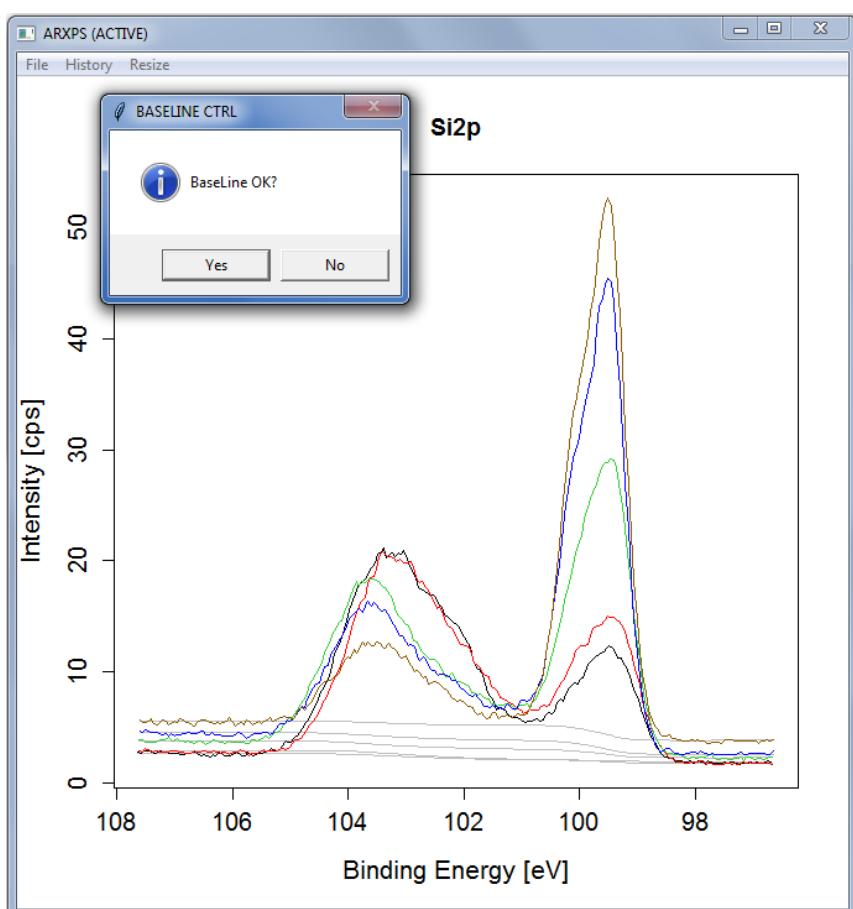
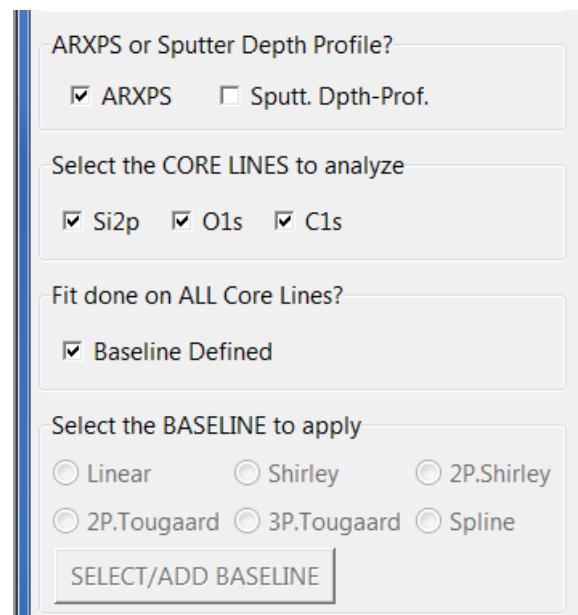
- **Save & Exit:** to save changes in the software main memory end exit the *Move Baseline* procedure;
- **Exit:** to exit the *Move Baseline* procedure without saving.



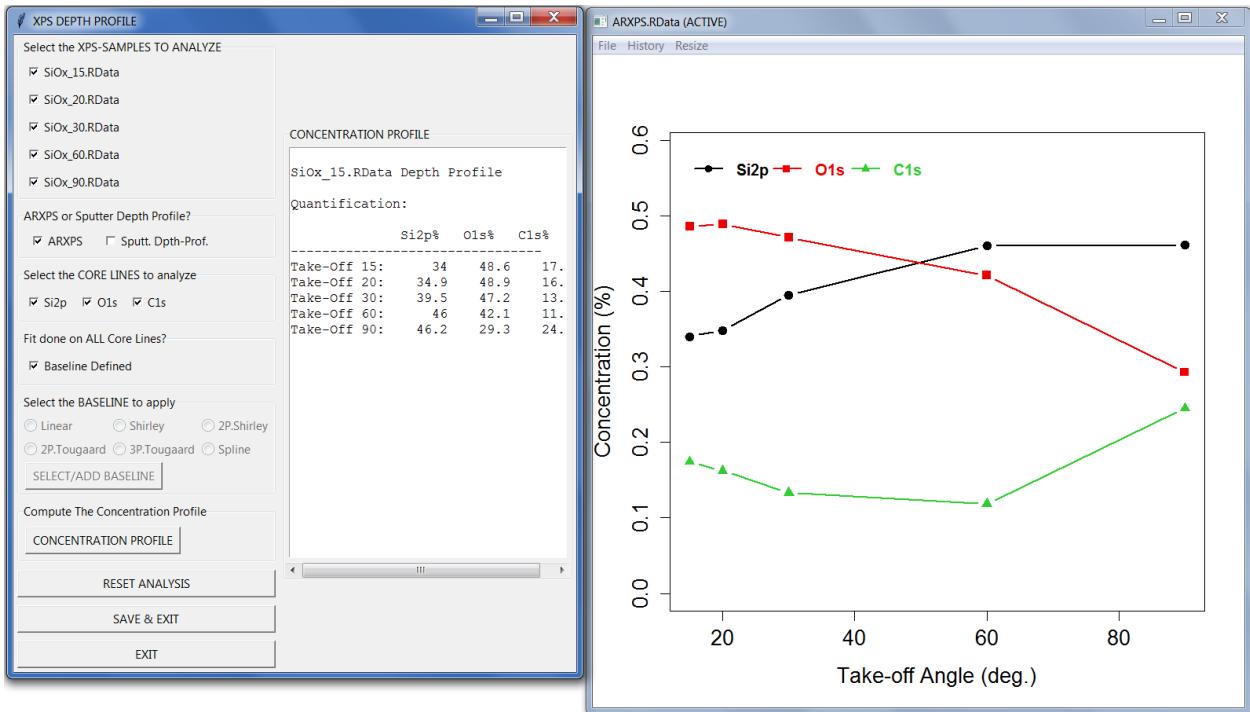
DEPTH PROFILE: this option computes the element distribution with depth. The depth information can be obtained by changing tilting the sample in ARXPS or by sputter-etching the sample surface as in *Sputter Depth Profile*, In ARXPS the element distribution is mapped on a $0 - 3\lambda$ range where λ represents the inelastic mean free path and 3λ corresponds to the max sampling depth. In Sputter Depth Profile the sample surface is removed layer-by-layer using an ion gun. Both the kinds of XPSSamples can be analyzed applying the Depth Profile option. The example shows the use of the Depth to a list of XPSSamples recorderd at different take-off angles. One XPSSamples and ARXPS mode are selected a widow to define the take-off angles appears.



- **Select the source Data-files:** here 5 XPSSamples are recorder at different tilt angles;
- **Indicate the number of take-off angles** use to perform the ARXPS;
- **Check the ARXPS box:** a window will opened requiring the value of the take-off angles corresponding to each of the XPSSamples;

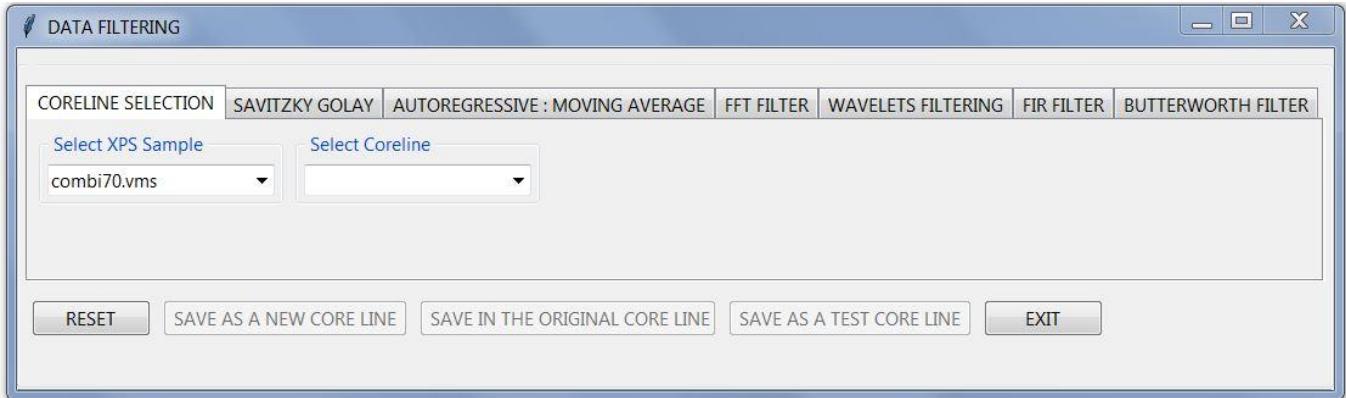


- After definition of the baseline end points the baselines for each of the loaded XPSSample is computed. This example shows the result of the baseline definition of the Si 2p core-lines of the XPSSamples acquired at the five different tilt angles.
- Definition of the baseline end-points must be made for all the selected elements (Si2p, O1s, C1s in this example).
- When the baselines are defined for all the elements then press the **CONCENTRATION PROFILING** button
- RxpsG will produce a plot describing the trend of the element concentration with the take-off angles used.
- Same procedure is applied if the spectra are acquired with successive sputtering cycles.



Example of ARXPS Depth Profile.

⇒ **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:



For *Sawitzky-Golay*, *Autoregressive*, *Moving Average*, *FFT* filters the smoothing power corresponds to the Degree of Noise Rejection: the higher the degree the higher the noise rejection.

For *Wavelets*, *FIR*, *Butterworth* filters there are two parameters:

- the Filter Order corresponds to the N. Wavelets or coefficients used for filtering. The higher the order the higher the noise rejection (increases the filter steepness from pass_band to stop_band).
- the filter Degree of Noise Rejection varies the amount of noise to reject (power of smoothing).

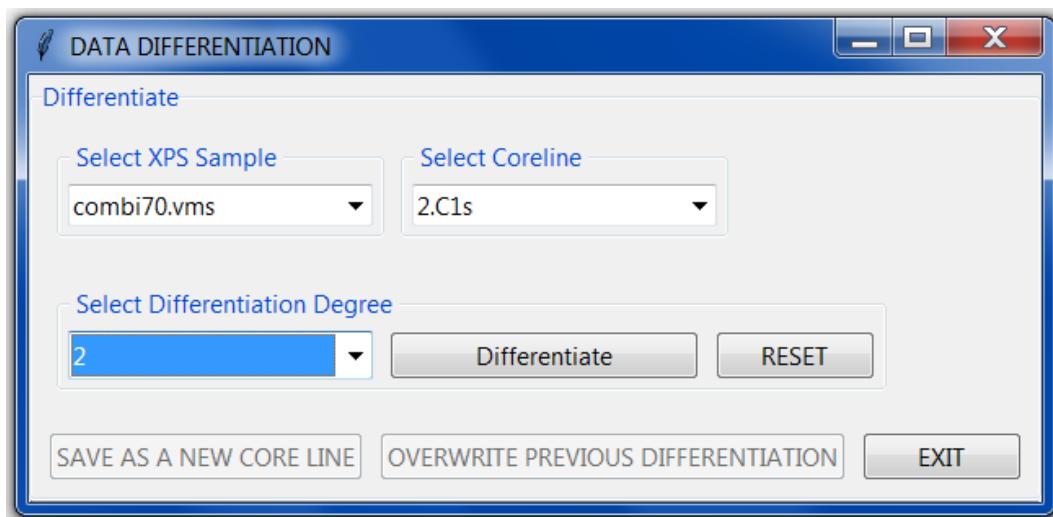
For any kind of filter it is possible to change the filter parameters and re-filter the spectrum as many times as desired.

- **Select SPSSample:** here the XPS-Sample data file to smooth is selected;

- **Core-Line Selection:** here the Core-Line to smooth is selected;
 - **Sawitzky Golay:** is one of the most popular filters used to perform smoothing. In *Sawitzky Golay* filtering the output at point i is the weighted average of data $w_{i-n} * y_{i-n} \dots w_i * y_i \dots w_{i+n} * y_{i+n}$ where w_i are the Sawitzky Golay coefficient. Select the Degree of Noise Rejection: the higher the degree the higher the number of filter coefficient used, the higher the noise rejection. Make sure that you are 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 subtraction* is checked 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 $i-n \dots i \dots i+n$. The higher the Degree of Noise Rejection the higher the rejection of the noise for both the filters. *Filter button* and *BKG subtraction* work as described above
 - **FFT filtering:** apply the FFT transform to perform filtering. Filtering corresponds to elimination of the high frequency component of the FFT_transformed spectrum. Filtered data are then obtained by applying the inverseFFT. Again the higher the filter degree the higher number of frequencies eliminated, the higher the noise rejection. *Filter button* and *BKG subtraction* works as described above.
 - **Wavelets Filtering:** uses the wavelets to perform filtering. Here the wavelets are used to model the noise. More wavelets correspond to higher degree of information rejection. The default is 5. Select the Degree of Noise Rejection 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 (filter steepness). Select the Degree of Noise Rejection (it would correspond to the cutoff freq. in the time dimain) 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). Also in this case the higher the number of coeff. the higher the filter precision (filter steepness). Differently from the FIR, the *Butterworth* filters can introduce signal distortions. Select the Degree of Noise Rejection and press *Filter* button;
 - **Save as a New Core Line:** preserves the original data and save the smoothed Core-Line in a new core line having the same name as the original. Now it is possible to select another Core-Line and proceed with another smoothing.
 - **Save in the Original Core Line:** to save (overwrite) the results of filtering in the original coreline. Use this option when type of filter and filter condition are known since original data are lost;
 - **Save as a Test Core Line:** use this option when filter and filtering parameters are unknown. This option will preserve the original spectra and filtered data will be saved always in a separated “test-Core Line”. This enables to select the better filter and find the optimal filter conditions: (i) apply the filter to the original data and save in the Test – Core Line. (ii) Verify if the filtering corresponds to the desired result: for example does the filter reject the noise enough? (iii) if required, change the filter type or the filter parameter and filter again. Apply steps (i), (ii) and (iii) to optimize filtering.
- N.B. test core lines are identified with “T.” followed by the core line name (*T.C1s* for example refers to a *test_C1s* core line).
- **Exit:** to exit the procedure without saving.

⇒ **DIFFERENTIATION:** this option is used to differentiate the selected spectral data.

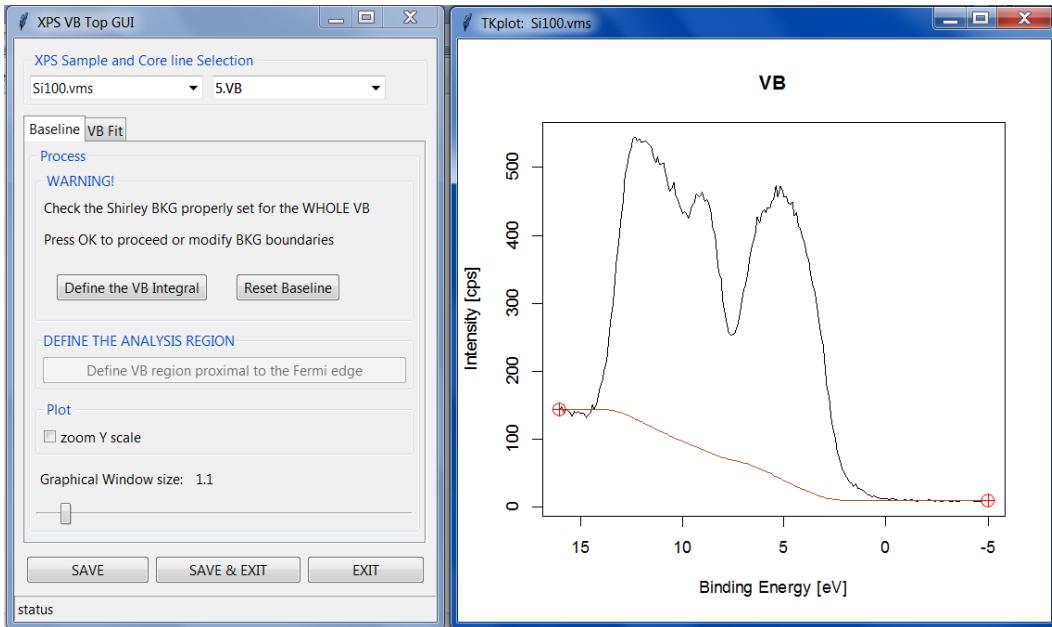
- **Select the XPS Sample:** Select the desired Data File among the loaded data;
- **Select the Core Line:** select the desired spectral data to be differentiated;
- **Select the Differentiation degree:** it is possible to perform differentiations till to the fifth degree (degree 1 corresponds to the first derivative etc.). However one can apply differentiation on already differentiated data.
- **Differentiate button:** performs the differentiation on the selected spectrum following the chosen degree;
- **Reset:** resets analysis to restart from beginning;
- **Save as a new Core Line:** saves differentiated data in a new core line to preserve then original data;
- **Overwrite previous differentiation:** differentiated data are generally rather noisy and need noise to be removed using the smoothing option; Since the “force” of the filter is not known a priori, generally some tests are needed to find the correct filtering conditions to obtain reasonable differentiated data. In this case one selects the smoothing and filters the desired spectral data. Then *Save data as a new core line*. Now it is possible to generate new filtered data and reapply differentiation to see the effect of the filter. During these attempts, one can select *Overwrite previous differentiation* to avoid generation of too many new core lines.



N.B. Differentiation is identified with “D.” followed by the degree of differentiation and by the core line name (*D.2.C1s* for example refers to the second derivative of the C1s core line). This convention is used also in the core line informations.

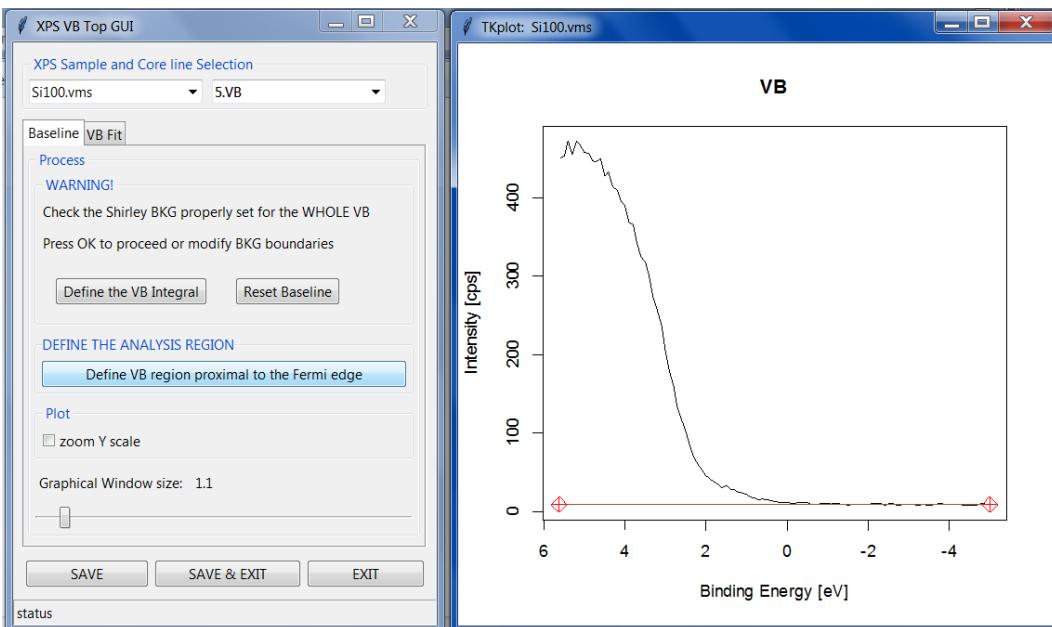
⇒ **VB-TOP ESTIMATION:** this option allows the estimate of the VB top position. Two methods are implemented: (1) Linear fitting on the VB tail descending towards the Fermi edge and on the background after the Fermi level. The intersection of the two fits defines the position of the VB top; (2) Non linear fitting: using this method a fit on the whole descending tail and background A threshold defined on the basis of the VB mean intensity is used to estimate the VB top position. To compute a meaningful threshold this method requires the whole VB to be acquired (background present on both the sides of the VB).

When the **VB top estimation** option is selected it will appear a panel showing all the core-lines. In the following example the VB was replicated using Core Line Processing to perform both **Linear** and **Non Linear fitting**.



- **Background definition:** a Shirley background is automatically generated on the whole VB region to define the integral of the VB intensity in this range. Adjust the edges of the Background.

- **Reset Baseline:** resets the Baseline to the initial values. Moving the red markers it is possible to manually redefine the Shirley baseline ;
- **OK button:** to approve the *Baseline subtraction*. This operation removes the Shirley background and enables the selection of the VB portion where performing the VB top analysis.



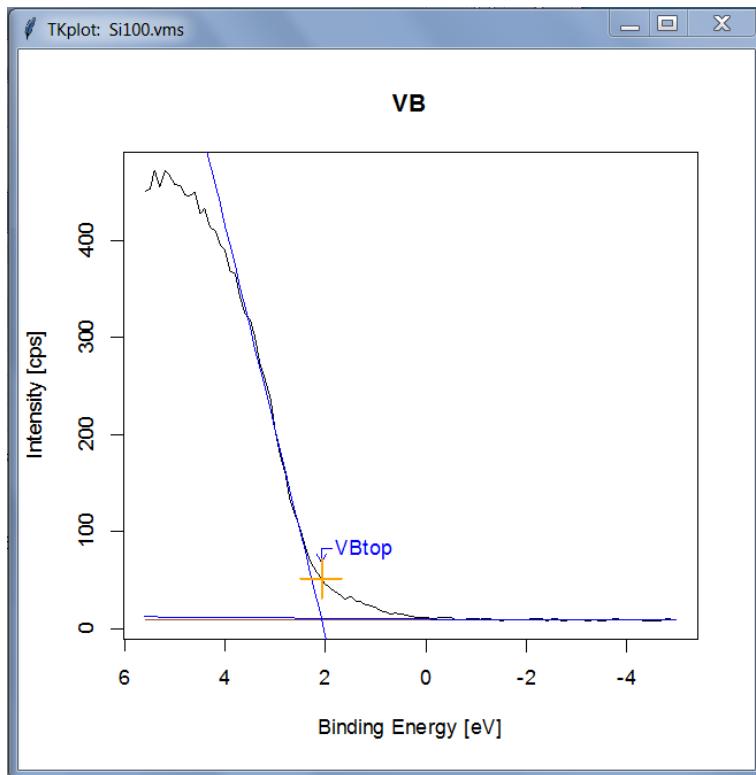
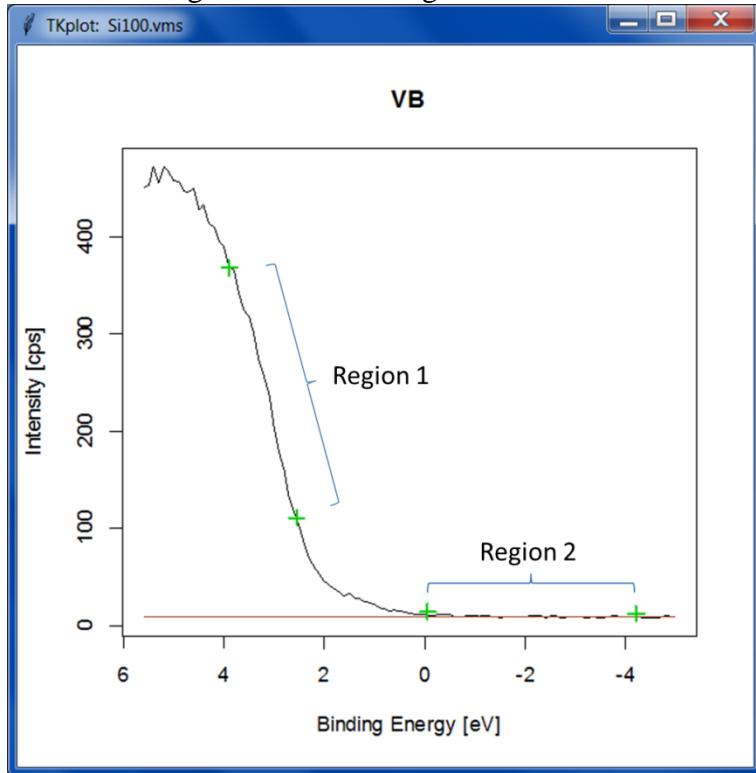
- **Define de region proximal to VB:** automatically the Shirley background is replaced by a flat horizontal line defining the region where to perform the analysis. Move the red markers at edges to define the region

proximal to the Fermi Edge where carry out the Linear or Non-Linear or Hill Sigmoid fitting.

- **VB Region Boundaries OK button:** to approve the VB region where performing the analysis.

Now switch to the second page of the menu to select the *Linear*, *Non-Linear* or *Hill Sigmoid* fitting procedure.

- ❖ **Linear Fit:** this method is selected by default. VB top is estimated by linear fitting the descending tail and the background of the VB.



VB defined in the selected region

- Just click with the left mouse button to define the regions where the linear fits have to be performed. Green crosses will appear on the VB tail.

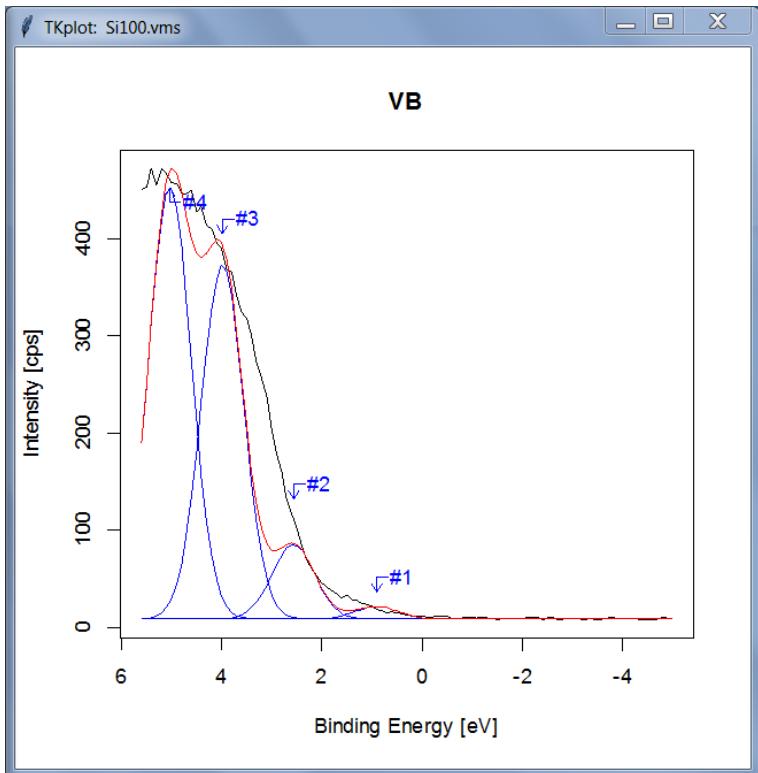
- **Reset button:** to reset the fit region boundaries;

- **Fit button:** performs the linear fitting in the defined regions; **Estimate the VB top:** if the linear fits are reasonable, press this button to work out an estimate of the VB top position.

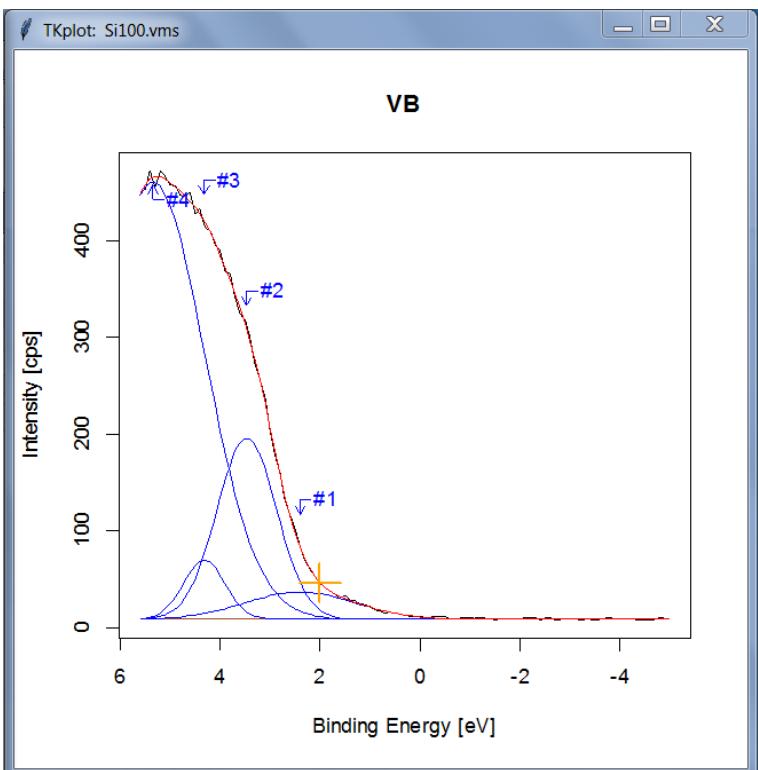
- **Save, Save & Exit buttons:** to save the analysis result and exit.

- ❖ **NON Linear fit:** consists in fitting the descending tail of the

- **Fit type:** select the desired fit function among those listed in the drop down menu;



- **Add button:** click with the mouse left button on the VB tail in the position where you want to add the selected fit function and then press the *add button* (in the example a sigmoid function added in the position #1). If Gaussian function is selected, you can use three or more components to fit the VB tail.



- **Fit button:** performs the VB tail fitting;
- **Delete Component button:** to delete the fit function;
- **Estimate the VB top:** when the fitting is reasonable, pressing this button works out an estimate of the VB top position.
- **Reset Analysis:** to restart the VB top analysis from beginning.
- **Save, Save & Exit buttons:** to save the analysis result and exit.

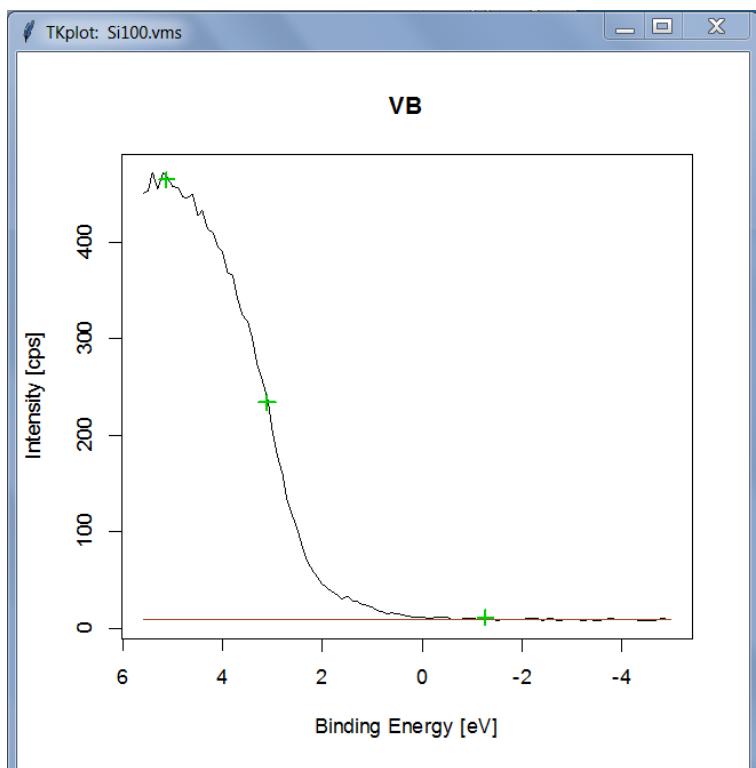
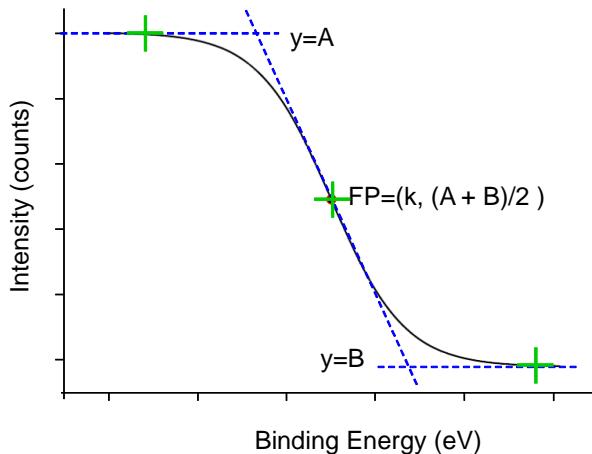
- ❖ **Hill Sigmoid fit:** consists in fitting the descending tail of the VB defined in the selected region utilizing a Hill Sigmoid curve. The advantage of this method lies in the fact that once the curve is

defined by fitting the sigmoid parameters on the experimental data, the VB top can be determined utilizing a mathematical relation.

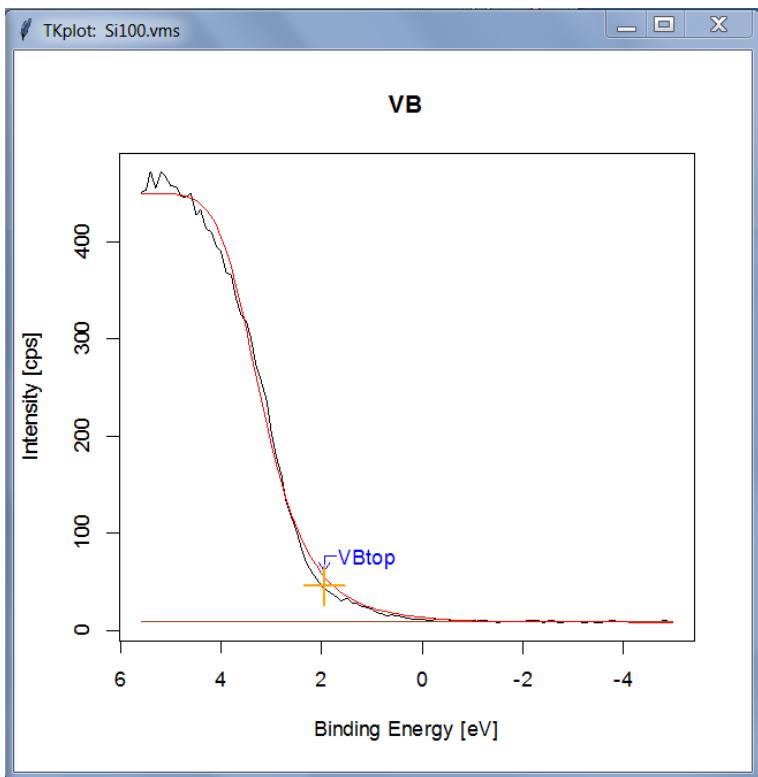
The Hill Sigmoid is defined by the equation:

$$y = A + (A - B) x^n / (k^n + x^n)$$

A, B and k are defined as shown in figure. To start the Hill Sigmoid fitting, the descending tail of the VB towards the Fermi edge has to be defined as described above.



- **Define the sigmoid maximum, flex and minimum points:** to describe the Hill sigmoid, its maximum, the flex point and the minimum level have to be defined. These points are indicated with green crosses in the above figure.
- **Add the Hill Sigmoid:** Add the Hill Sigmoid to the VB data;



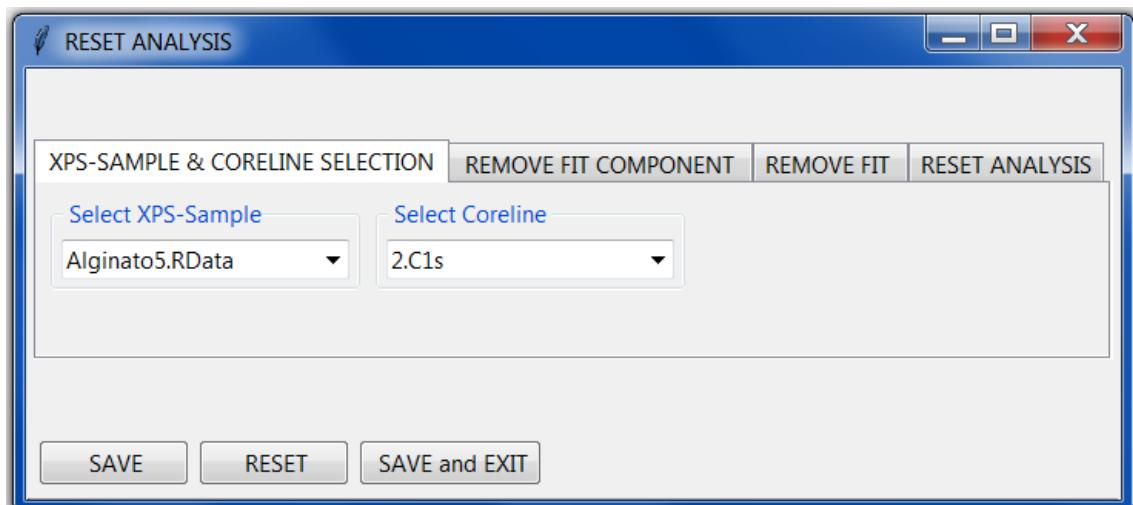
- **Fit:** model the VB in the region near to the Fermi Edge fitting the spectral data using the Hill Sigmoid
- **Estimate the VB top:** once the best fit is obtained, it is possible to estimate the VB top mathematically. In particular the VB top coincides with the abscissa of the intersection of the straight line passing for FP and the $y=B$ (see figure above). This value is given by:

$$x=k*(1+2/n)$$

For more details see Ruben Bartali et al. "Critical relative indentation depth in carbon based thin films", Progr Nat. Sci. Mater. Int. Sci. (2014), 24, 287-290.

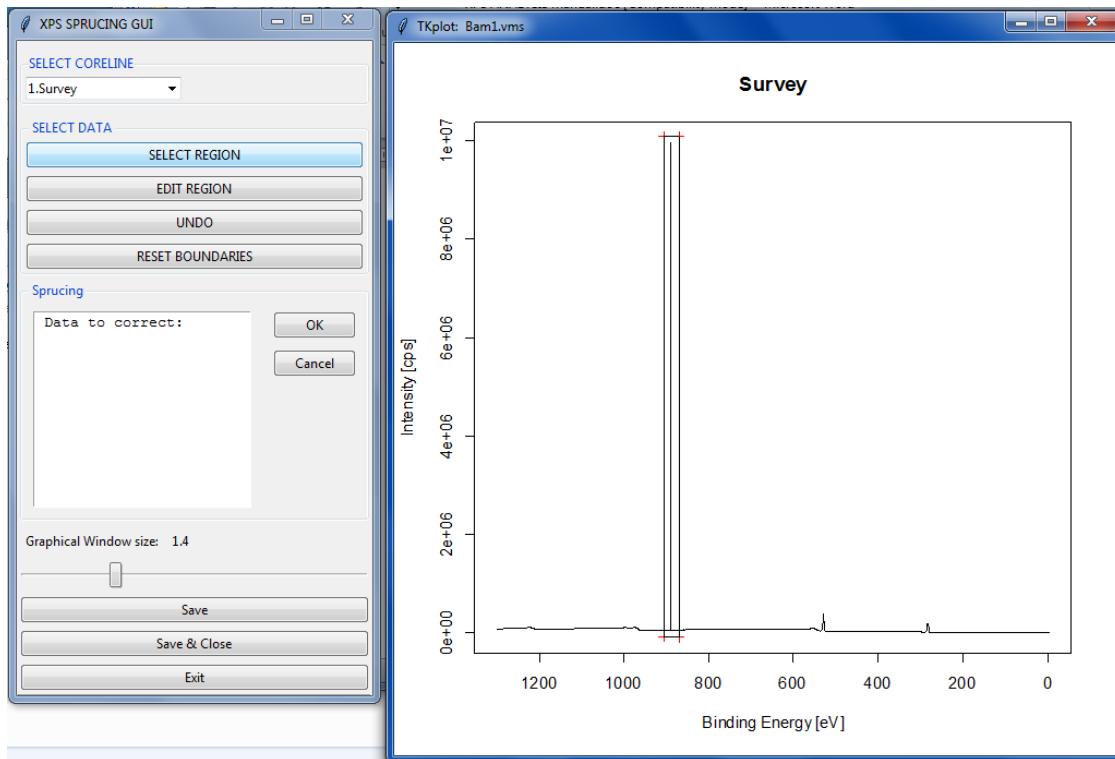
- ⇒ **RESET ANALYSIS:** this option allows to partially or totally reset the results of a Core-Line analysis. This option activate the following window:

- **XPS-Sample & Core line selection:** select an XPS-Sample and the desired Core Line: the active XPS-Sample and active Core Line are presented by default;
- **Remove fit component:** it is possible to remove a single fit component among the those of the peak fitting. This operation causes the loss of the fit constraints;
- **Remove fit:** removes the best fit and components, fit region and baseline survive;
- **Reset analysis:** resets 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.

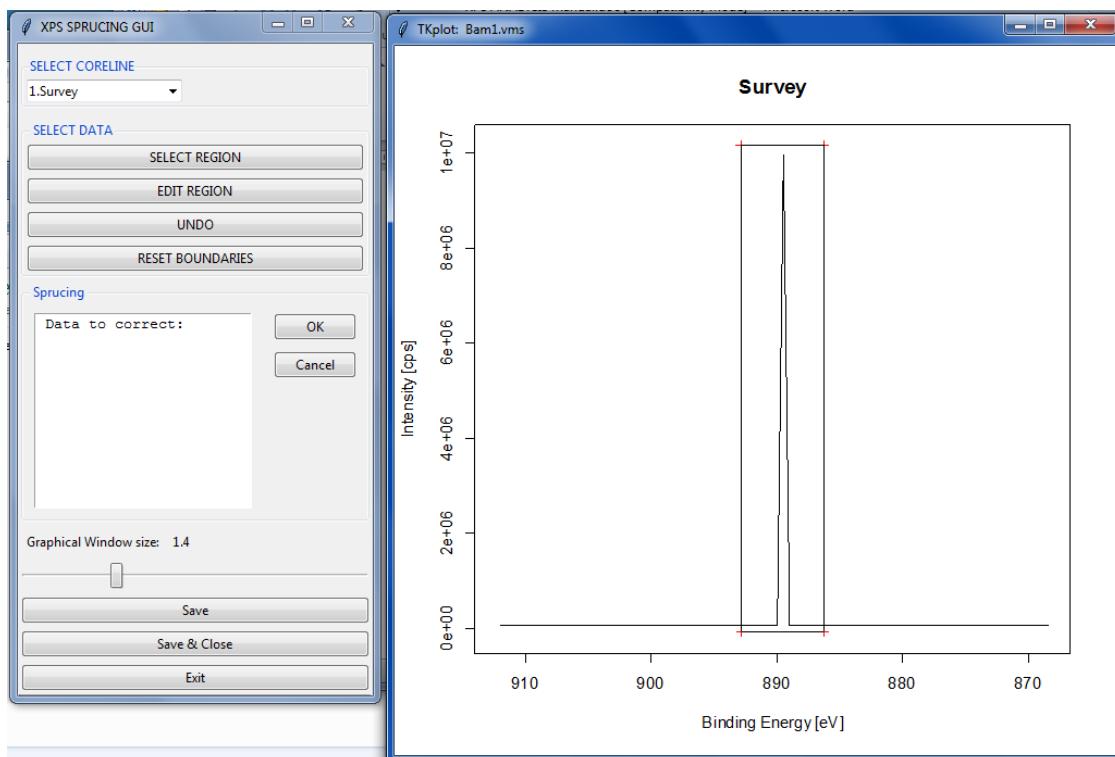


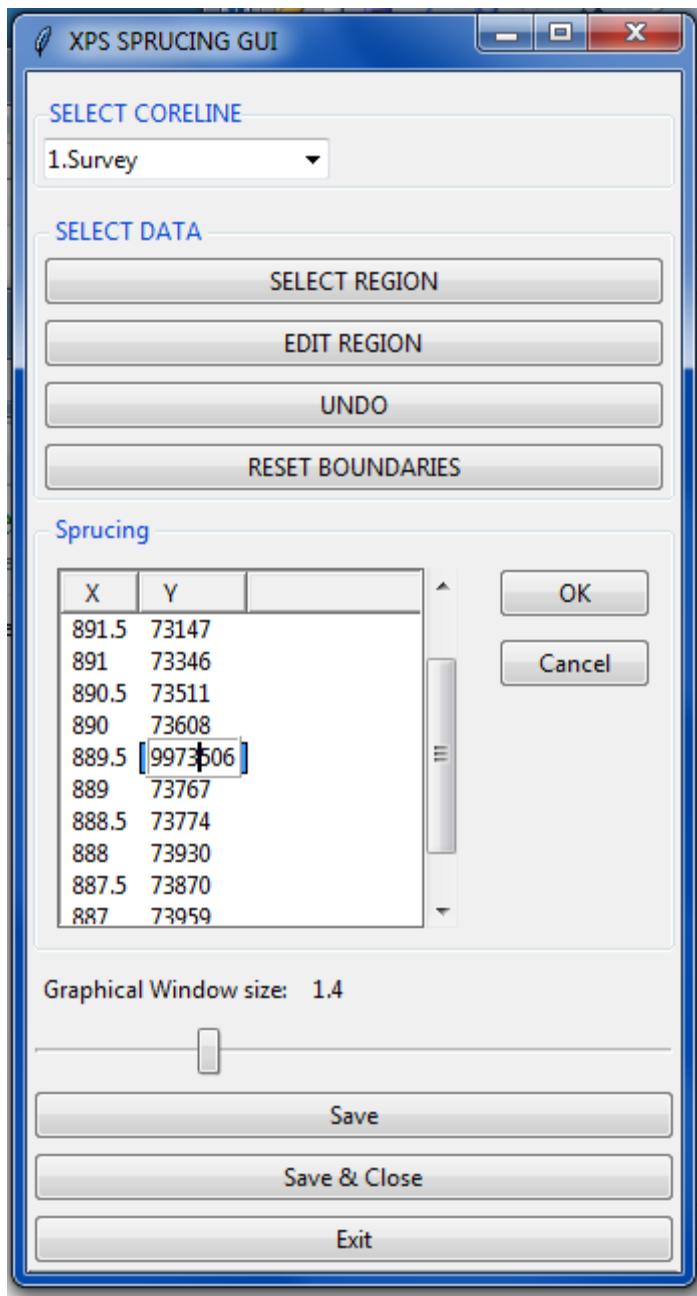
⇒ ***SPRUCING UP:*** this option allows data editing to make corrections. It may happen that there are wrong data in your spectra such as spikes as in the example shown in the figure below. After selection of the desired Core Line open the *Sprucing Up* option:

- ***Identify the region containing data to correct:*** move the cross markers (+) to identify the region around the data to correct;



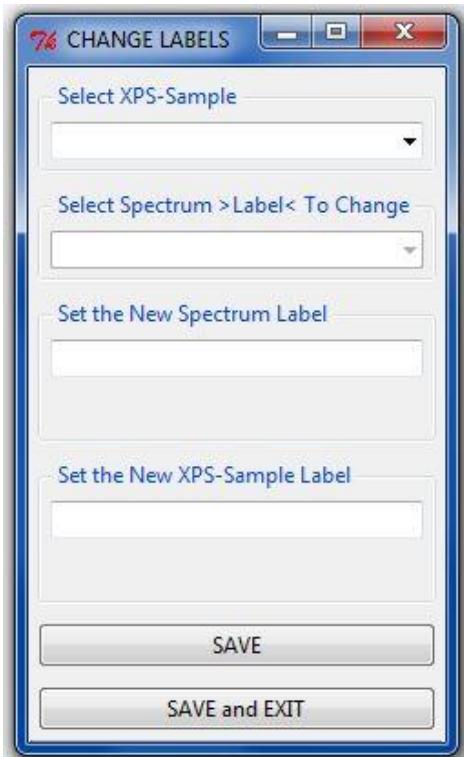
- ***Select Region:*** This will plot the selected area to better identify the region around the wrong data;





- **Edit Data:** pressing this button will edit the data identified by the frame around the wrong data: search for the wrong data and correct. Pressing the *OK* button will replace the wrong data with the corrected ones. Pressing the *Cancel* button will close the edit window.
- **Save:** this button saves the changes in the program main memory;
- **Save & Exit:** save results and exit the *Sprucing Up* option.

- ⇒ **CHANGE SPECTRUM LABEL:** sometimes it happens that the name given to one (or more) of the Core Lines is inappropriate. This option allows changing the Core-Line name.

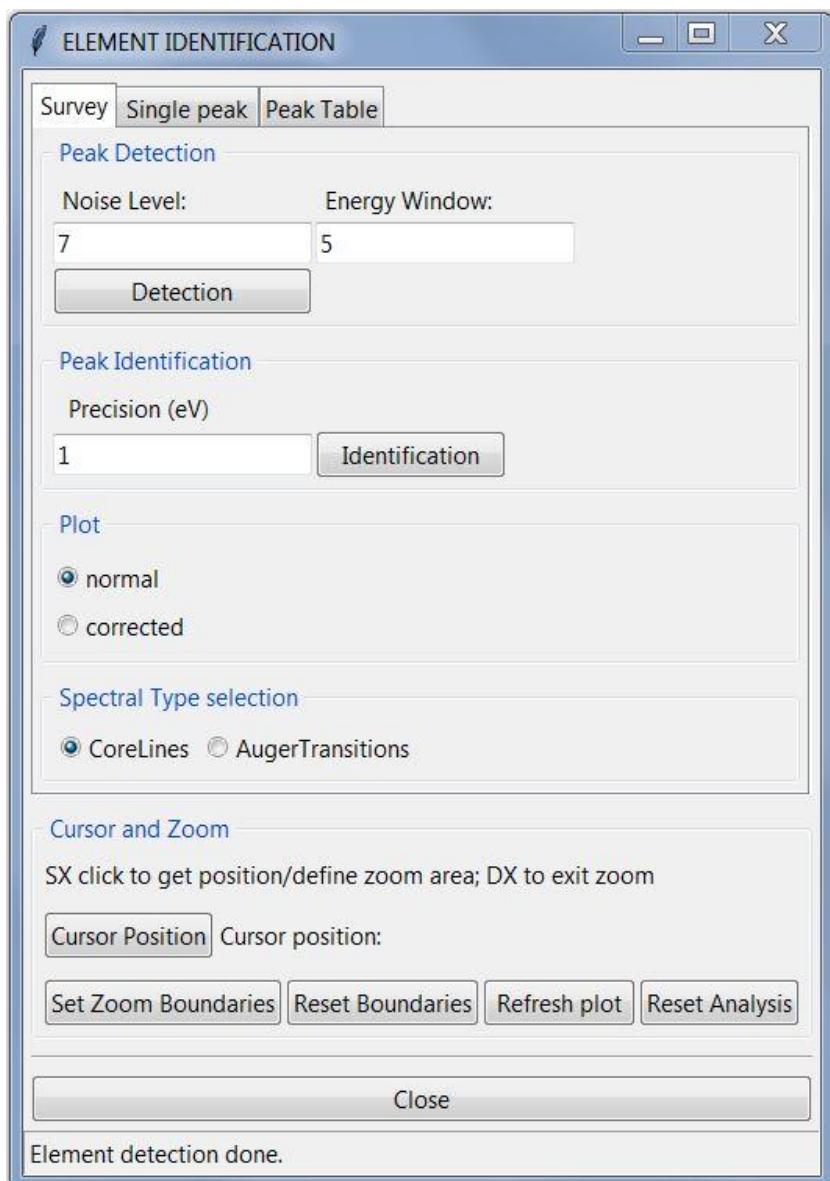


- **Select the XPS-Sample:** select the XPS-Sample using the drop-down list. After selection the XPS-Sample name will appear in the bottom-text-box;
- **Select the Spectrum Label to change:** for the selected XPS-Sample the list of Core Lines is give in this drop-down list. Names are written between >...< symbols (for example >survey< to correctly identify all the characters of the core line name)
- **Set the new Spectrum Label:** write in this text-box the new core line name;
- **Set the new XPS-Sample Label:** in this text-box appears the selected XPS-Sample name. If needed it is possible to change the XPS-Sample-Name info which will be saved inside the Rdata file. The XPS-File-Name used to identify the XPS-Sample listed in the main panel is retained.
- **Save&Exit:** to save the smoothed Core-Line 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.

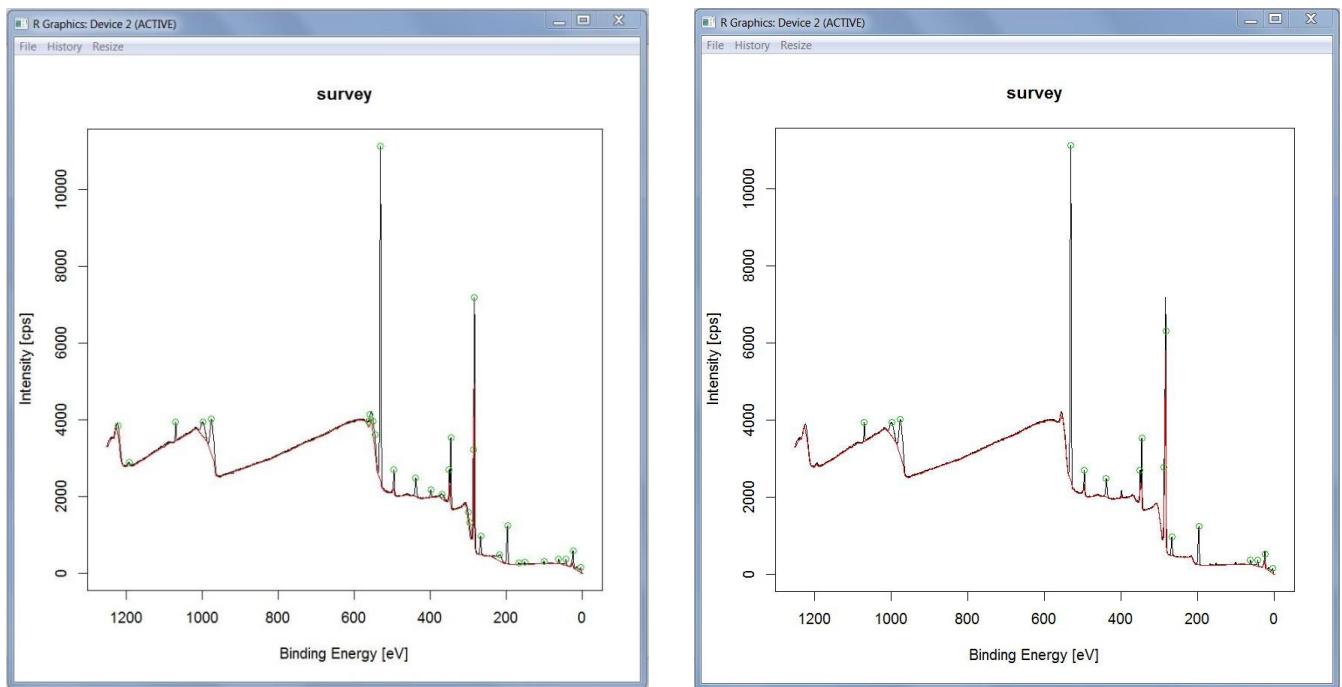
❖ **Survey page:**

- **Noise level:** the default is 7 but it is possible to increase the noise level in case of high spectral noise.



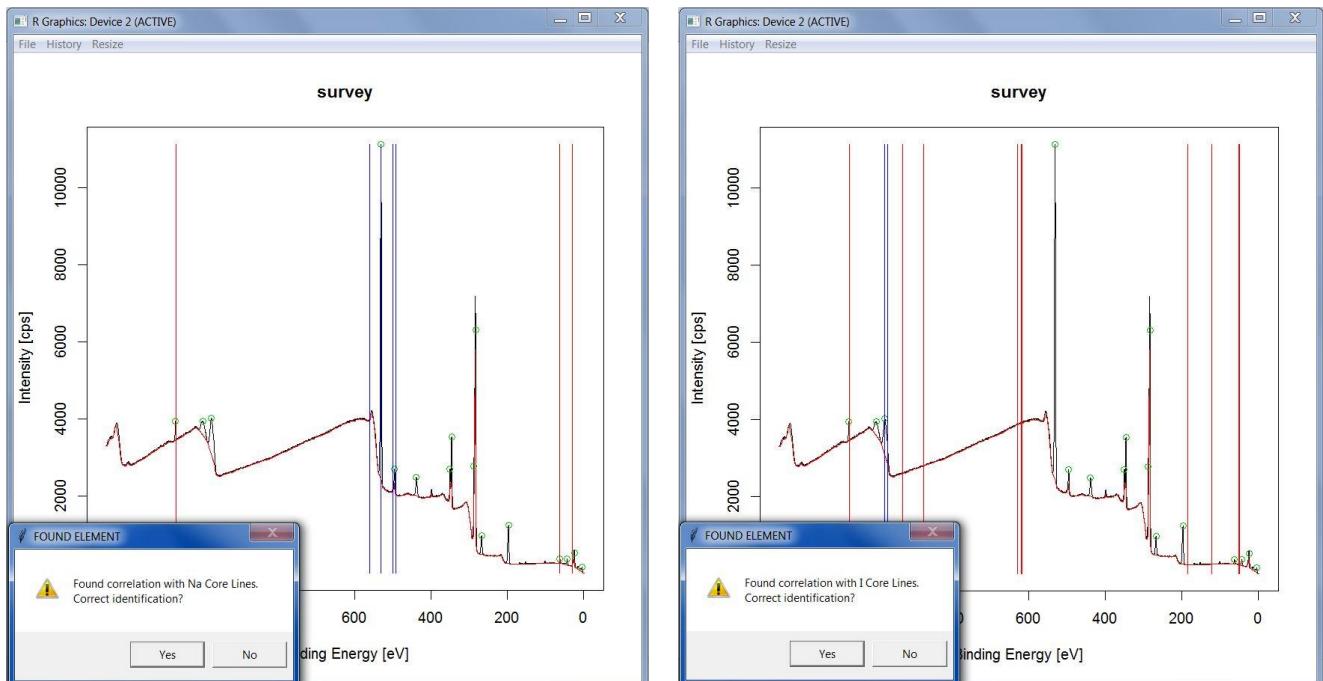
- **Energy range:** 5eV is the default. The energy window is used to increase/decrease the data smoothing for the identification of peaks. The smaller the energy window, the higher the precision the smoothed signal follows the original data.
- **Detection:** activate the detection of peaks. A green marker 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 console;
- **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!).

N.B. detection of Auger energy loss features can be avoided by increasing noise level and setting an appropriate energy window (i.e. Noise Level = 20, Energy Window = 3 eV) and pressing *Detection* button.



Difference in peak detection using Noise Level = 7 Energy Window = 5 (left) and Noise Level = 25 Energy Window = 3.

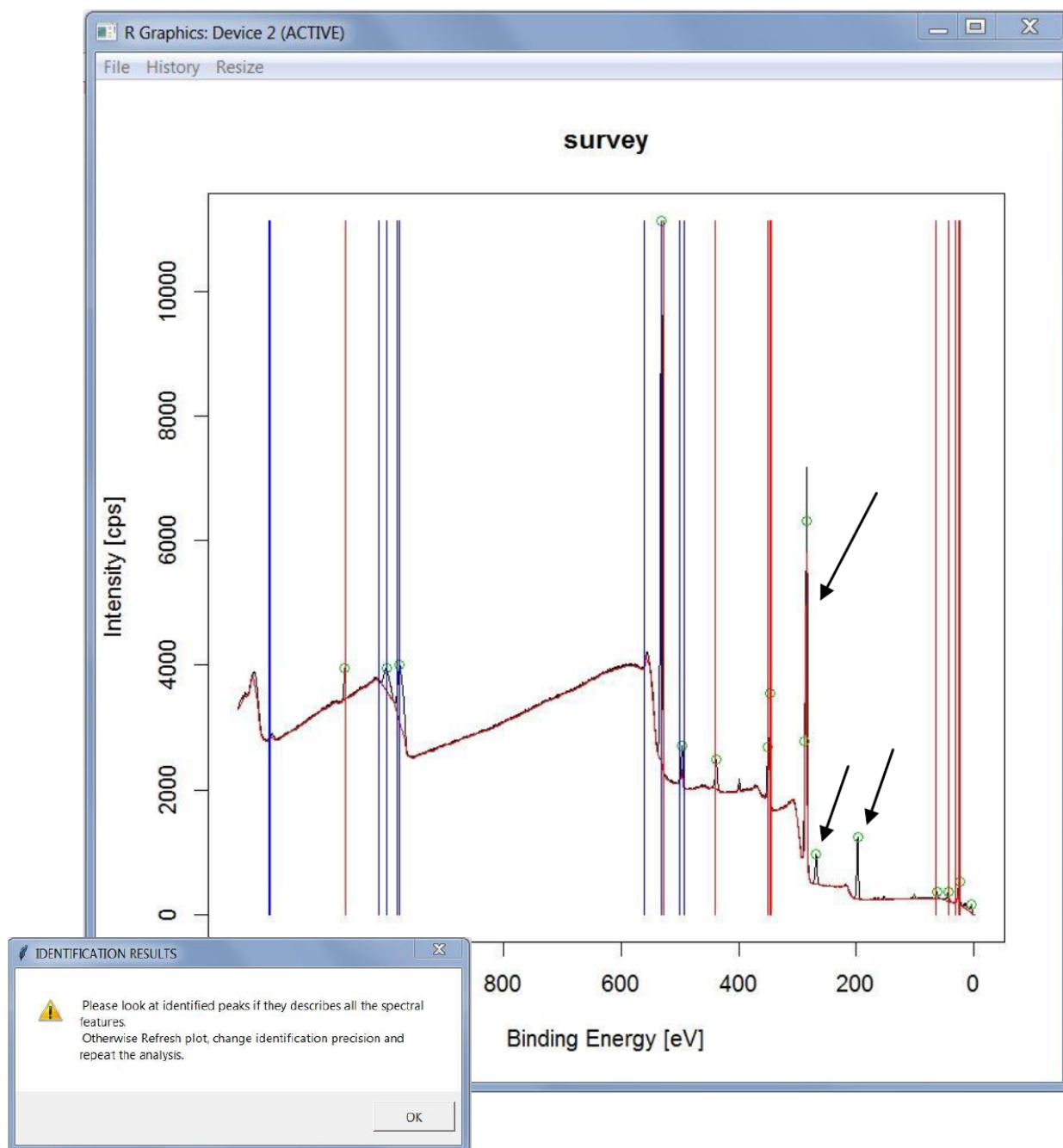
Pressing the *Identification* button RxpsG will show you all the possible candidate having Core Lines matching with a peak detected in your survey. Assignment is made controlling if all the element Core Lines (in red) and Auger features (in blue) fit with the spectral features of your survey spectrum



In the left panel above, the spectral features of Na perfectly fit with the spectral features of the survey you will assign Na pressing YES. In the right panel iodine spectra Auger features match with the survey structures (blue lines) but I 3p, I 3d, I 4s and I 4p does not have any correspondent peak in the survey. You will discard I pressing NO.

Finally the GUI will show you all the Core Lines and Auger features of the assigned elements as shown in the next figure.

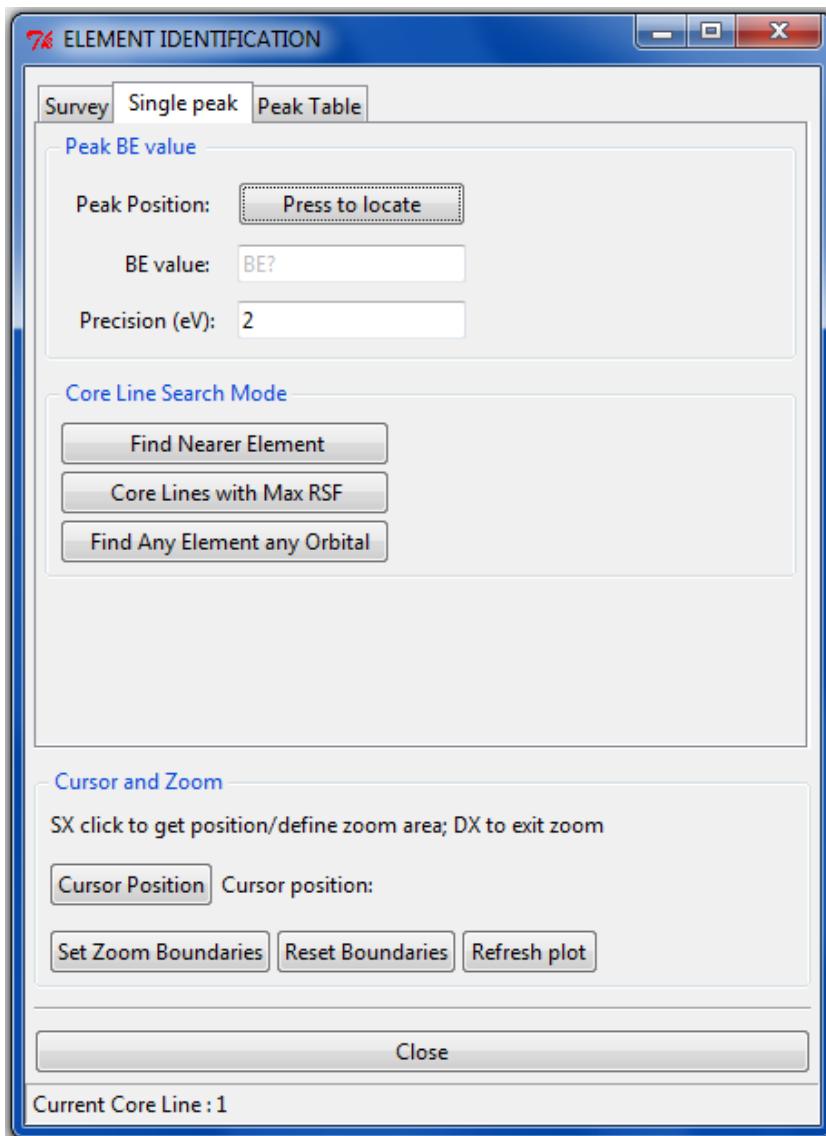
N.B. correct element assignment requires knowledge of the analyzed sample to discard possible candidates.



Although intense, some detected peaks are not assigned. Consider that the peak identification is made using Core Line / Auger energy positions of pure elements. Chemical shifts and possible charging effects may be present. In this last case, an energy alignment prior to peak identification and assignment may be important to correctly assign peaks.

To identify not assigned peaks you can proceed with the options in the second page of the GUI.

- ❖ **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.



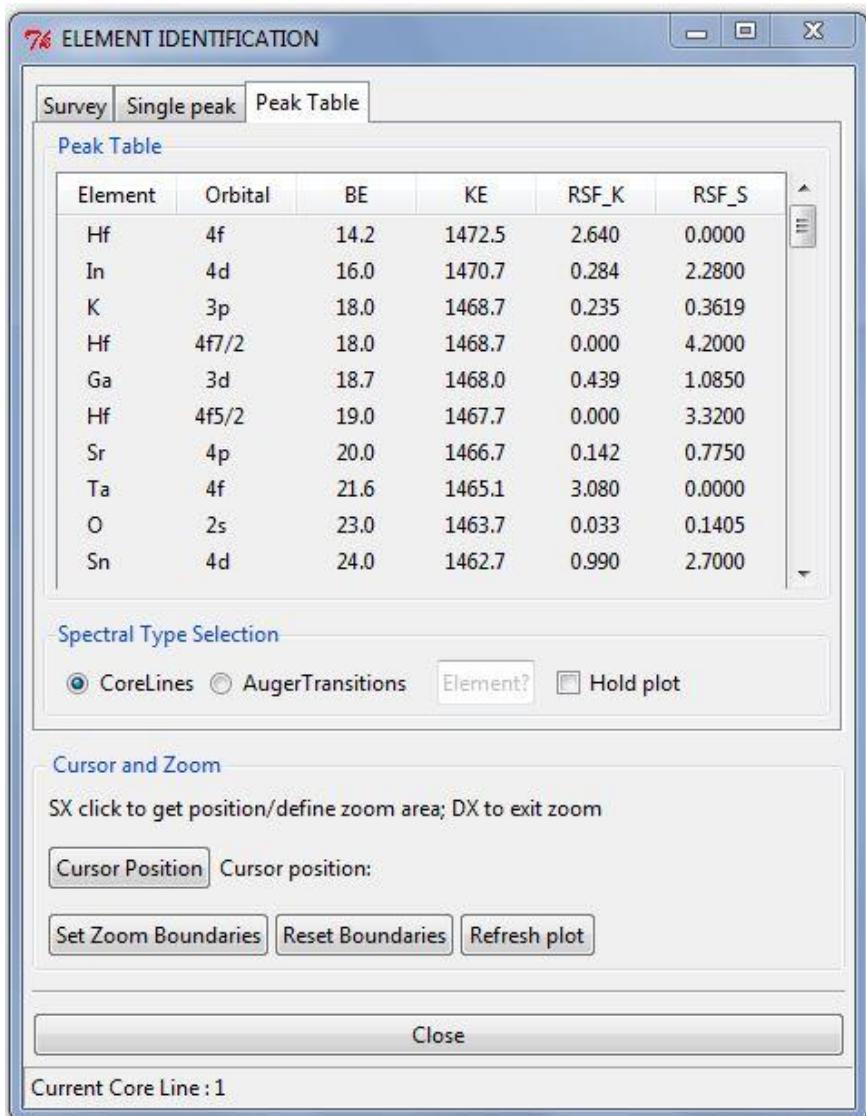
- **Cursor position:** press **to locate** button to identify the position of the peak with the mouse left button.
- **BE value:** the binding energy value of the peak to be identified. It will appear when the peak is located with the mouse or the BE value can be directly written in this window.
- **Precision(eV):** 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 any Element any Orbital:** a list of elements falling inside the “precision” energy range will be produced without any particular selection rule.

Assign element when good matching is found between the element core line position (red lines) and spectral features of the survey. This is made in the Peak Table page.

- ❖ **Peak Table page:** in this notebook page, by default it is shown the table of the core lines. Selecting Auger Transition in the *Spectral Type Selection* area, Auger components will be shown in the table



- **Spectral Type selection:** the detection may be applied to identify *Core Lines* or *Auger* transition selecting the correspondent radio-button.
- **Element?:** red (blue) bars in the position of core lines (Auger transitions) of the element selected with the editable box, will be shown on the survey.
- **Hold plot:** the plot is hold to overlap core lines or Auger transitions positions of more elements.

Common Buttons:

- **Cursor Position:** click with the left mouse button on the desired spectra feature to get its position;
- **Set Zoom Boundaries:** to define the corners of the area to be zoomed through left mouse button, DX button to exit and zoom;
- **Reset Boundaries:** to reset/re-define the zoom boundaries;
- **Refresh plot:** to reset the plot to its original view.

- ⇒ **CORE-LINE AUGER TABLES:** this option shows the tables of the core lines and of the Auger Transition. Double Clicking on the element or on the Transition, line positions or Auger component positions will be shown on the survey.

CORE LINES AND AUGER ELEMENT TABLES

Peak Table					
Element	Orbital	BE	KE	RSF_K	RSF_S
Hf	4f	14.2	1472.4	2.6390	NA
In	4d	16.0	1470.6	0.2840	2.2800
U	6p3/2	17.0	1469.6	NA	NA
K	3p	18.0	1468.6	0.2350	0.3619
Hf	4f7/2	18.0	1468.6	NA	4.2000
Np	6p3/2	18.0	1468.6	NA	NA
Ga	3d	18.7	1467.9	0.4390	1.0850
Hf	4f5/2	19.0	1467.6	NA	3.3200
Sr	4p	20.0	1466.6	0.1420	0.7750
O	2s	23.0	1463.6	0.0330	0.1405
Y	4p	24.0	1462.6	0.1410	0.0910
Sn	4d	24.0	1462.6	0.9900	2.7000
Ta	4f7/2	25.0	1461.6	3.0820	4.8200

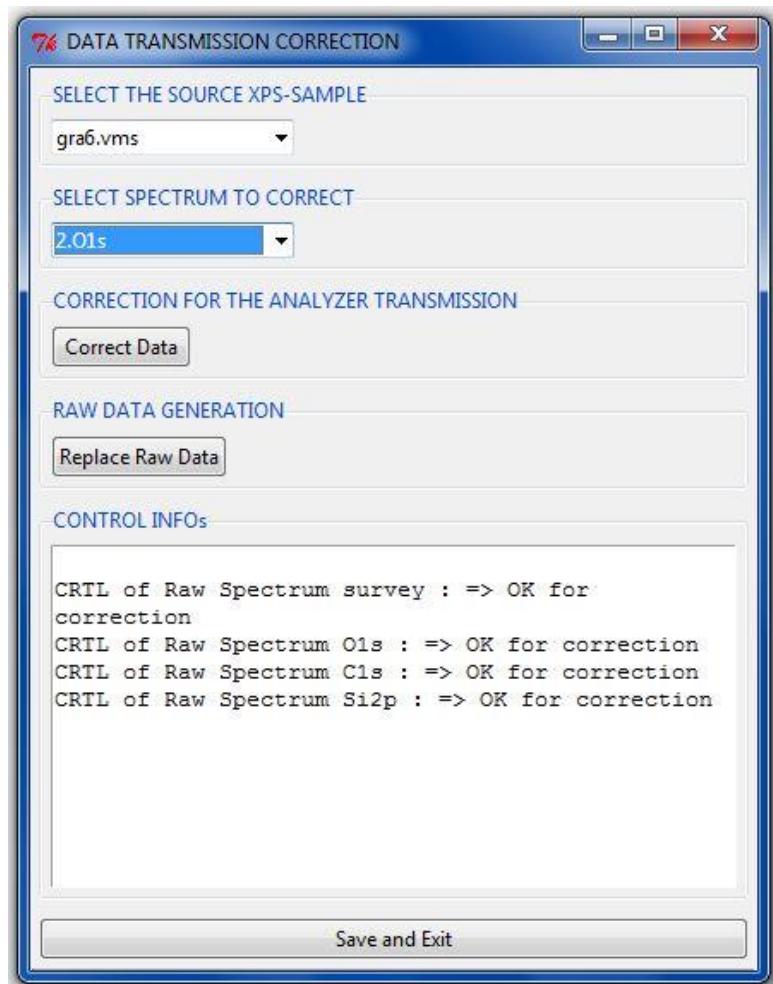
Auger Transitions					
Element	Transition	BE	KE	RSF_K	RSF_S
Ru	NOO	1453.6	33.0	0.96	0
I	NOO	1450.6	36.0	0.60	0
Rh	NOO	1449.6	37.0	0.43	0
Li	KLL	1448.6	38.0	0.37	0
Pd	NOO	1446.6	40.0	0.43	0
Cs	NOO	1441.6	45.0	0.27	0
Fe	MNN	1441.6	45.0	1.00	0
Ir	OPP	1435.6	51.0	1.45	0
Co	MNN	1435.6	51.0	1.21	0
Ba	NOO	1434.6	52.0	0.30	0
Br	MNN	1433.6	53.0	0.75	0
Ga	MNN	1433.6	53.0	0.32	0
Ba	NOO	1431.6	55.0	0.20	0

- **Element? :** core lines of a given element are shown just entering the chemical symbol of that element in the editable box on the bottom left;
- **Core Lines:** enables plotting the position of element corelines;
- **Auger Transitions:** enables plotting the position of element Auger features;
- **Hold Plot:** to show the core line or Auger Transition position of more than one element;
- **Cursor position:** allows reading the position of spectral features with a cursor;
- **Undo:** cancels the last added element when *hold* is activated;
- **Refresh:** to refresh the survey for displaying new set of spectra component;
- **Close:** to exit the Corelines & Auger Tables.

⇒ **VMS DATA TRANSMISSION CORRECTION: ONLY FOR KRATOS VAMAS FILES.**

Raw Vamas files contain information to correct data for the transmission of the analyzer. The transmission is a function of the kinetic energy and is characteristic of any individual analyzer. Then the transmission coefficients are instrument dependent and should be generated by the *raw-data to Vamas* conversion routine provided by the manufacturer.

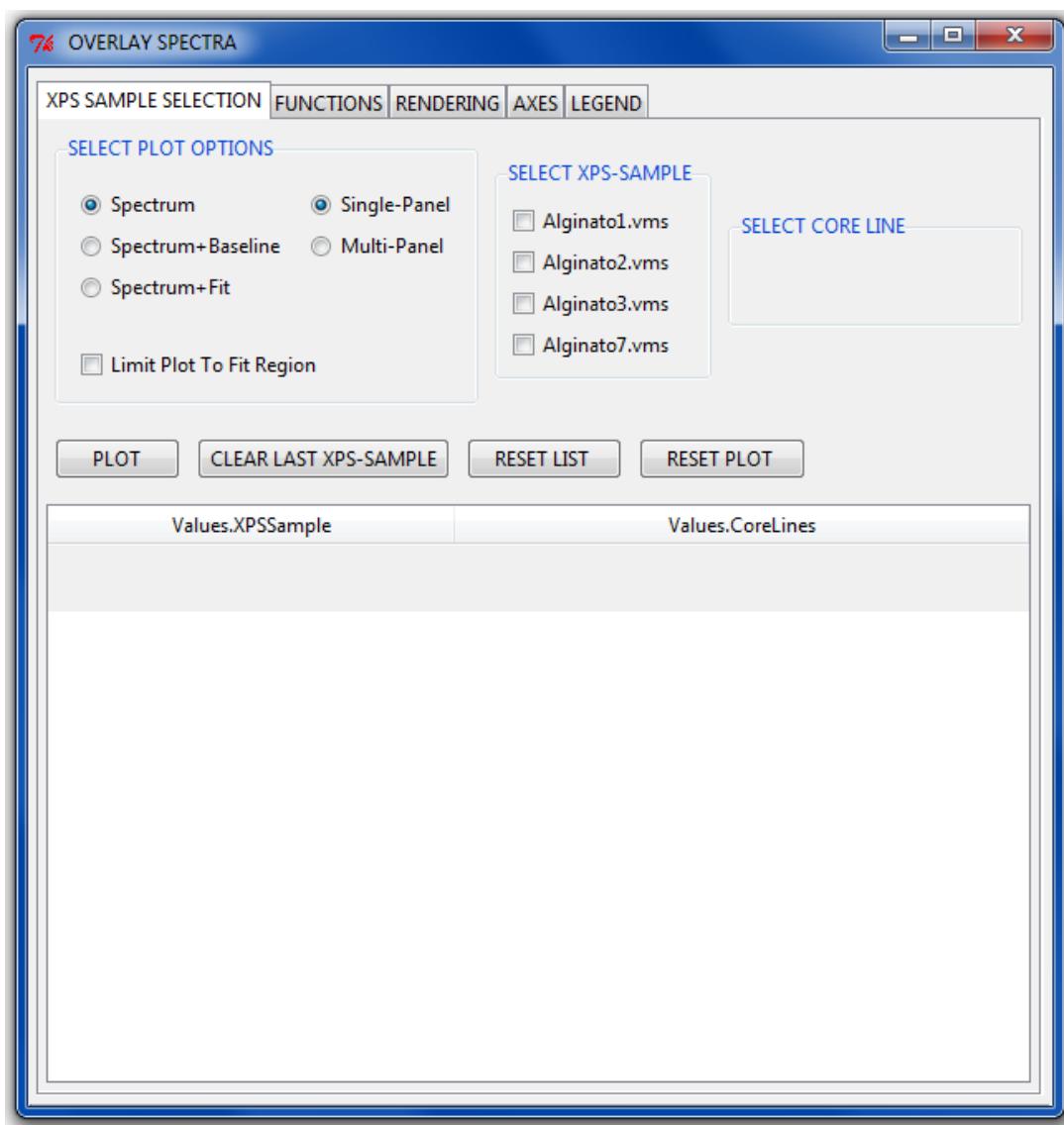
When Vamas spectra are read, the correction for the transmission factor is automatically applied. However for some reason it is possible to go back to the original raw data or apply the transmission correction to uncorrected raw Vamas data utilizing the *VMS Data Transmission Correction*.



- **Select the XPS-Sample:** in the drop down list select the XPS-Sample containing the corelines to process: in the CONTROL INFOs window will appear the list of corelines and if they are ready to be corrected or if they do not need correction;
- **Select the Core-Line to process:** in the drop down list select the single Core-Line or *all* the corelines to process;
- **Correct Data button:** press the button to correct the Vamas data
- **Replace Raw Data:** press this button to go back to raw Vamas data previously corrected.

PLOT menu:

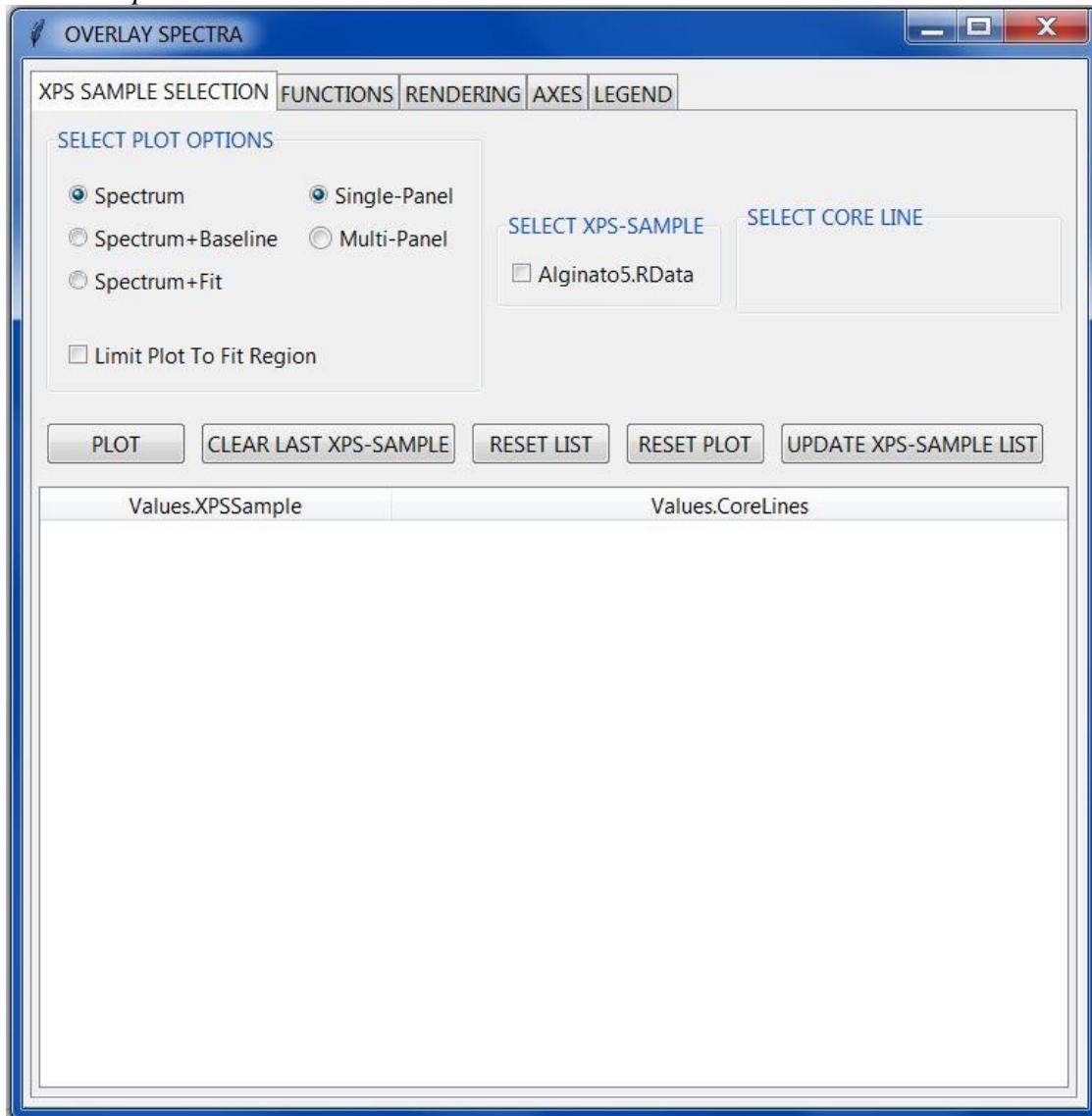
- ⇒ **PLOT:** plots the active XPS-Sample including wide spectra, corelines and peak fittings when present. Due to limited extension of the graphic window, only the first 12 spectra are plotted. Next corelines may be visualized right-clicking on the XPS-Sample name and selecting the desired Core-Line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

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 Core-Line 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:

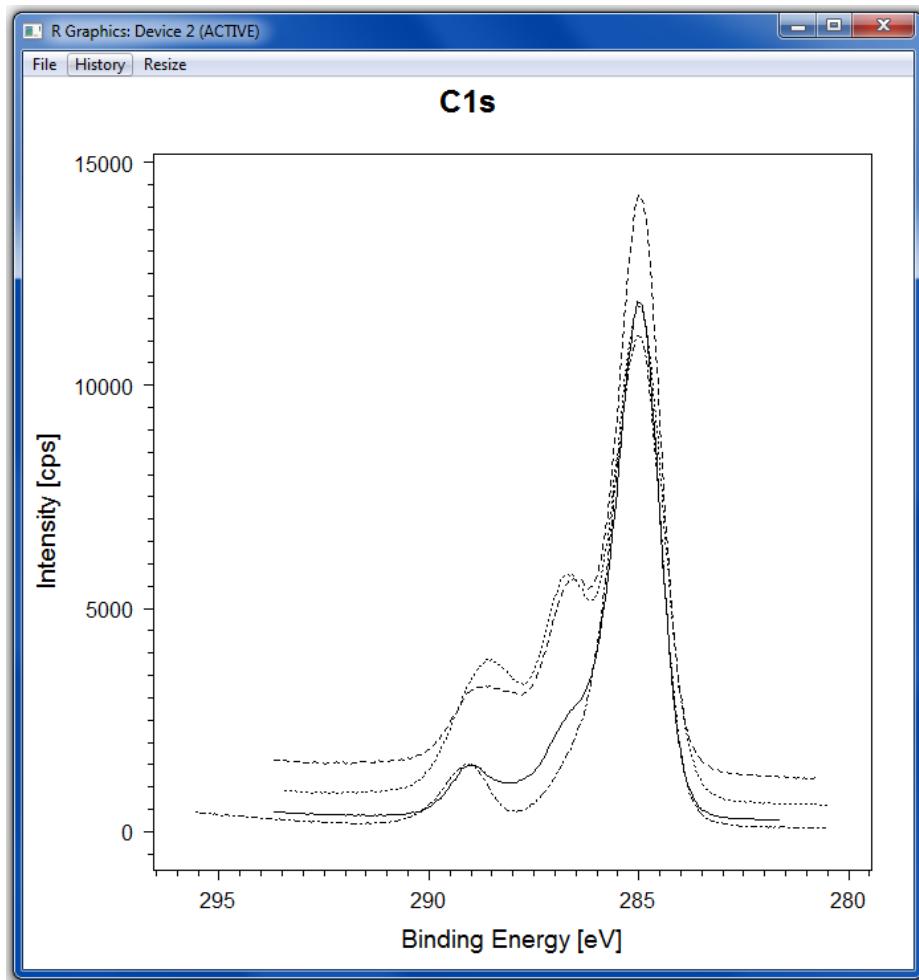
- **Spectrum:** just the original data will be plotted;
- **Spectrum + Baseline:** spectrum + baseline will be plotted;
- **Spectrum + Fit:** spectrum + complete fit will be plotted;

These spectral details will be plotted either in

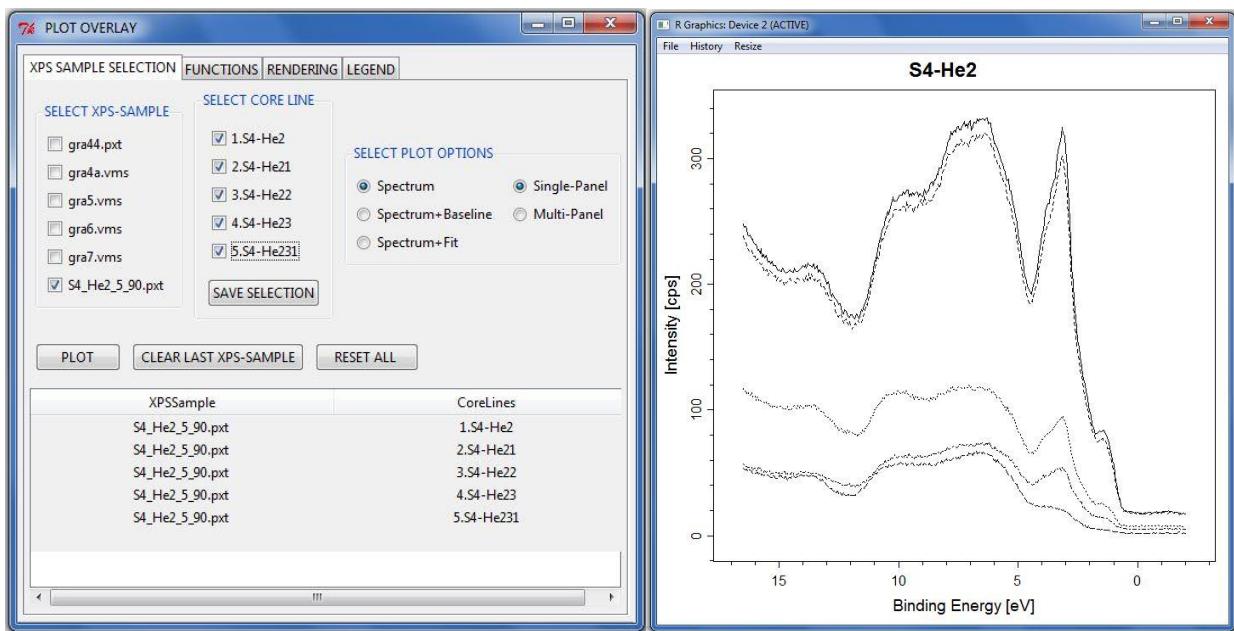
- **Single panel:** all the spectra overlapped in a single graphic panel;
- **Multi-panel:** the different corelines provided with the selected details will be plotted in separated panels.

- **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 List:** resets the list of the spectra to be plotted maintaining the options which will be applied to the new list of corelines;
- **Reset Plot:** resets the list of spectra, the plot and the plot options;
- **Update XPS-Sample List:** if you load a new XPS datafile in RXPG, you can update the XPS-Sample list of XPSOverlay routine to plot it;

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

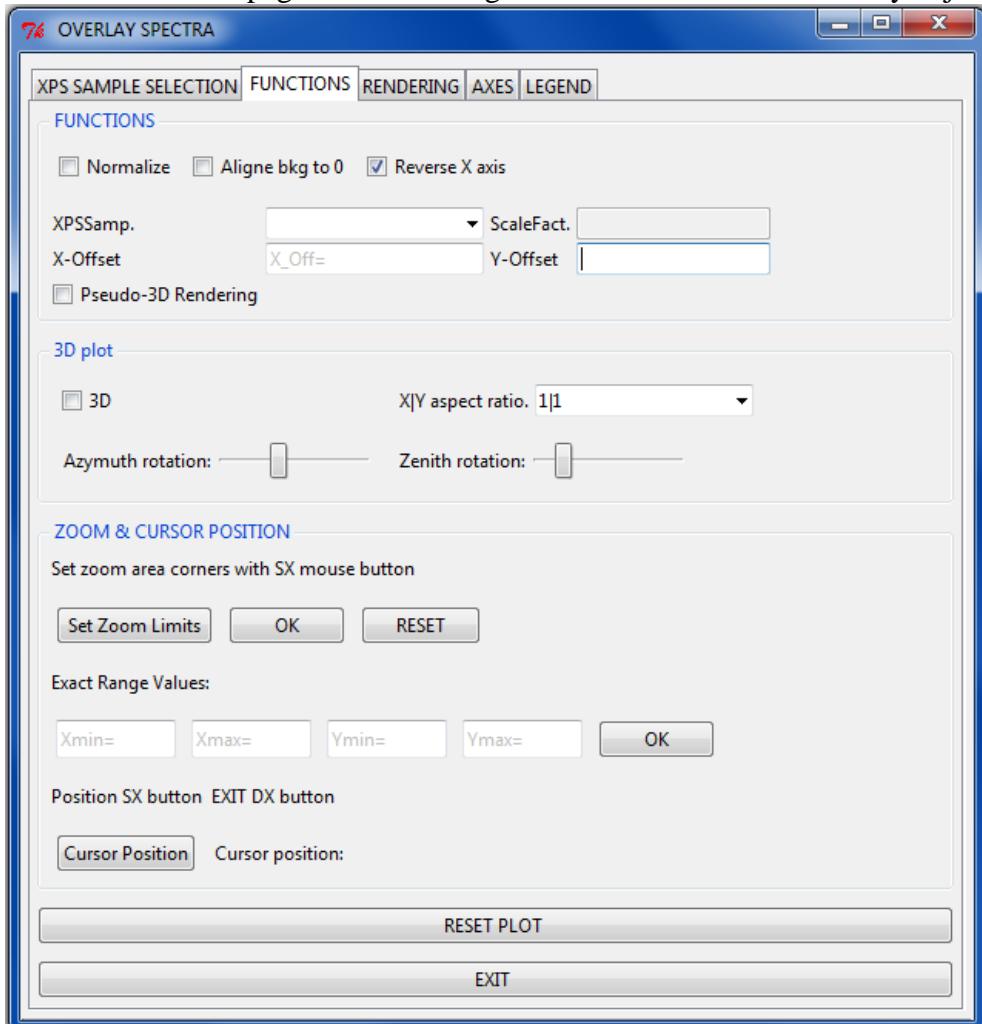


It could happen that a single XPS-Sample file contains more than one Core-Line you want to overlap (for example a depth profile or same Core-Line acquired at different tilt angles etc...). In this case after selection of the XPS-Sample, select all the relative corelines to overlap:

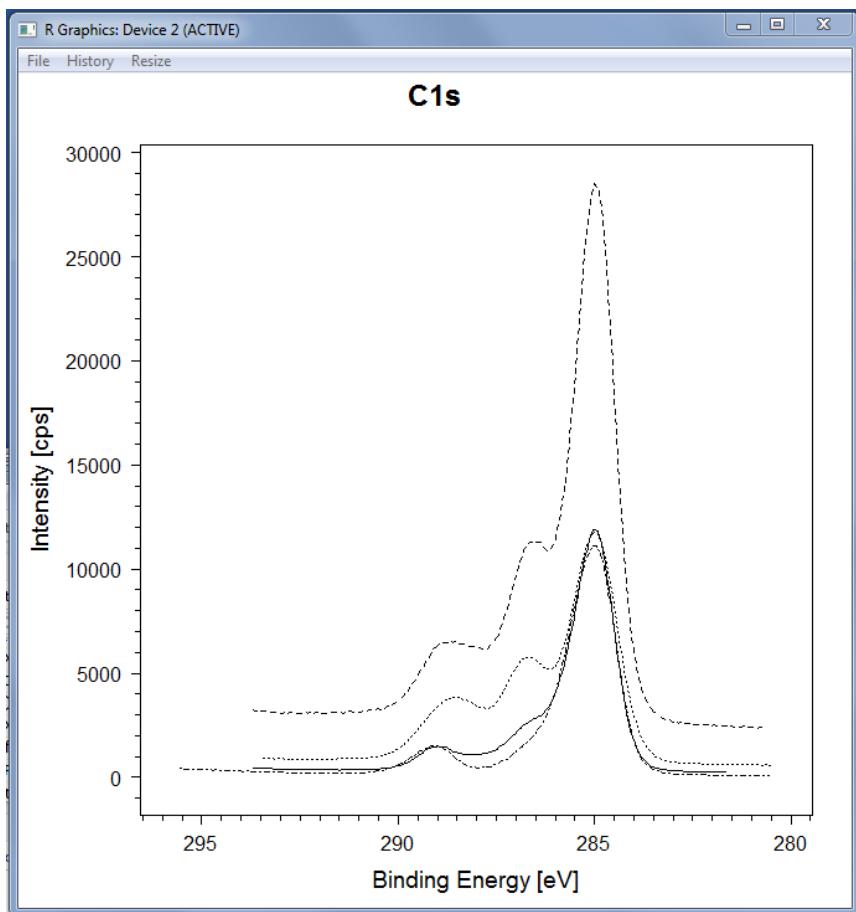
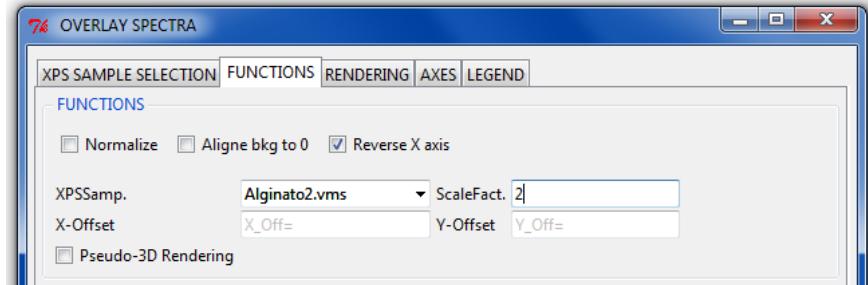


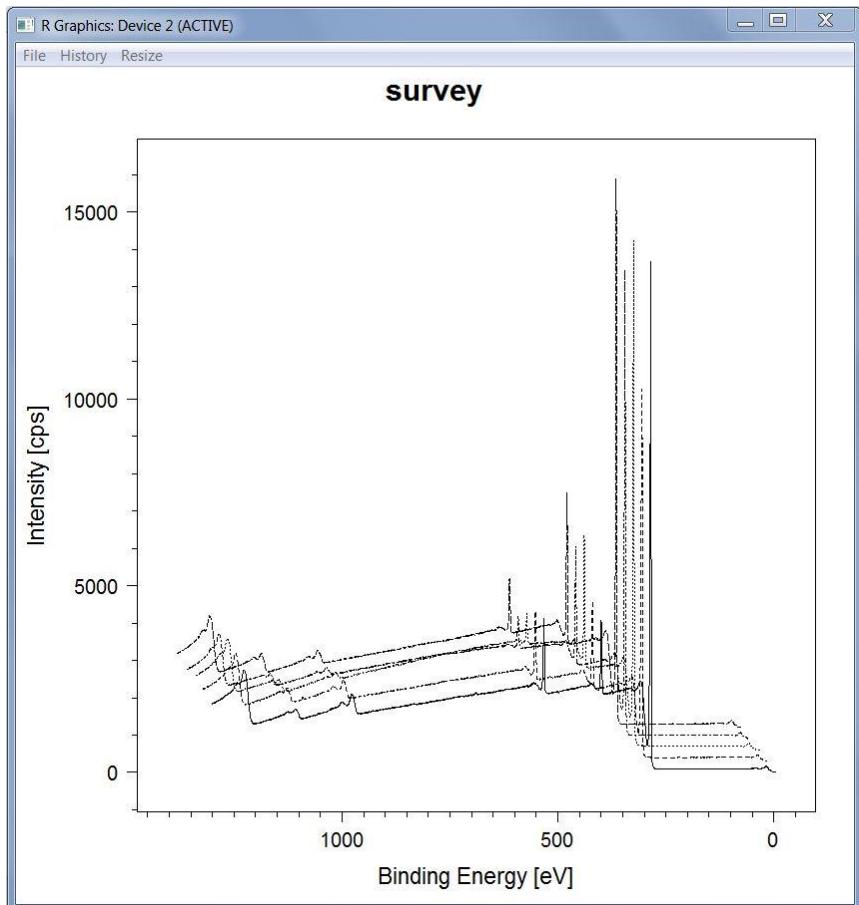
In this example the XPS-Sample S4_He2_5_90.pxt contains a series of five VBs which are selected and overlapped in a unique figure.

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

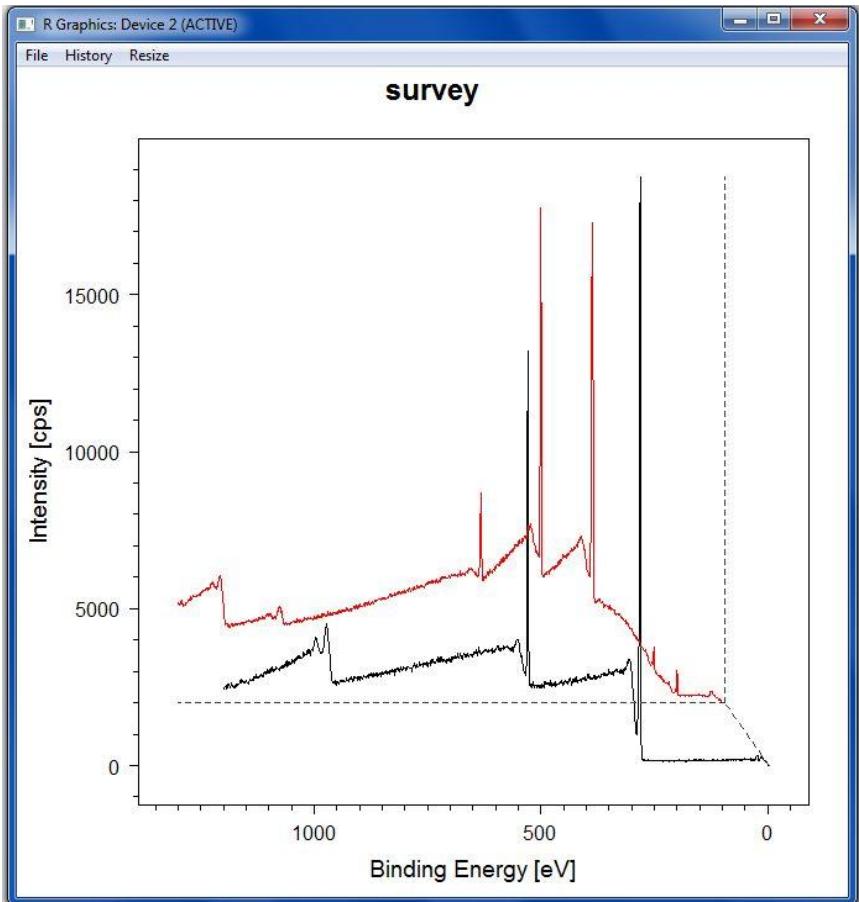


- **Normalize:** to normalize all the spectra to intensity = 1.
- **Aligne bkg to 0:** for each of the spectra this option puts the background minimum = 0;
- **Revers X-axis:** reverse the X axis (this to plot in binding energy);
- **Rescaling the single spectrum: XPSSamp:** select the XPS-Sample of the Core-Line to rescale with the drop-down list; input the **Scale-Factor** to amplify/reduce the intensity of the selected spectrum;
- **XPS-Samp:** select the XPS Sample among the list of data loaded in the Overlay function;
- **Scale Fact:** the scale factor to amplify/reduce the Core-Line of the selected XPS-Sample;

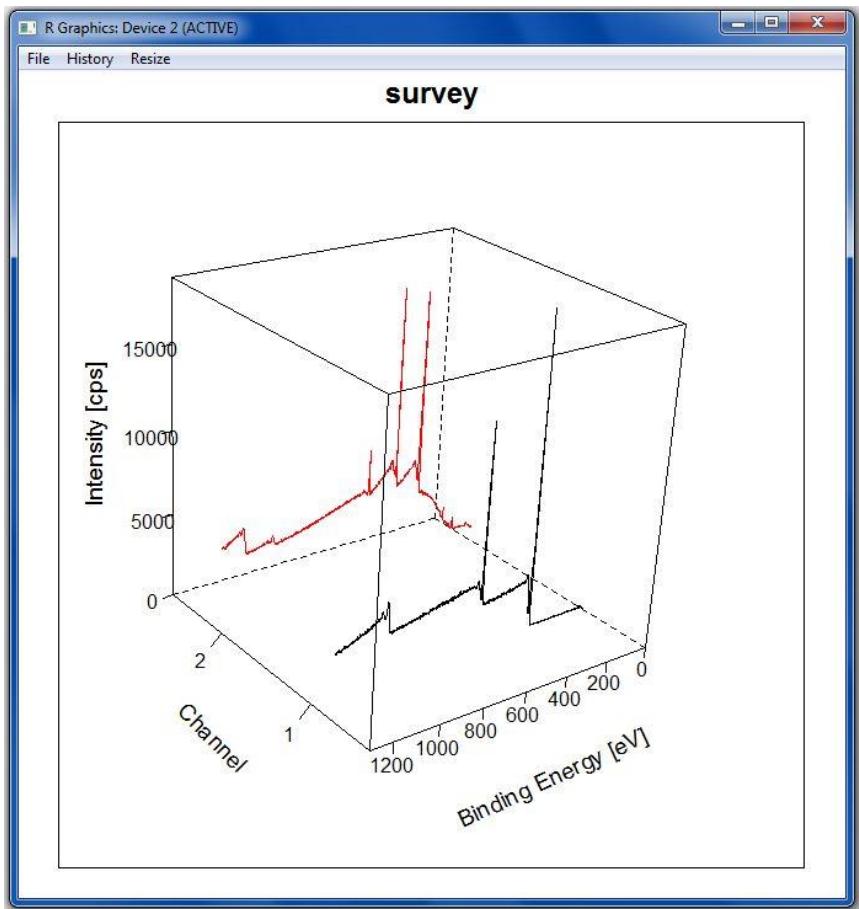




- **X-Offset, Y-Offset:** to apply a shift along the X and Y direction to all the spectra;



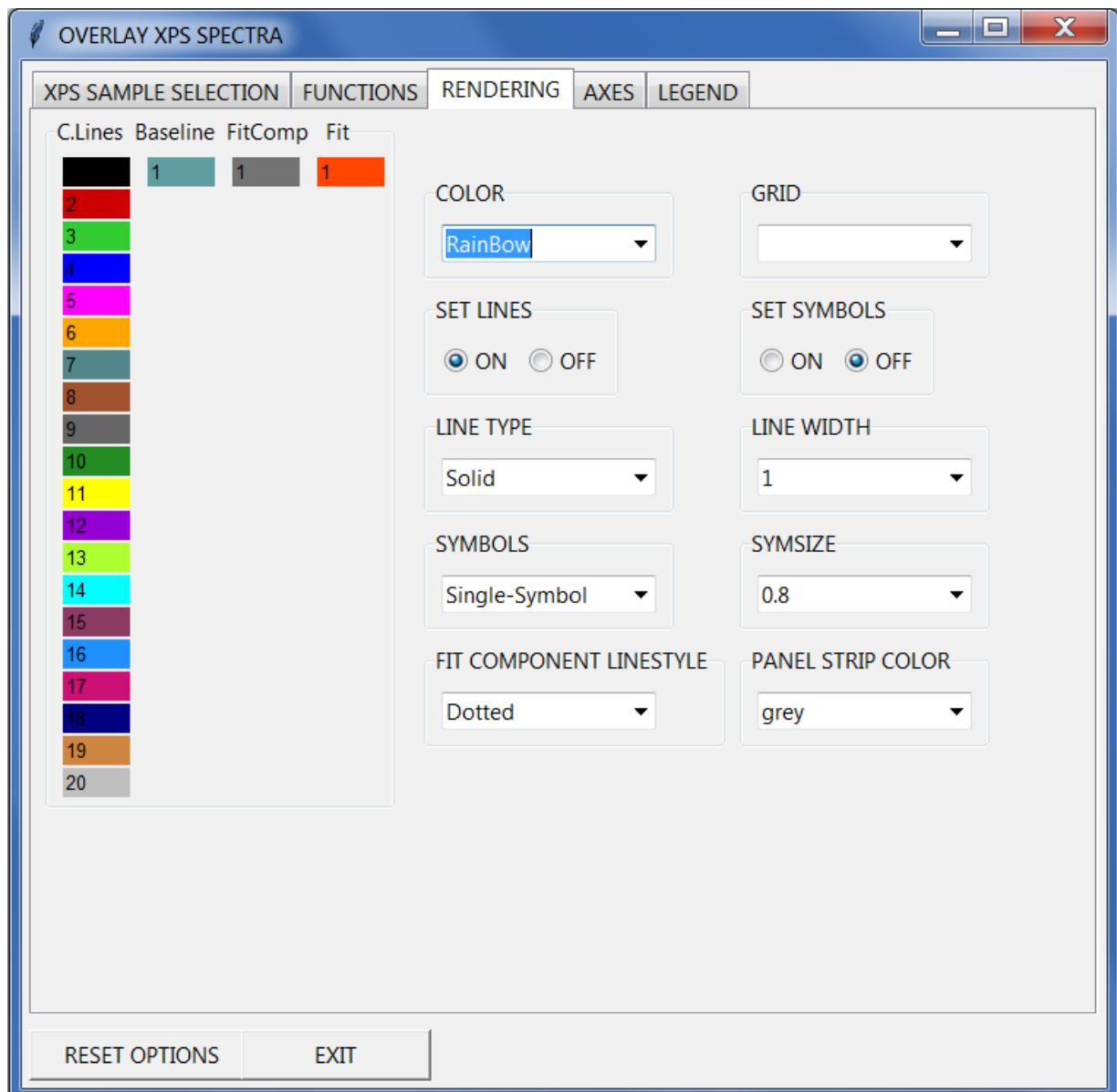
- **3D Pseudo rendering:** in presence of both X and Y offsets plots dashed axes to render 3D perspective as shown in the figure;



- **3D:** checking this box will visualize the spectra in a real 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 left 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:



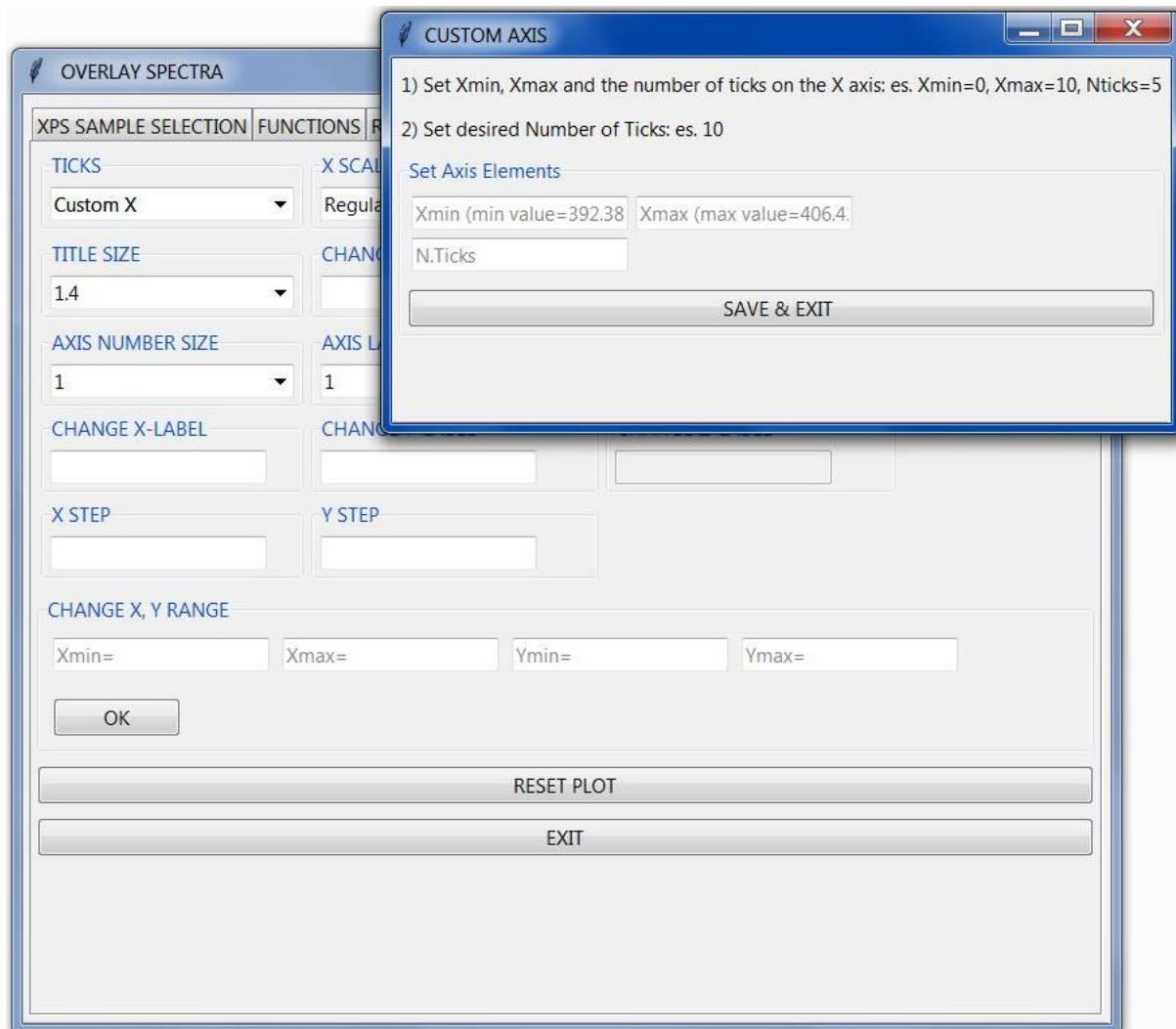
This page contains self explaining options acting on the figure:

- **Set Core-Line Palette, Set Fit Palette:** personalized color plot may be obtained by clicking on the related color. Palette is provided for corelines, baseline and fit components (in this example monochrome option in *Preferences* was set) and spectral fits.
- **B/W color:** to use black/white or color lines
- **Grid:** to set a grid on/off;
- **Set Lines:** the default is ON: lines will be used for the plot;
- **Set Symbols:** the default is OFF. When set ON symbols will be used for the plot.
- **Line Type:** when colors are selected lines can be solid or different patters can be chosen;
- **Line Width:** to select the line weight;
- **Symbols:** when colors are selected single symbol or multiple symbols can be chosen;
- **Symsize:** to select the symbol size.

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

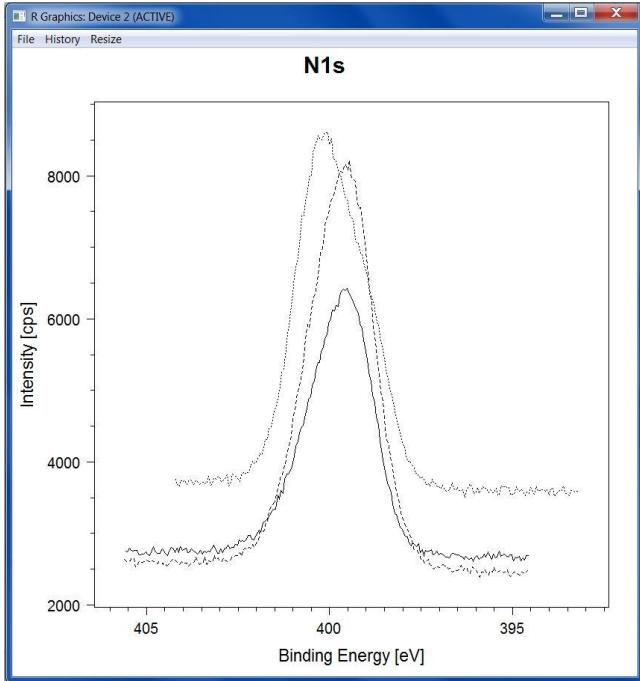
❖ **AXES:** in this page are the some general options used to optimize the figure rendering:

- **Ticks:** to set which axis should have ticks.
- **Custom X, Y:** to customize tick intervals on X, Y scale.

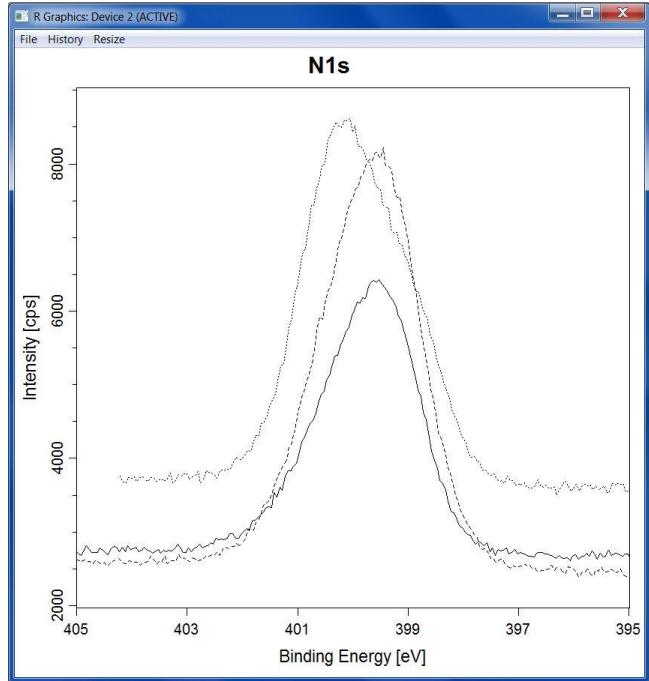


The X scale will be modified will be replotted following the custom X (Y) range and the relative number of ticks.

ORIGINAL VIEW



AFTER CUSTOM X

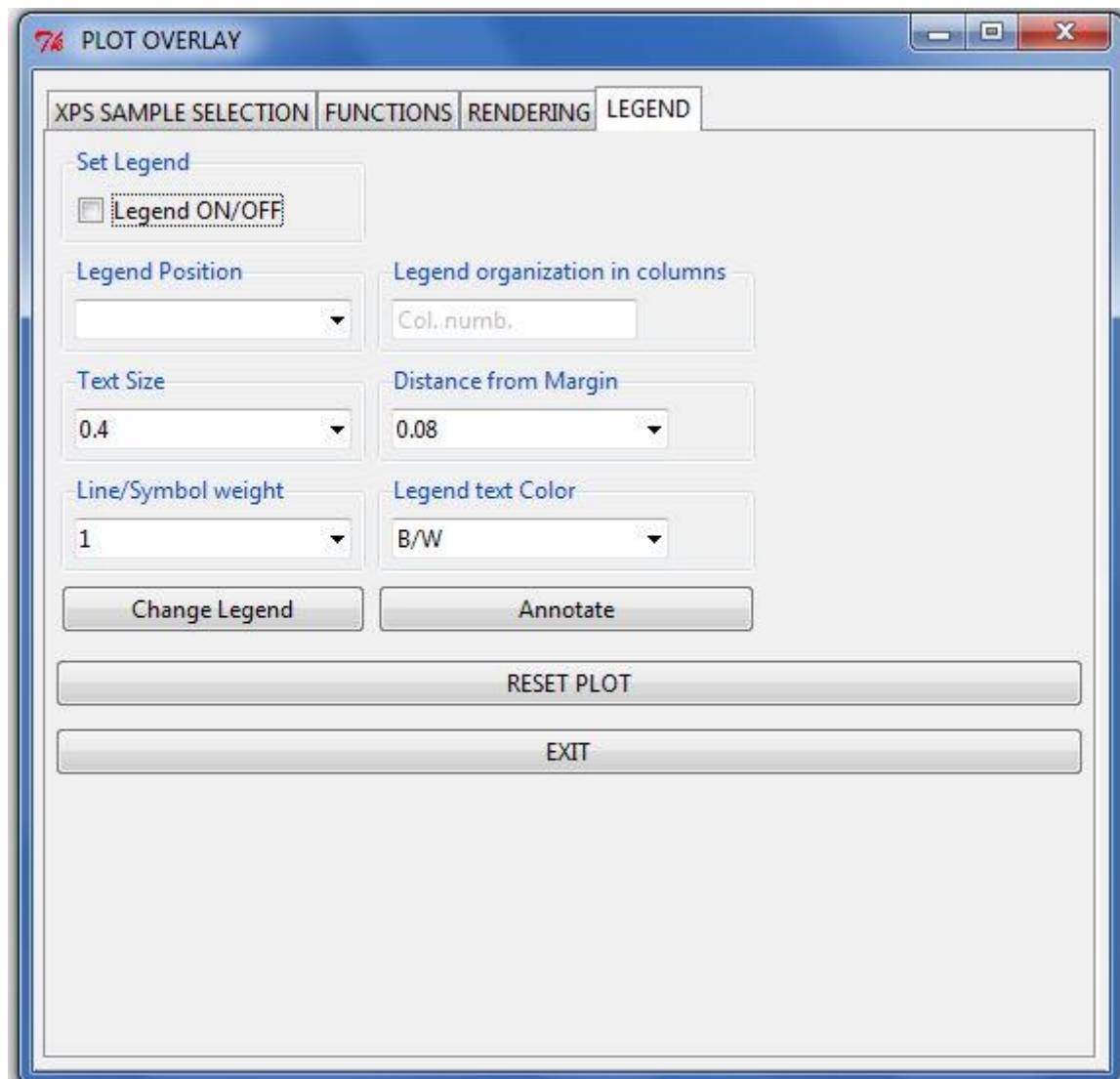


Selection of *Custom X* (*Custom Y*) will open a new window where to set the X minimum, X maximum, the number of ticks and as many tick-labels as the ticks. Number, letters and also white spaces can be used for the tick-labels.

Es: Xmin=0, Xmax=10, NTicks = 6, TickLabels = 0, 2, 4, 6, 8, 10

- ***Log. Scale:*** to set logarithmic scale on X axis, Y axis, both;
- ***Title size:*** to set the size of the title characters;
- ***Change Main Title:*** to change the plot title;
- ***Axis Label Size:*** to set the size of the axis labels: both axis are affected;
- ***Axis Name Size:*** to set the size of the axis Names: both axis are affected;
- ***Change X, Y, Z Name:*** to change the relative axis name: Z enabled only in 3D;
- ***Axis Label Size:*** to set the size of the axis labels;
- ***Xstep, Ystep:*** to change the X or Y scale increment. X, Y step is rounded on an integer value. This value is affected by the extension of the X, Y range;
- ***Change X, Y range:*** to change the X or Y scale on the desired range;
- ***OK button:*** to set the desired X,Y scale.
- ***Reset plot button:*** to reset the changes done and replot spectra as initially done.
- ***Exit:*** to exit the overlay procedure.

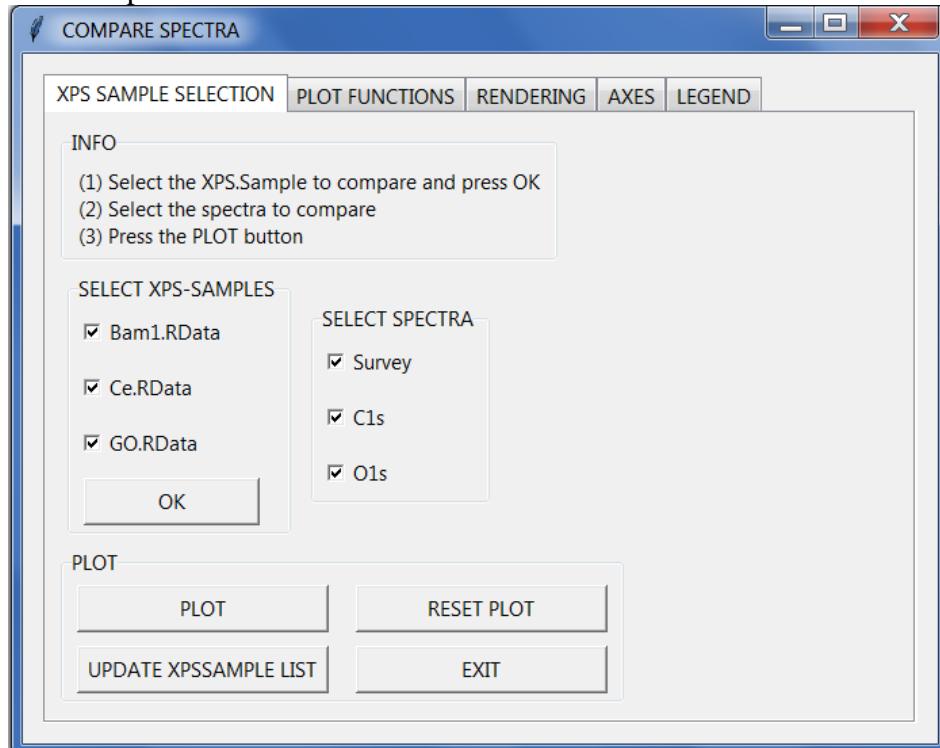
- ❖ ***LEGEND :*** to add text to the figure:



- **Set legend:** to set plot legends on/off;
- **Legend 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.

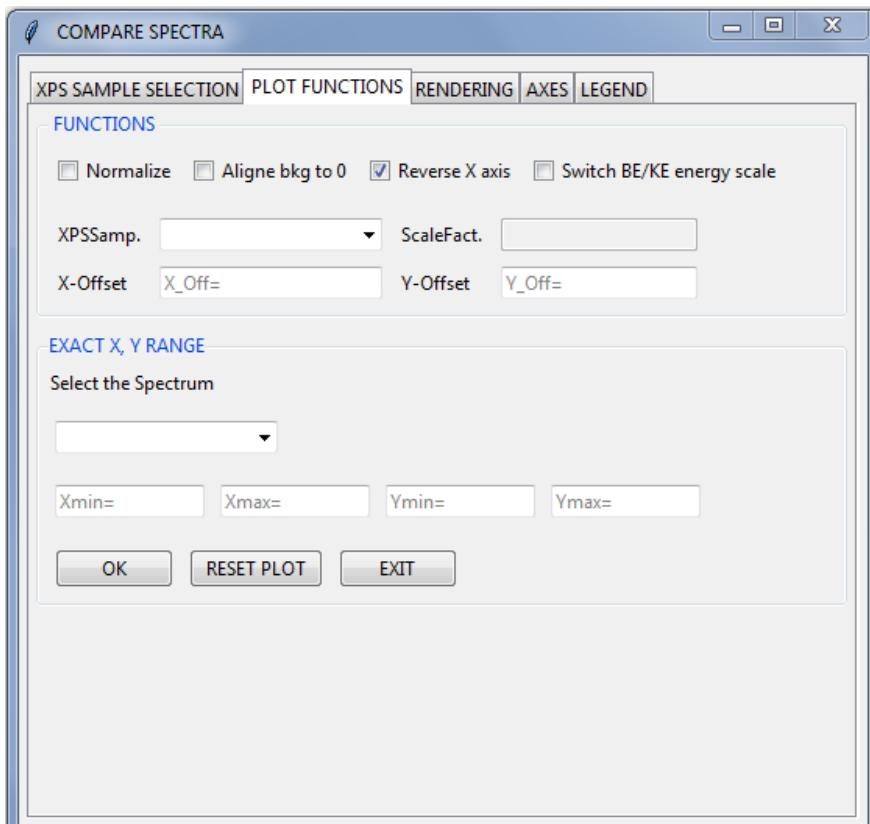
⇒ **COMPARE XPS-SAMPLES:** this function allows comparing different core-lines of different XPS-Samples. The different core-lines are plotted in separated panels. This option is organized as the *Overlay Spectra* options, offering almost the same options. Here we will provide the base information to proceed. Please refer to the *Overlay Spectra* for more details

❖ **XPS-SAMPLE SELECTION:** here are selected the XPS-Sample and common Core-Lines to compare



As far as the XPS-Samples are selected the list of spectra common to the selected XPS-Samples are indicated on the right check box-group. Common core-lines can be selected and plotted. In the example Bam1.RData contains Survey, C1s, O1s, N1s Core-Lines. When also Ce.RData and GO.RData are selected, common Core-Lines to be compared are only Survey, C1s and O1s. The corelines of the selected XPS-Samples will be plotted in individual panels. No fit option is available in *Compare Spectra* function.

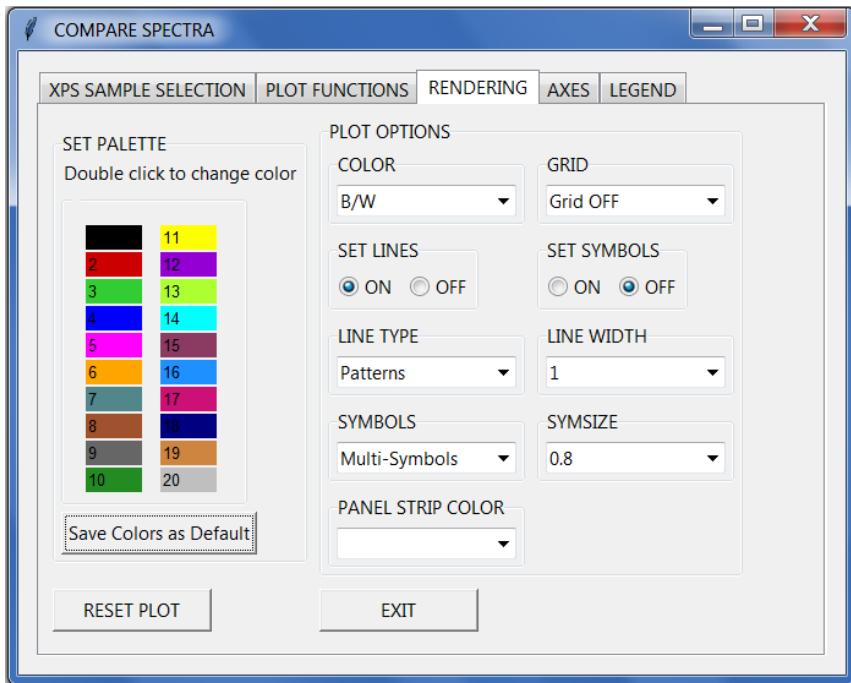
❖ **PLOT FUNCTIONS:** this page contains options to optimize the plot of the spectra



- **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 Core-Line to rescale with the drop-down list; input the **Scale-Factor** to amplify/reduce the intensity of the selected spectrum;
- **XPS-Samp:** select the XPS Sample among the list of data loaded in the Overlay function;

- **Scale Fact:** the scale factor to amplify/reduce the Core-Line of the selected XPS-Sample;
- **Exact X, Y range:** it is possible to change the default X, Y range to plot spectra following the own needs. First *Select the Spectrum* you want to modify the X,Y range. Therefore, input values for Xmin, Xmax, Ymin, Ymax.

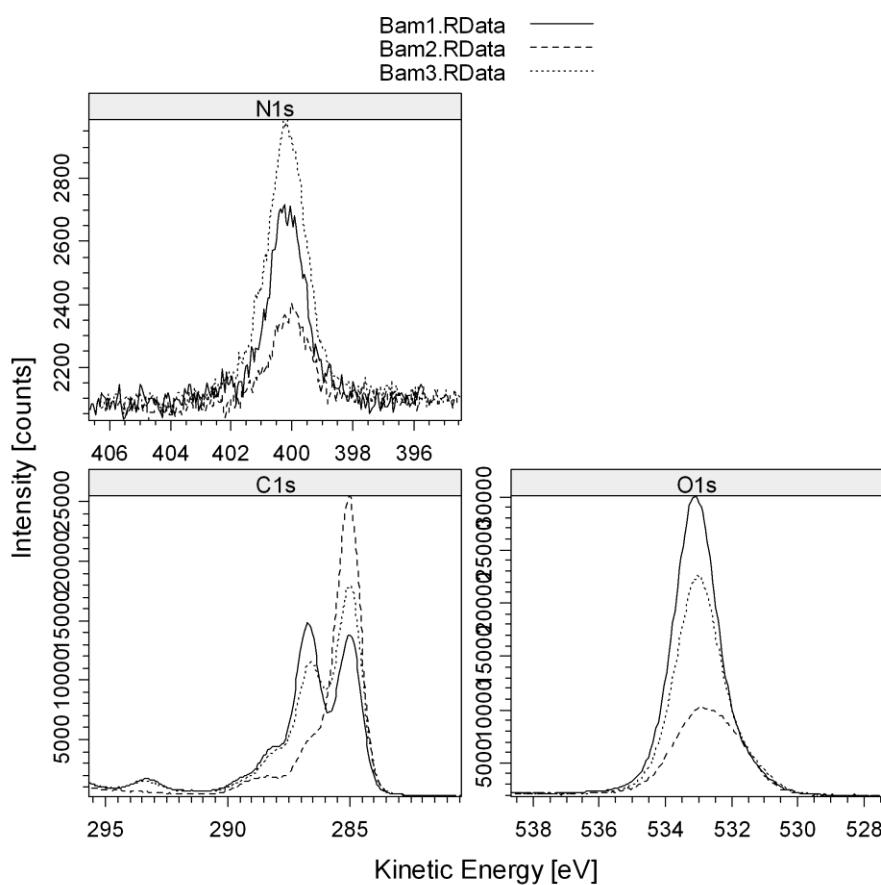
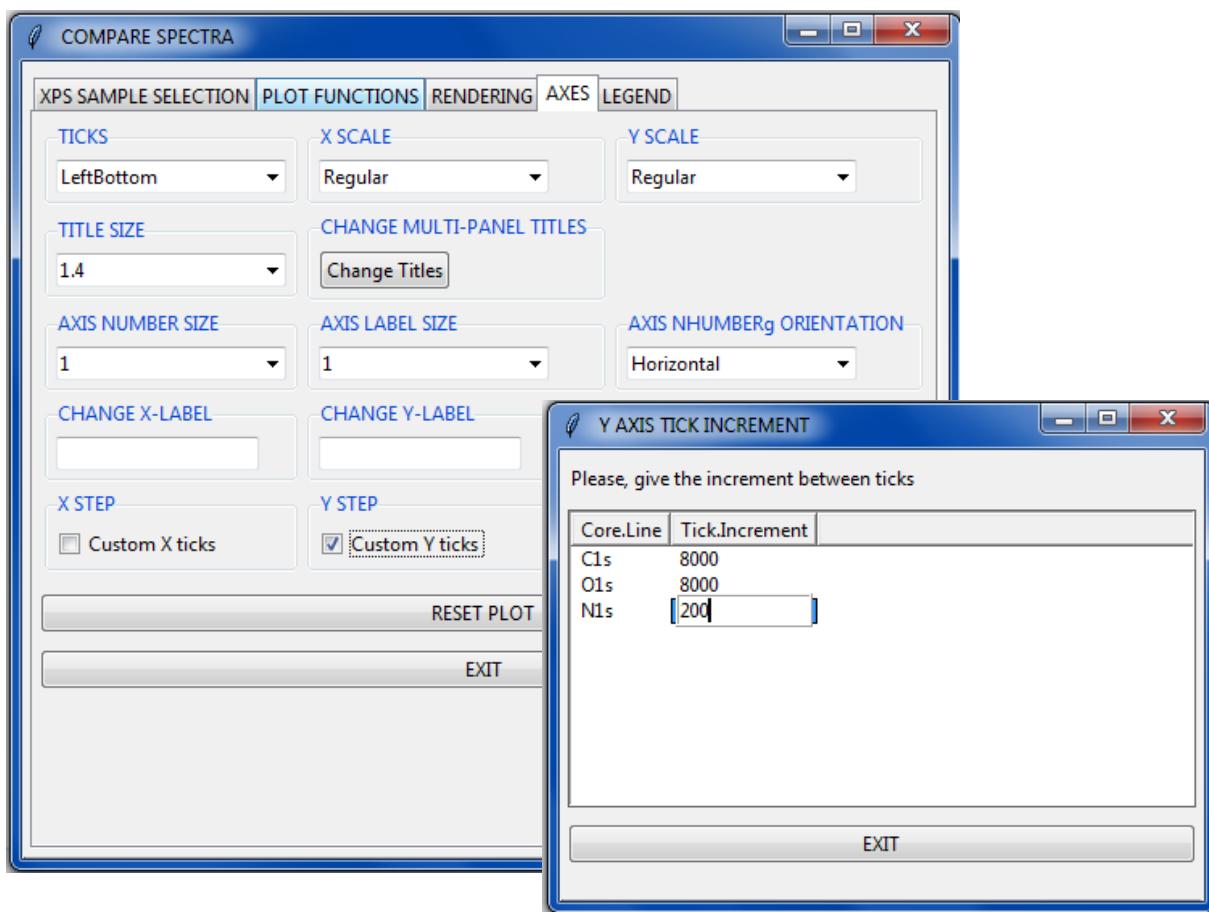
❖ **RENDERING:** this page contains self explaining options acting on the figure:



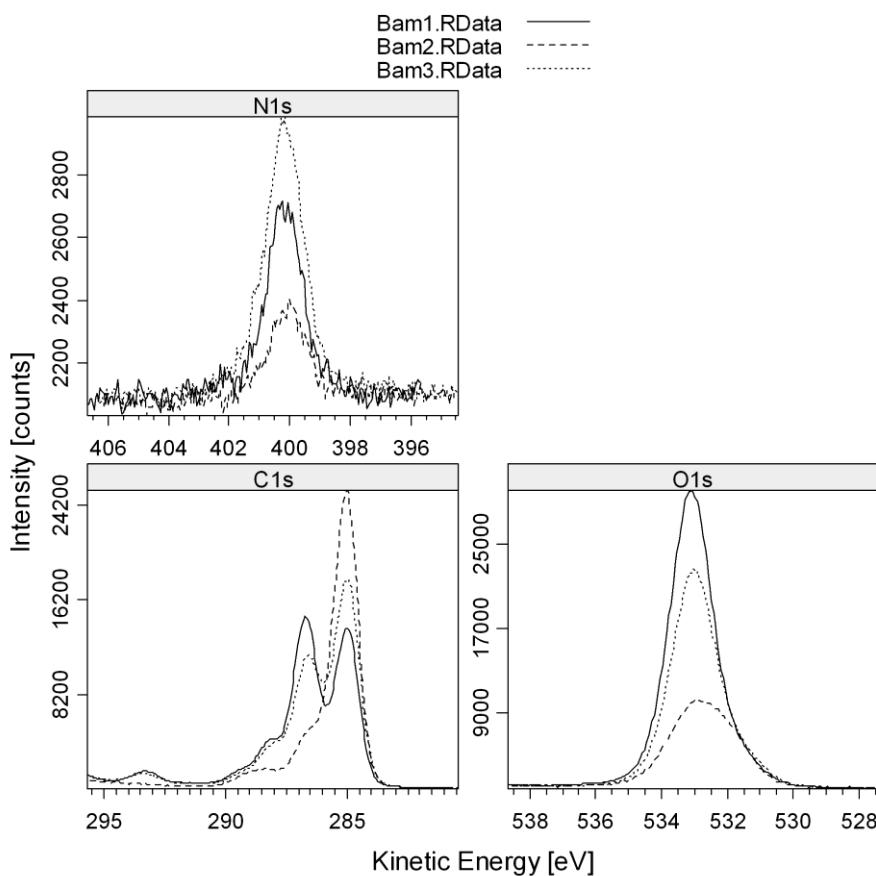
- **Set Core-Line Palette, Set Fit Palette:** personalized color plot may be obtained double-clicking on the correspondent color.
- **B/W color:** to use black/white or color lines
- **Grid:** to set a grid on/off;
- **Set Lines:** the default is ON: lines will be used for the plot;
- **Set Symbols:** the default is OFF. When set ON symbols will be used for the plot.
- **Line Type:** when colors are selected lines can be solid or different patters can be chosen;
- **Line Width:** to select the line weight;
- **Symbols:** when colors are selected single symbol or multiple symbols can be chosen;
- **Symsize:** to select the symbol size.
- **Panel strip color:** to change the color of the title bar of each of the panels used to plot the corelines

❖ **AXES:** this page is dedicated to customize the axes appearance:

- **Ticks:** option to change the tick position: default is *Left Bottom. Top Right* is available as well as *Both* to draw ticks on all the four axis.
- **X Scale, Y Scale:** possible type of scales used for the X, Y axis. *Regular, Power, Log.10, Log.e* are the scale type used to plot data.
- **Title size:** to set the size of the title characters;
- **Change Titles:** to change the panel title for the selected core-line;
- **Axis Number Size:** to set the size of the axis numbers: both axis are affected;
- **Axis Label Size:** to set the size of the axis Names: both axis are affected;
- **Axis Number Orientation:** orientation of the
- **Change X, Y Label:** to change the relative axis Label;
- **Xstep, Ystep:** to change the X or Y tick increment. When option selected, a window is opened requiring the input of tick increment for each of the plotted Core-line. As shown in the following example, the original plot is shown.

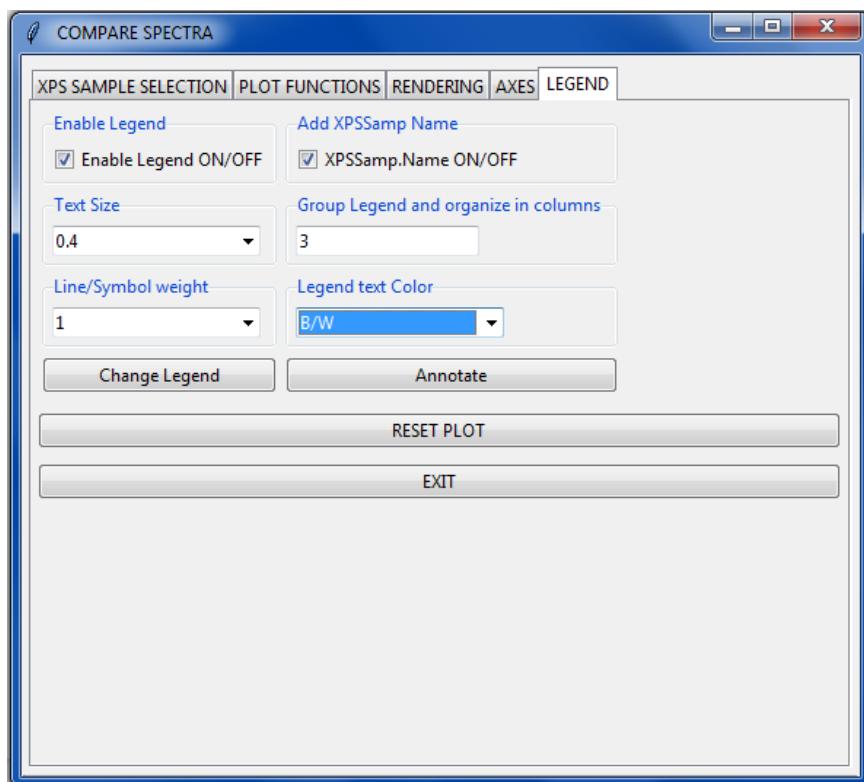


In the following example the Y axis of C1s and O1s are not properly plotted. The Y tick step is then modified for all the Core-Lines as shown in the previous figure.



Now the Y scale of all the plotted Core-Lines are modified following the custom tick-step given.

- ❖ **LEGEND:** this page regards the possibility to add legends to the plot:

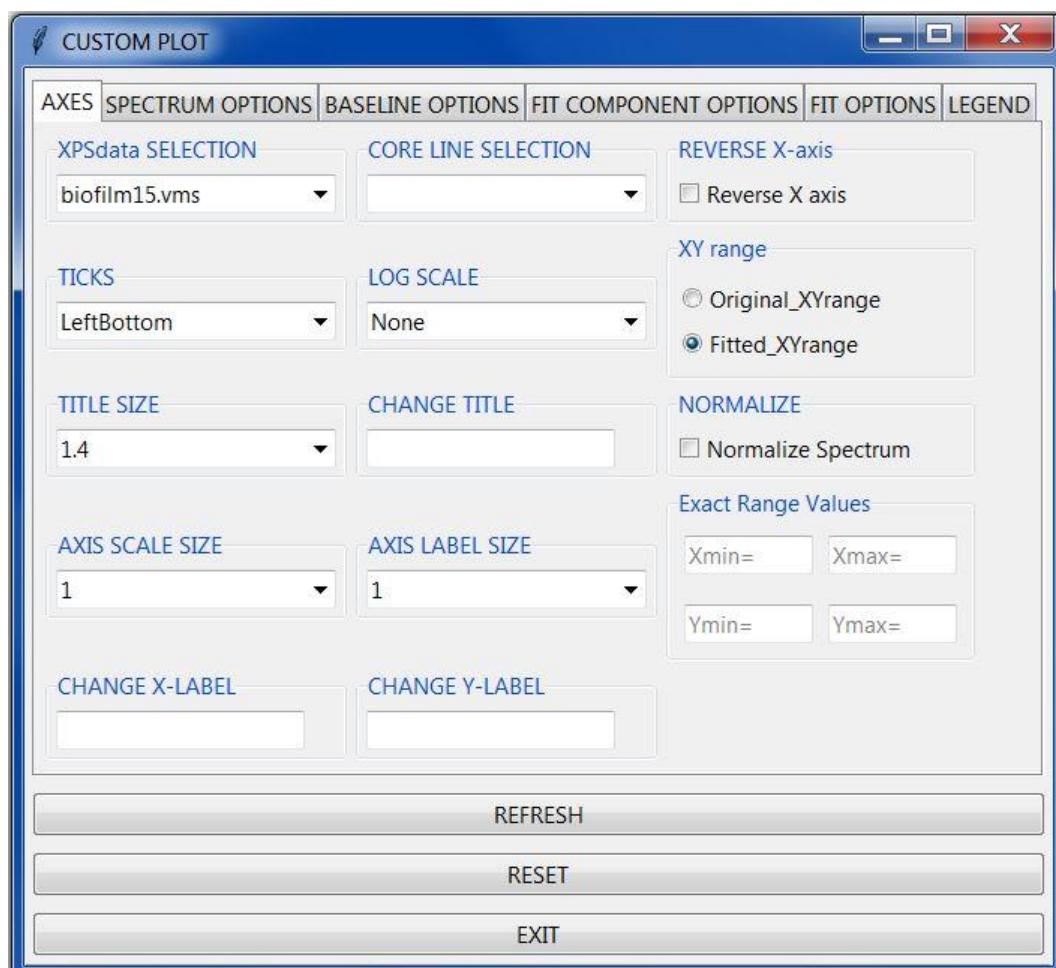


- **Enable Legend:** enables the legend to be added to plots. This option is active by default;
- **Add XPS Sample Name:** adds the name of the XPS Samples used to compare the corelines.
- **Text size:** size of the legend text.
- **Group Legend and organize in columns:** draw legends in the indicated number of columns.
- **Line, Symbol weight:** weight of the line, symbol used in the legend.
- **Legend text color:** the legend text may be written using the same color of the correspondent spectrum.

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

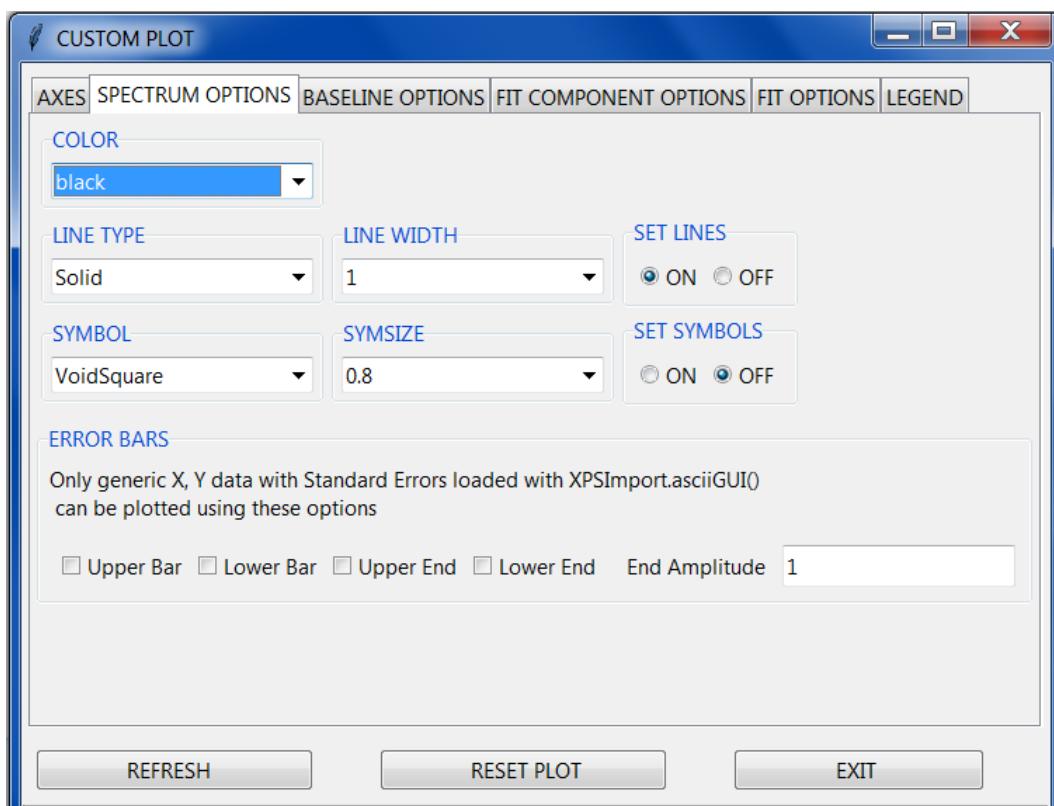
❖ **AXES:** this page contains the options regarding the axes format:

- **Core-Line selection:** to select the Core-Line 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;
- **Reverse X-axis:** to reverse the X-axis direction (to use if Binding Energy is set);
- **Original-XY Fitted-XY:** original XY plots data as acquired, Fitted-XY restrict the XY range to the extension of the fitted region;
- **Normalize:** to normalize spectra;
- **Exact Range Values:** set the plot area to the given values;
- **Reset button:** to reset the changes done and replot spectra as initially done..:

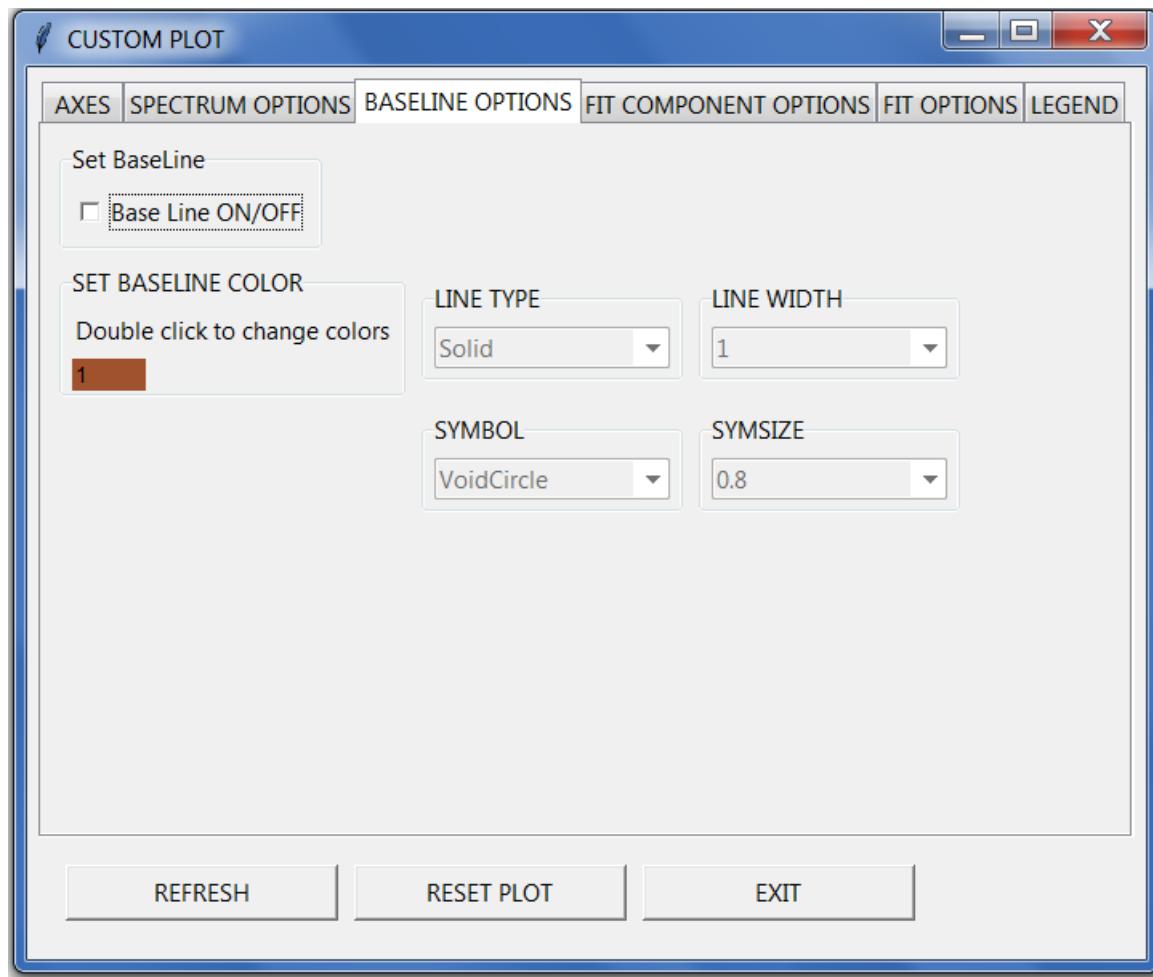


❖ **SPECTRUM OPTIONS:** this page contains options regarding the axes format:

- **Color:** to select B/W or color representation;
- **Line Type:** when colors are selected lines can be solid or different patterns can be chosen;
- **Linewidth:** to select the weight of the lines
- **Symbol:** to use symbols instead of lines for replotting;
- **Symsize:** to select the symbol size.
- **Error bars:** when data are loaded together with their standard error it is possible to plot the error bars or part of the bars. Corresponding checkboxes will appear automatically.
- **End Amplitude:** is a proportional factor to modify the horizontal segment at the end of the error bars 
- **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:

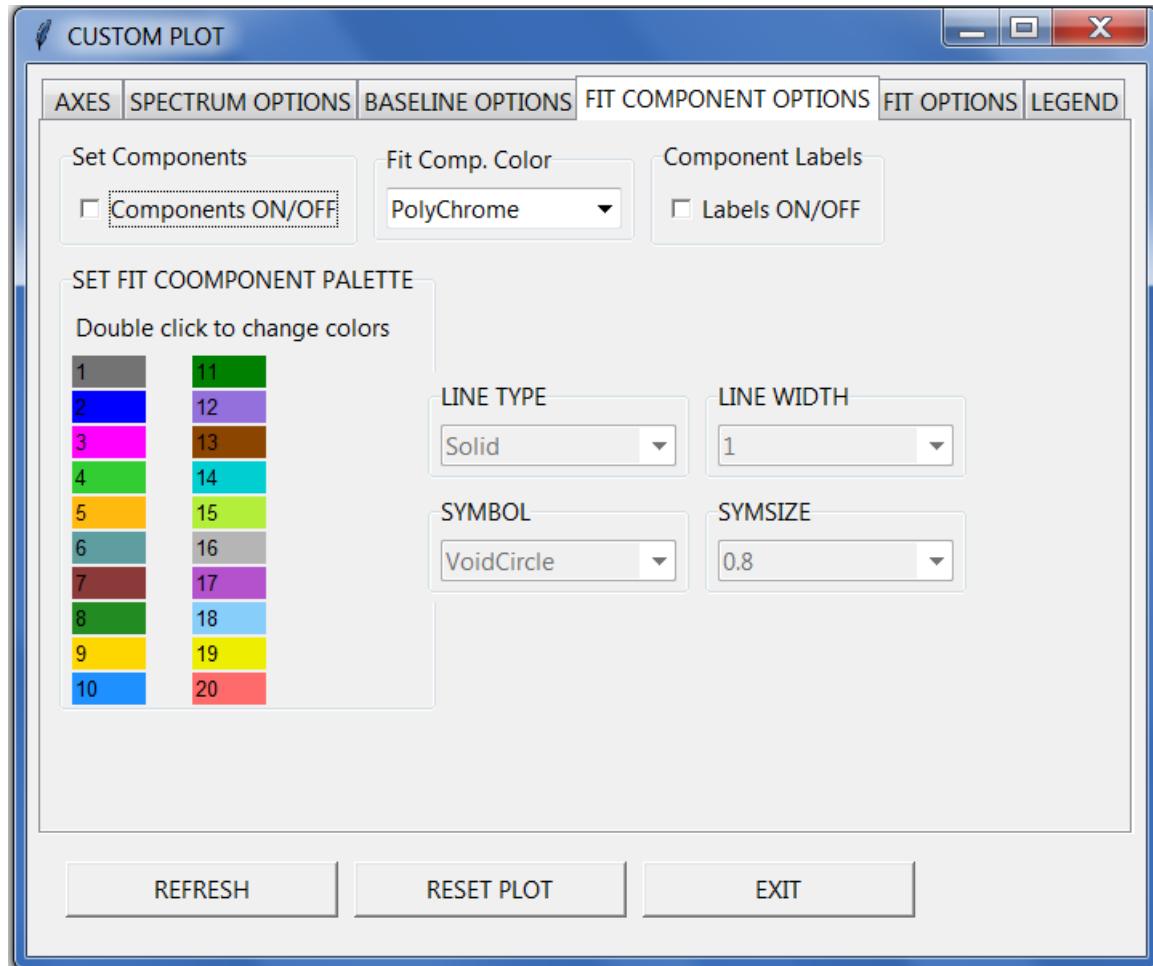


- **Set Baseline:** to set Baseline visualization ON/OFF;
- **Color:** to select the baseline color double-click on the correspondent rectangle;
- **Line Type:** when colors are selected lines can be solid or different patters can be chosen;
- **Linewidth:** to select the weight of the lines
- **Symbol:** 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:

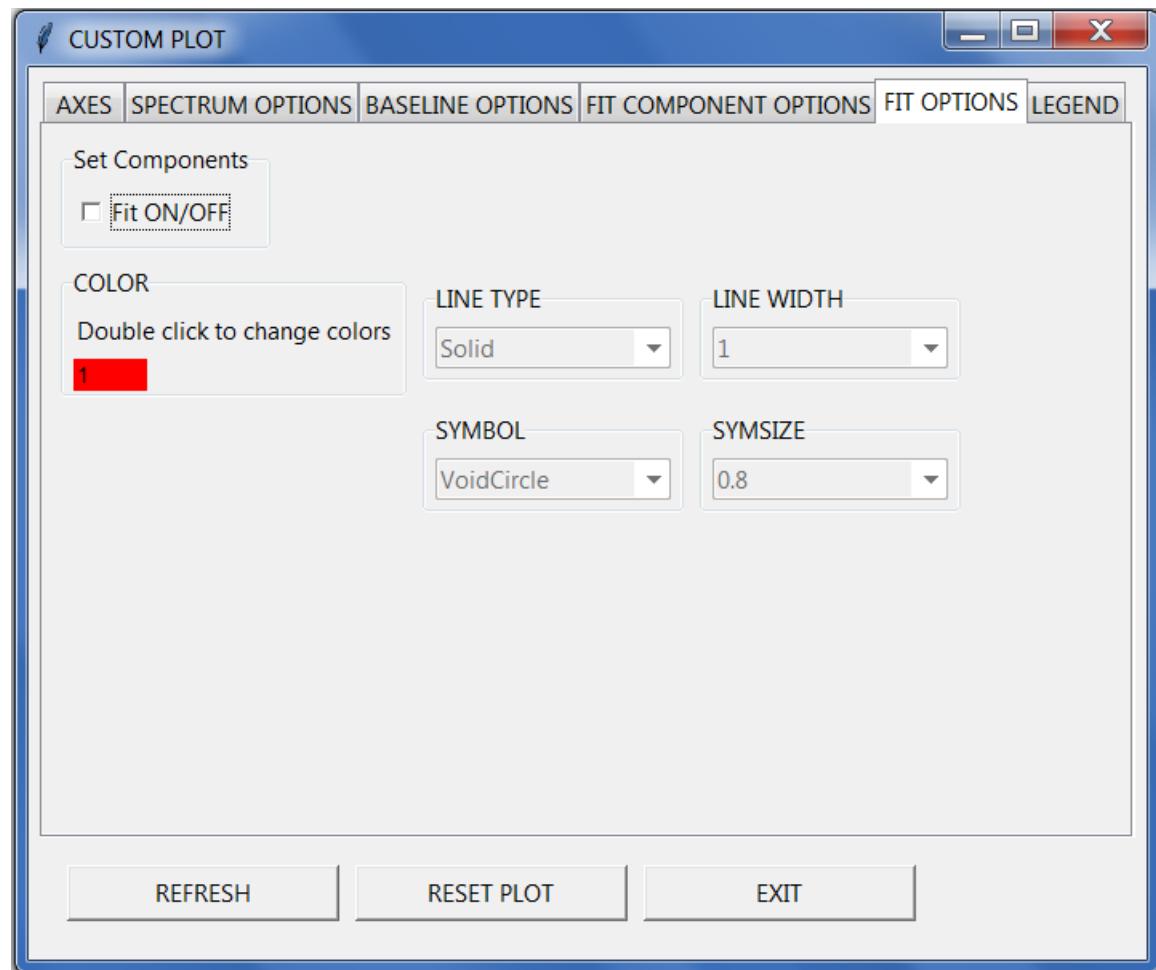
- **Set Fit Components:** to set Fit Components visualization ON/OFF;
- **Color:** *Monochrome* or *Polychrome* options are available to plot the fit components using the same or different colors respectively. In the example, Polychrome option is selected and the correspondent list of colors are shown on the left side of the GUI.
- **Fit Component Palette:** by double clicking on each color it is possible to personalize the palette.
- **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.

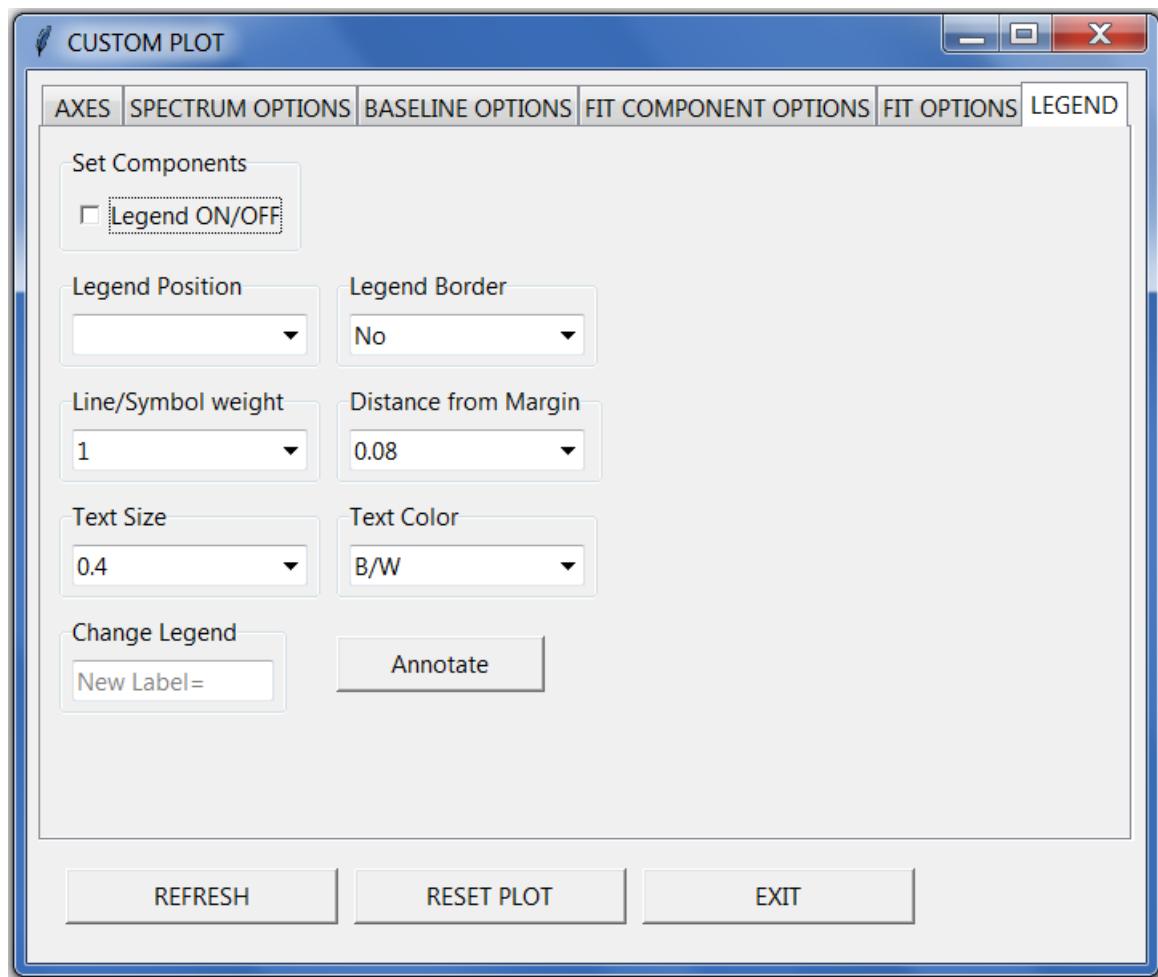


❖ **FIT OPTION:** this page contains options for plotting the spectrum Best Fit:

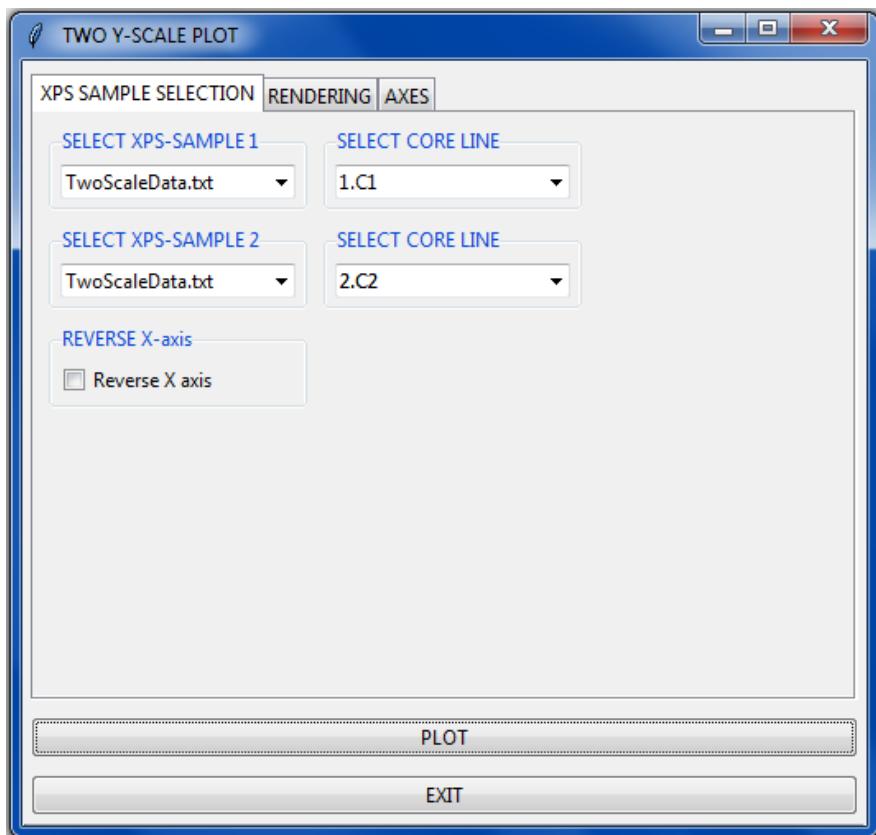
- **Set Fit:** to set the Best Fit visualization ON/OFF;
- **Color:** by double clicking on the *Fit color* it is possible to select custom colors for the fit.
- **Line Type:** when colors are selected lines can be solid or different patters can be chosen;
- **Linewidth:** to select the weight of the 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:

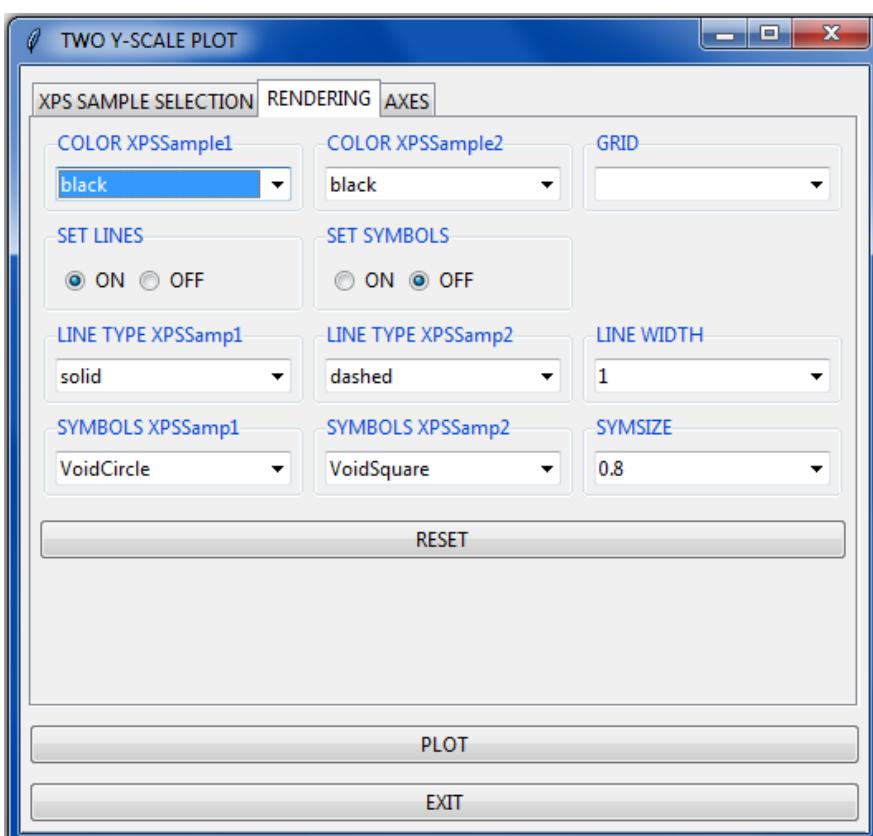


- **Set legend:** to set plot legends on/off;
 - **Legend position:** there are 8 different positions available for the legend corresponding to the four corners in inner and outside position;
 - **Legend orientation:** vertical or horizontal organization of the legend names;
 - **Distance from margin:** 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.
- ⇒ **TWO Y-SCALE PLOT:** this options allows for plotting data using different Y scales.
- ❖ **XPS-SAMPLE SELECTION:** this page contains options for drawing the legends:



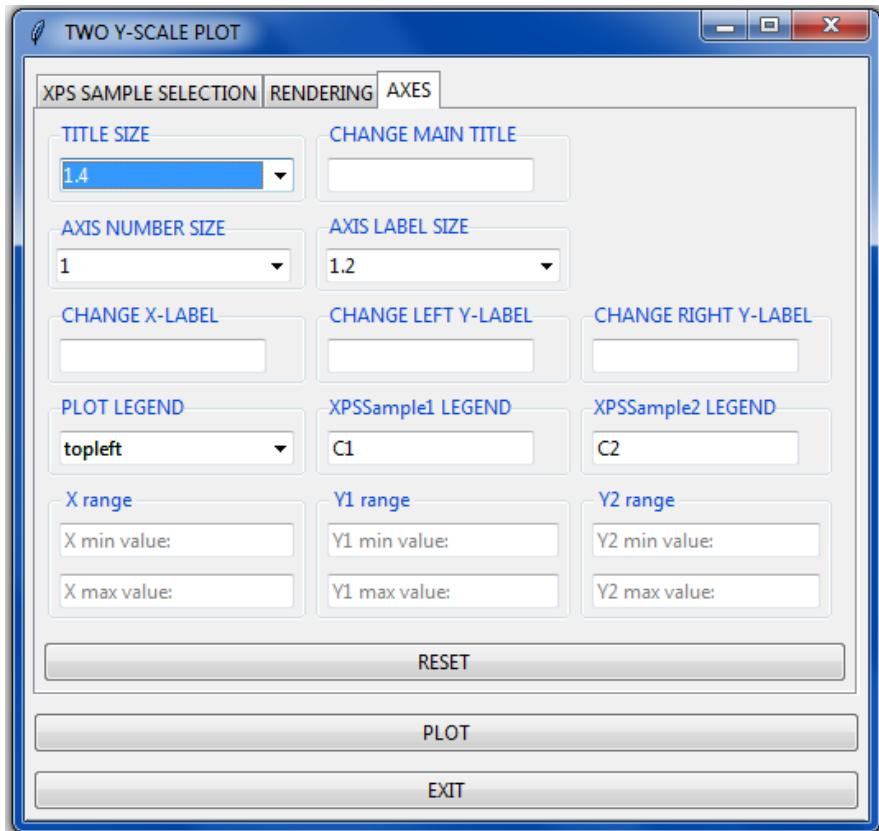
- **Select XPS-Sample1:** select the first data file;
- **Select Core Line:** select the first core line to plot;
- **Select XPS-Sample2:** select the second data file;
- **Select Core Line:** select the second core line to plot;
- **Reverse X axis:** reverse the X-axis
- **PLOT:** plot the data using two different left/right Y axis.

❖ **RENDERING:** this page contains options for customizing the plot.

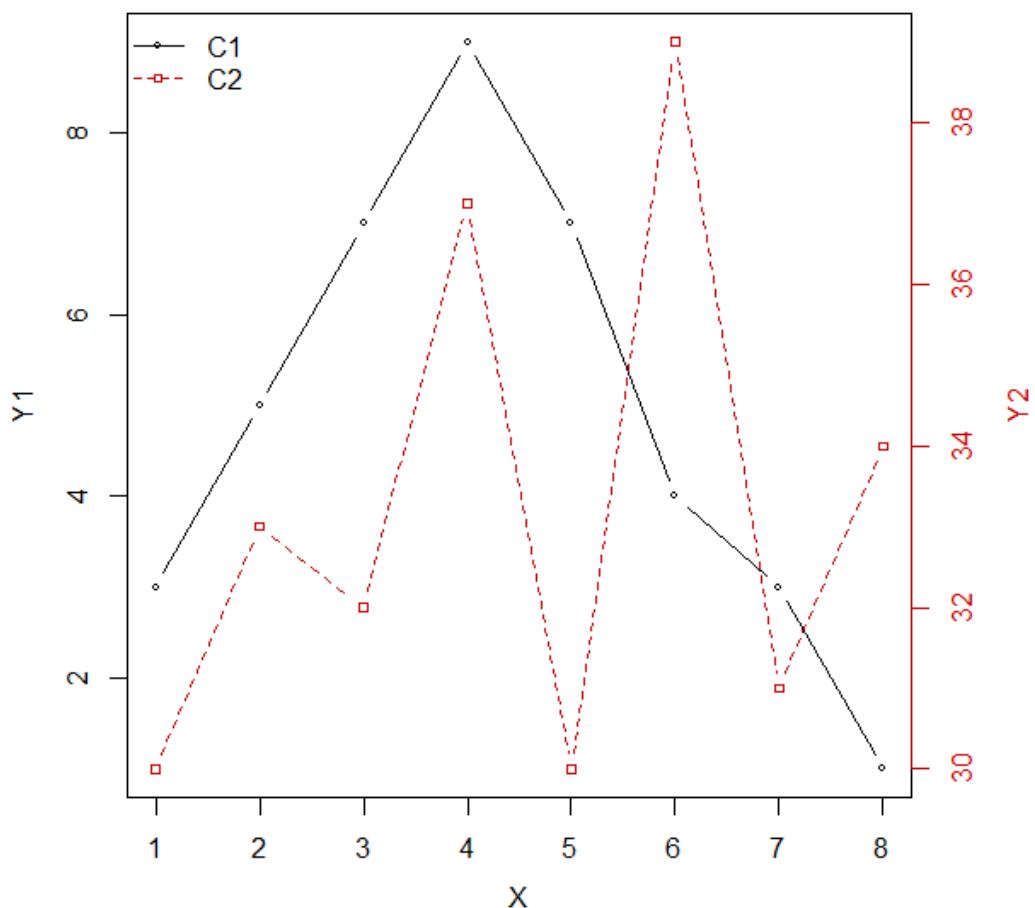


- **Color XPS-Sample1:** color of core-line 1;
- **Color XPS-Sample2:** color of core-line 2;
- **Grid:** enables the grid;
- **Set lines, set Symbol:** enables plot data using lines, symbols or both
- **Line Type, Symbols Sample1:** select the line type/symbols for the first coreline;
- **Line Type Symbols Sample2:** select the line type/symbols for the second coreline;
- **Line width, SymSize:** select the linewidth, symbol size.
- **Reset:** reset the plot to the default values.

- ❖ **AXES:** this page contains options for customizing the plot axes.



NB: it is possible to use *Import ascii* to load desired data into an XPSSample in two different core-lines



and use
TWO-Y-scale
Plot to plot
data as shown
in this
example.

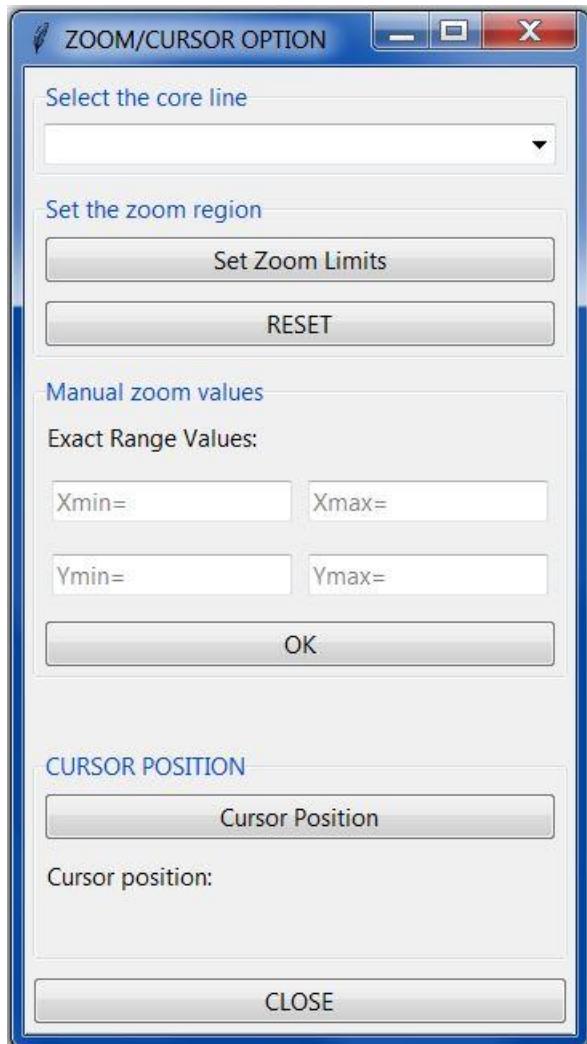
- ⇒ **ANNOTATE:** this options allows for adding text to a figure.

NB: It might happen that an error occurs if the previous plots were done *Custom Plot or Overlay* options. These routines contain their *Annotate* option.

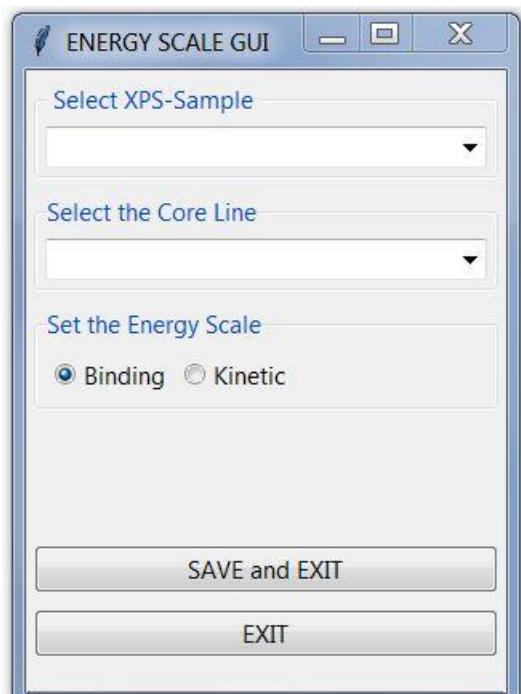
To recover errors the graphic window must be reset opening the *Graphic device Options* selecting the proper operative system and pressing OK. This will generate a new Graphic Window and all the plots will be lost



- **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.

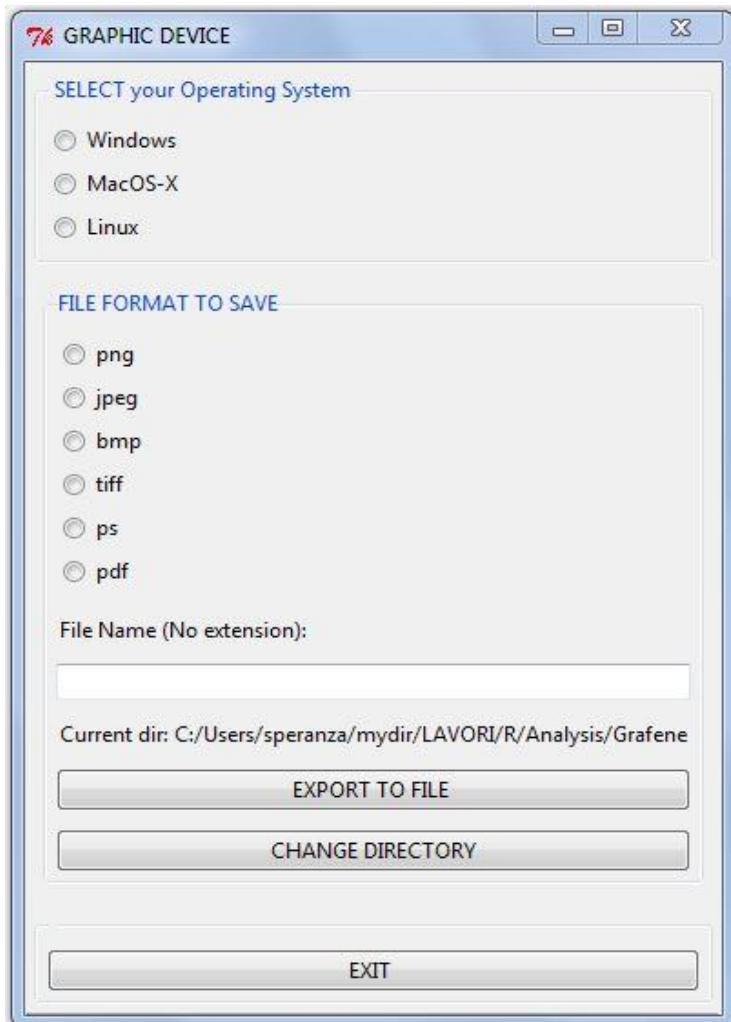


- ⇒ **ZOOM AND CURSOR:** allows zooming the active spectrum.
- **Select the core line:** self explaining
 - **Set zoom area:** with left mouse button click on the spectrum to define the corners of the area to be zoomed. The red corners can be adjusted by clicking with the SX button. DX button exit the definition of the corners;
 - **Reset button:** to reset the zoom to the original visualization;
 - **Exact range values:** you can define Xmin, Xmax, Ymin, Ymax to replot the spectral data pressing OK button.
 - **Cursor Position button:** click on the spectrum with the SX button to read the mouse position (i.e. binding energy, intensity). The DX button exit reading the mouse position;
 - **Close:** to exit the *Zoom & Cursor* option.



- ⇒ **SWITCH BE/KE SCALE:** to plot spectral data vs. Binding Energy or Kinetic Energy scale.
- **Select XPS-Sample:** select the desired XPS-Sample;
 - **Select the Core Line:** select the core line to be visualized vs. the desired energy scale. *All* is also present as option to represent all the core lines in the desired energy scale;
 - **Set the Energy Scale:** select the desired energy scale to visualize spectral data;
 - **Save & Exit button:** to save the changes and exit the routine;
 - **Exit button:** to exit the routine letting the original data representation.

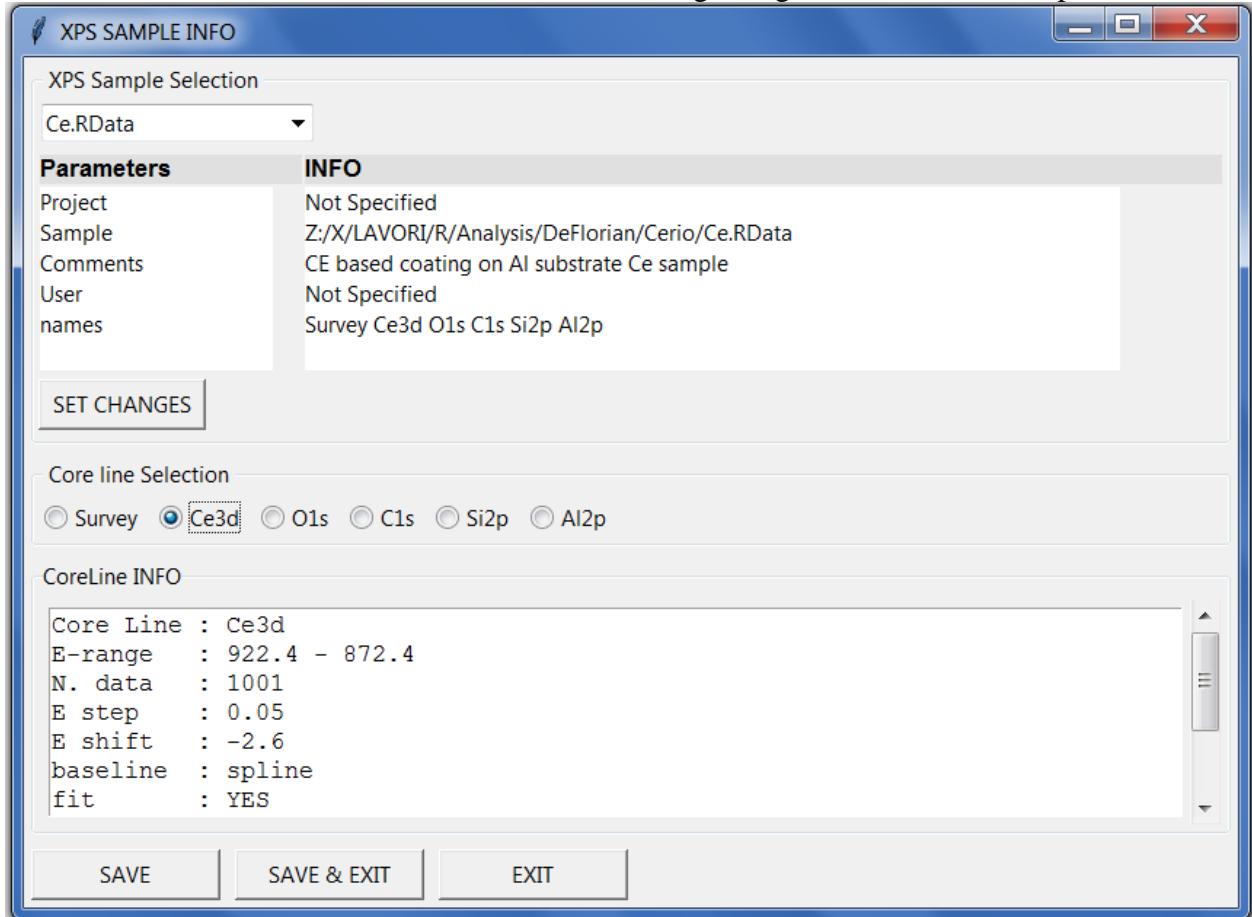
- ⇒ **GRAPHIC DEVICE OPTIONS:** to select a graphic window in agreement with the operative system (Windows by default), reset the graphic window and save figure in files using different formats.



- **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.

INFO & HELP menu.

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



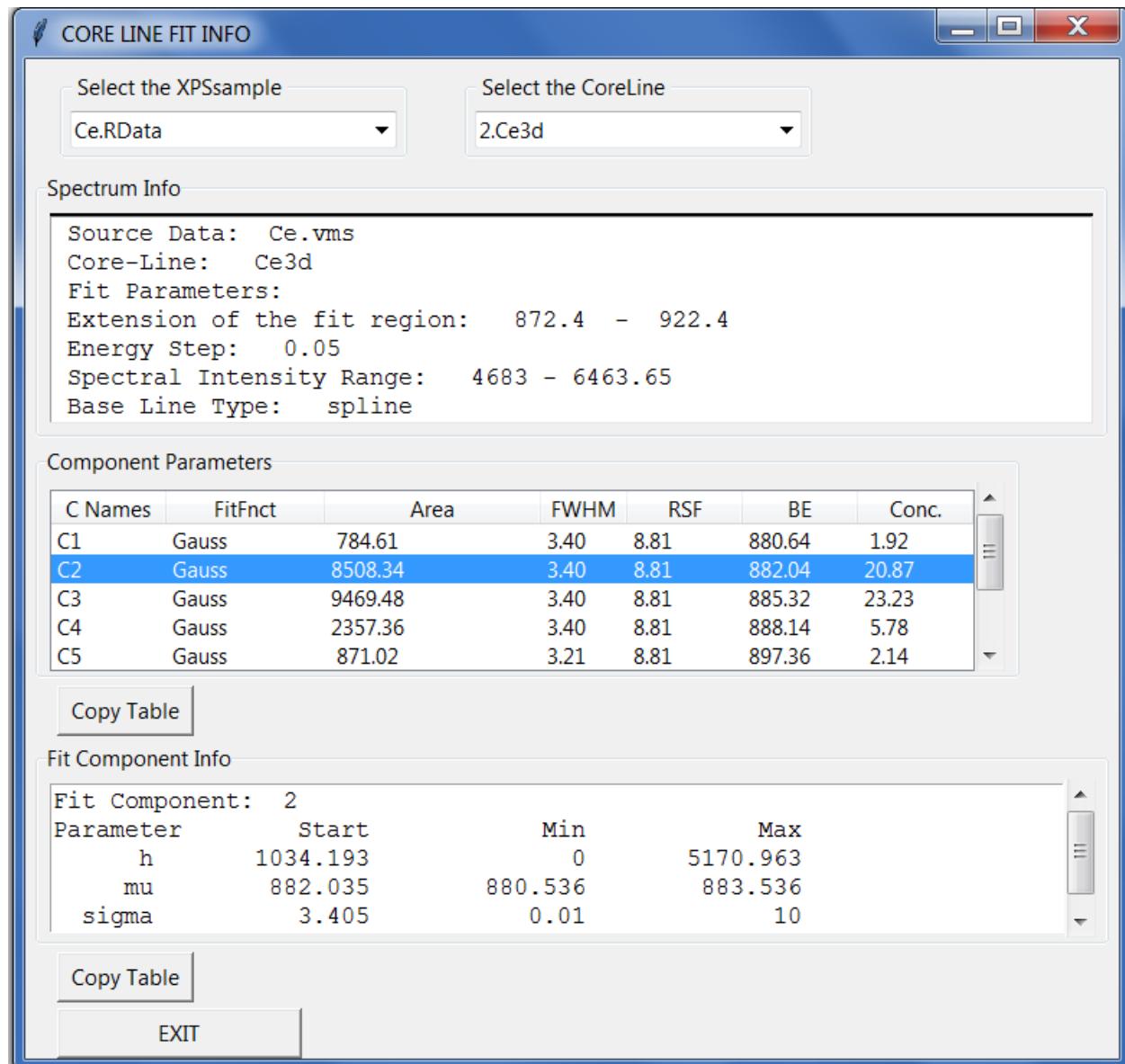
- **Select the XPS-Sample:** select the XPS-Sample containing the desired core-line. Upon selection acquisition information will be visualized as well as the containing list of acquired core lines
- **Core-Line selection:** selecting the desired core-line the spectral information will be visualized

- ⇒ **CORE-LINE INFO:** displays a list of parameters regarding the core line fitting components:

- **Select the XPS-Sample:** select the XPS-Sample containing the desired core-line. Upon selection acquisition information will be visualized as well as the containing list of acquired core lines
- **Core-Line selection:** selecting the desired core-line the spectral information will be visualized

The list parameters of the fit components relative to the chosen core-line 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 variability ranges.



- ⇒ **ANALYSIS REPORT:** displays a summary of parameters describing the spectral analysis carried out.

XPS Sample Report

SELECT XPSsample
HOPGtest.RData

Select Core-Lines and the Report Format
Fitted: 3.C1s 5.CKVV 6.VBt

Fit report Quantification report **MAKE REPORT** **RESET**

Other: 1.Survey 2.C1s 4.VB 7.ST.VB 8.D.2.ST.VB

Standard report **MAKE REPORT** **RESET**

```
==> File Name: HOPGtest.RData

*** C1s Core-Line Fit Info:
Pass Energy: NAEnergy Step: 0.03

BaseLine applied: 4p.tougaard

Components Fit Funct. Area (cps) Intensity FWHM Position Weight(%)
C1 D.S.Gauss 44.95 10.21 0.25 284.32 66.45
C2 Gauss 0.58 0.06 2.50 288.46 0.85
C3 Gauss 2.98 0.29 2.83 291.04 4.41
C4 Gauss 1.11 0.11 2.70 294.00 1.63
C5 Gauss 1.38 0.07 5.66 304.97 2.04
C6 Gauss 8.74 0.29 8.50 311.13 12.92
C7 Gauss 5.52 0.21 7.42 317.77 8.16
C8 Gauss 2.39 0.10 6.54 323.20 3.54

*** CKVV Core-Line Fit Info:
Pass Energy: NAEnergy Step: 0.1

BaseLine applied: shirley

Components Fit Funct. Area (cps) Intensity FWHM Position Weight(%)
C1 Gauss 0.40 0.05 7.96 1206.55 0.29
```

- **Select the XPS-Sample:** select the XPS-Sample containing the desired core-line;
 - **Select the Core-Line:** select the desired core-line to describe in the Report
 - **Select the Report type:** core-lines are grouped in *Fitted Corelines* and *Normal*. For fitted core-lines *Fit Report* or *Quantification Report* are available. For *Normal* core-lines *Standard Report* must be selected since baseline and fit are lacking.
 - **MAKE REPORT:** press this button to display the selected kind of *Report*.
 - **RESET Button:** resets the selected core-lines and type of *Report*.
 -
- ⇒ **HELP:** to open the *HELP* page on the Rstudio console. From here one can access this RxpsG manual.

Table of colors

R colors

1	white	#FFFFFF	255	255	255
2	aliceblue	#F0F8FF	240	248	255
3	antiquewhite	#FAEBD7	250	235	215
4	antiquewhite1	#FFEFD8	255	239	219
5	antiquewhite2	#EEDFCC	238	223	204
6	antiquewhite3	#CDC0B0	205	192	176
7	antiquewhite4	#B88378	139	131	120
8	aquamarine	#7FFFAD	127	255	212
9	aquamarine1	#7FFFAD	127	255	212
10	aquamarine2	#76EEC6	118	238	198
11	aquamarine3	#66CDAA	102	205	170
12	aquamarine4	#458B74	69	139	116
13	azure	#F0FFFF	240	255	255
14	azure1	#F0FFFF	240	255	255
15	azure2	#E0EEEE	224	238	238
16	azure3	#CDCDCD	193	205	205
17	azure4	#B8B8B8	131	139	139
18	beige	#F5F5DC	245	245	220
19	bisque	#FFE4C4	255	228	196
20	bisque1	#FFE4C4	255	228	196
21	bisque2	#EED5B7	238	213	183
22	bisque3	#CDB79E	205	183	158
23	bisque4	#BB7D6B	139	125	107
24	black	#000000	0	0	0
25	blanchedalmond	#FFEBCD	255	235	205
26	blue	#0000FF	0	0	255
27	blue1	#0000FF	0	0	255
28	blue2	#0000EE	0	0	238
29	blue3	#0000CD	0	0	205
30	blue4	#00008B	0	0	139
31	blueviolet	#8A2BE2	138	43	226
32	brown	#A52A2A	165	42	42
33	brown1	#FF4040	255	64	64
34	brown2	#EE3B3B	238	59	59
35	brown3	#CD3333	205	51	51
36	brown4	#B22222	139	35	35
37	burlywood	#DEB887	222	184	135
38	burlywood1	#FFD39B	255	211	155
39	burlywood2	#ECC591	238	197	145
40	burlywood3	#CDAA7D	205	170	125
41	burlywood4	#B87355	139	115	85
42	cadetblue	#5F9EA0	95	158	160
43	cadetblue1	#98FBFF	152	245	255
44	cadetblue2	#8EE5EE	142	229	238
45	cadetblue3	#7AC5CD	122	197	205
46	cadetblue4	#53868B	83	134	139
47	chartreuse	#7FFF00	127	255	0
48	chartreuse1	#7FFF00	127	255	0
49	chartreuse2	#76EE00	118	238	0
50	chartreuse3	#66CD00	102	205	0
51	chartreuse4	#458B00	69	139	0
52	chocolate	#D2691E	210	105	30
53	chocolate1	#FF7F24	255	127	36
54	chocolate2	#EE7621	238	118	33
55	chocolate3	#CD661D	205	102	29
56	chocolate4	#8B4513	139	69	19
57	coral	#FF7F50	255	127	80
58	coral1	#FF7256	255	114	86
59	coral2	#EE6A50	238	106	80
60	coral3	#CD5B45	205	91	69
61	coral4	#8B3E2F	139	62	47
62	cornflowerblue	#6495ED	100	149	237
63	cornsilk	#FFF8DC	255	248	220
64	cornsilk1	#FFF8DC	255	248	220
65	cornsilk2	#EEE8CD	238	232	205
66	cornsilk3	#CDC8B1	205	200	177
67	cornsilk4	#B88878	139	136	120
68	cyan	#00FFFF	0	255	255
69	cyan1	#00FFFF	0	255	255
70	cyan2	#00EEEE	0	238	238
71	cyan3	#00CDCD	0	205	205
72	cyan4	#008B8B	0	139	139
73	darkblue	#00008B	0	0	139
74	darkcyan	#008B8B	0	139	139
75	darkgoldenrod	#B8860B	184	134	11
76	darkgoldenrod1	#FFB90F	255	185	15
77	darkgoldenrod2	#EEAD0E	238	173	14
78	darkgoldenrod3	#CD950C	205	149	12
79	darkgoldenrod4	#B86508	139	101	8
80	darkgray	#A9A9A9	169	169	169
81	darkgreen	#006400	0	100	0
82	darkgrey	#A9A9A9	169	169	169
83	darkkhaki	#BDB76B	189	183	107
84	darkmagenta	#8B008B	139	0	139
85	darkolivedgreen	#556B2F	85	107	47
86	darkolivedgreen1	#CAFF70	202	255	112
87	darkolivedgreen2	#BCEE68	188	238	104
88	darkolivedgreen3	#A2CD5A	162	205	90
89	darkolivedgreen4	#6E8B3D	110	139	61
90	darkorange	#FF8C00	255	140	0
91	darkorange1	#FF7F00	255	127	0
92	darkorange2	#EB7600	238	118	0
93	darkorange3	#CD6600	205	102	0
94	darkorange4	#8B4500	139	69	0
95	darkorchid	#9932CC	153	50	204
96	darkorchid1	#BF3EFF	191	62	255
97	darkorchid2	#B23AEE	178	58	238
98	darkorchid3	#9A32CD	154	50	205
99	darkorchid4	#68228B	104	34	139
100	darkred	#8B0000	139	0	0

R colors

101	darksalmon	#E9967A	233	150	122		151	goldenrod4	#8B6914	139	105	20
102	darkseagreen	#8FB8BF	143	188	143		152	gray	#BEBEBE	190	190	190
103	darkseagreen1	#C1FFC1	193	255	193		153	gray0	#000000	0	0	0
104	darkseagreen2	#B4E8E4	180	238	180		154	gray1	#030303	3	3	3
105	darkseagreen3	#9BCD9B	155	205	155		155	gray2	#050505	5	5	5
106	darkseagreen4	#698B69	105	139	105		156	gray3	#080808	8	8	8
107	darkslateblue	#483D8B	72	61	139		157	gray4	#0AOA0A	10	10	10
108	darkslategray	#2F4F4F	47	79	79		158	gray5	#0DODOD	13	13	13
109	darkslategray1	#97FFFF	151	255	255		159	gray6	#0FOFOF	15	15	15
110	darkslategray2	#8DEEEE	141	238	238		160	gray7	#121212	18	18	18
111	darkslategray3	#79CDCD	121	205	205		161	gray8	#141414	20	20	20
112	darkslategray4	#528B8B	82	139	139		162	gray9	#171717	23	23	23
113	darkslategrey	#2F4F4F	47	79	79		163	gray10	#1A1A1A	26	26	26
114	darkturquoise	#00CED1	0	206	209		164	gray11	#1C1C1C	28	28	28
115	darkviolet	#9400D3	148	0	211		165	gray12	#1F1F1F	31	31	31
116	deeppink	#FF1493	255	20	147		166	gray13	#212121	33	33	33
117	deeppink1	#FF1493	255	20	147		167	gray14	#242424	36	36	36
118	deeppink2	#EE1289	238	18	137		168	gray15	#262626	38	38	38
119	deeppink3	#CD1076	205	16	118		169	gray16	#292929	41	41	41
120	deeppink4	#8B0A50	139	10	80		170	gray17	#2B2B2B	43	43	43
121	deepskyblue	#00BFFF	0	191	255		171	gray18	#2B2B2B	46	46	46
122	deepskyblue1	#00BFFF	0	191	255		172	gray19	#303030	48	48	48
123	deepskyblue2	#00B2EE	0	178	238		173	gray20	#333333	51	51	51
124	deepskyblue3	#009ACD	0	154	205		174	gray21	#363636	54	54	54
125	deepskyblue4	#00688B	0	104	139		175	gray22	#383838	56	56	56
126	dimgray	#696969	105	105	105		176	gray23	#3B3B3B	59	59	59
127	dimgrey	#696969	105	105	105		177	gray24	#3D3D3D	61	61	61
128	dodgerblue	#1E90FF	30	144	255		178	gray25	#404040	64	64	64
129	dodgerblue1	#1E90FF	30	144	255		179	gray26	#424242	66	66	66
130	dodgerblue2	#1C86EE	28	134	238		180	gray27	#454545	69	69	69
131	dodgerblue3	#1874CD	24	116	205		181	gray28	#474747	71	71	71
132	dodgerblue4	#104E8B	16	78	139		182	gray29	#4A4A4A	74	74	74
133	firebrick	#B22222	178	34	34		183	gray30	#4D4D4D	77	77	77
134	firebrick1	#FF3030	255	48	48		184	gray31	#4F4F4F	79	79	79
135	firebrick2	#EE2C2C	238	44	44		185	gray32	#525252	82	82	82
136	firebrick3	#CD2626	205	38	38		186	gray33	#545454	84	84	84
137	firebrick4	#8B1A1A	139	26	26		187	gray34	#575757	87	87	87
138	floralwhite	#FFFFE0	255	250	240		188	gray35	#595959	89	89	89
139	forestgreen	#228B22	34	139	34		189	gray36	#5C5C5C	92	92	92
140	gainsboro	#DCDCDC	220	220	220		190	gray37	#5E5E5E	94	94	94
141	ghostwhite	#F8F8FF	248	248	255		191	gray38	#616161	97	97	97
142	gold	#FFD700	255	215	0		192	gray39	#636363	99	99	99
143	gold1	#FFD700	255	215	0		193	gray40	#666666	102	102	102
144	gold2	#EEC900	238	201	0		194	gray41	#696969	105	105	105
145	gold3	#CDAD00	205	173	0		195	gray42	#6B6B6B	107	107	107
146	gold4	#8B7500	139	117	0		196	gray43	#6B6B6B	110	110	110
147	goldenrod	#DAA520	218	165	32		197	gray44	#707070	112	112	112
148	goldenrod1	#FPC125	255	193	37		198	gray45	#737373	115	115	115
149	goldenrod2	#EEB422	238	180	34		199	gray46	#757575	117	117	117
150	goldenrod3	#CD9B1D	205	155	29		200	gray47	#787878	120	120	120

R colors

201	gray48	#7A7A7A	122	122	122
202	gray49	#7D7D7D	125	125	125
203	gray50	#7F7F7F	127	127	127
204	gray51	#828282	130	130	130
205	gray52	#858585	133	133	133
206	gray53	#878787	135	135	135
207	gray54	#8A8A8A	138	138	138
208	gray55	#8C8C8C	140	140	140
209	gray56	#8F8F8F	143	143	143
210	gray57	#919191	145	145	145
211	gray58	#949494	148	148	148
212	gray59	#969696	150	150	150
213	gray60	#999999	153	153	153
214	gray61	#9C9C9C	156	156	156
215	gray62	#9E9E9E	158	158	158
216	gray63	#A1A1A1	161	161	161
217	gray64	#A3A3A3	163	163	163
218	gray65	#A6A6A6	166	166	166
219	gray66	#A8A8A8	168	168	168
220	gray67	#ABABAB	171	171	171
221	gray68	#ADADAD	173	173	173
222	gray69	#B0B0B0	176	176	176
223	gray70	#B3B3B3	179	179	179
224	gray71	#B5B5B5	181	181	181
225	gray72	#B8B8B8	184	184	184
226	gray73	#BABABA	186	186	186
227	gray74	#BDBDBD	189	189	189
228	gray75	#BFBFBF	191	191	191
229	gray76	#C2C2C2	194	194	194
230	gray77	#C4C4C4	196	196	196
231	gray78	#C7C7C7	199	199	199
232	gray79	#C9C9C9	201	201	201
233	gray80	#CCCCCC	204	204	204
234	gray81	#CFCFCF	207	207	207
235	gray82	#D1D1D1	209	209	209
236	gray83	#D4D4D4	212	212	212
237	gray84	#D6D6D6	214	214	214
238	gray85	#D9D9D9	217	217	217
239	gray86	#DBDBDB	219	219	219
240	gray87	#DEDEDE	222	222	222
241	gray88	#E0E0E0	224	224	224
242	gray89	#E3E3E3	227	227	227
243	gray90	#E5E5E5	229	229	229
244	gray91	#E8E8E8	232	232	232
245	gray92	#EBEBEB	235	235	235
246	gray93	#EDEDED	237	237	237
247	gray94	#F0F0F0	240	240	240
248	gray95	#F2F2F2	242	242	242
249	gray96	#F5F5F5	245	245	245
250	gray97	#F7F7F7	247	247	247
251	gray98	#FAFAFA	250	250	250
252	gray99	#FCFCFC	252	252	252
253	gray100	#FFFFFF	255	255	255
254	green	#00FF00	0	255	0
255	green1	#00FF00	0	255	0
256	green2	#00EB00	0	238	0
257	green3	#00CD00	0	205	0
258	green4	#00BB00	0	139	0
259	greenyellow	#ADFF2F	173	255	47
260	grey	#BEBEBE	190	190	190
261	grey0	#000000	0	0	0
262	grey1	#030303	3	3	3
263	grey2	#050505	5	5	5
264	grey3	#080808	8	8	8
265	grey4	#0A0A0A	10	10	10
266	grey5	#0D0D0D	13	13	13
267	grey6	#0F0F0F	15	15	15
268	grey7	#121212	18	18	18
269	grey8	#141414	20	20	20
270	grey9	#171717	23	23	23
271	grey10	#1A1A1A	26	26	26
272	grey11	#1C1C1C	28	28	28
273	grey12	#1F1F1F	31	31	31
274	grey13	#212121	33	33	33
275	grey14	#242424	36	36	36
276	grey15	#262626	38	38	38
277	grey16	#292929	41	41	41
278	grey17	#2B2B2B	43	43	43
279	grey18	#2E2E2E	46	46	46
280	grey19	#303030	48	48	48
281	grey20	#333333	51	51	51
282	grey21	#363636	54	54	54
283	grey22	#383838	56	56	56
284	grey23	#3B3B3B	59	59	59
285	grey24	#3D3D3D	61	61	61
286	grey25	#404040	64	64	64
287	grey26	#424242	66	66	66
288	grey27	#454545	69	69	69
289	grey28	#474747	71	71	71
290	grey29	#4A4A4A	74	74	74
291	grey30	#4D4D4D	77	77	77
292	grey31	#4F4F4F	79	79	79
293	grey32	#525252	82	82	82
294	grey33	#545454	84	84	84
295	grey34	#575757	87	87	87
296	grey35	#595959	89	89	89
297	grey36	#5C5C5C	92	92	92
298	grey37	#5B5E5E	94	94	94
299	grey38	#616161	97	97	97
300	grey39	#636363	99	99	99

R colors

301	grey40	#666666	102	102	102
302	grey41	#696969	105	105	105
303	grey42	#6B6B6B	107	107	107
304	grey43	#6E6E6E	110	110	110
305	grey44	#707070	112	112	112
306	grey45	#737373	115	115	115
307	grey46	#757575	117	117	117
308	grey47	#787878	120	120	120
309	grey48	#7A7A7A	122	122	122
310	grey49	#7D7D7D	125	125	125
311	grey50	#7F7F7F	127	127	127
312	grey51	#828282	130	130	130
313	grey52	#858585	133	133	133
314	grey53	#878787	135	135	135
315	grey54	#8A8A8A	138	138	138
316	grey55	#8C8C8C	140	140	140
317	grey56	#8F8F8F	143	143	143
318	grey57	#919191	145	145	145
319	grey58	#949494	148	148	148
320	grey59	#969696	150	150	150
321	grey60	#999999	153	153	153
322	grey61	#9C9C9C	156	156	156
323	grey62	#9E9E9E	158	158	158
324	grey63	#A1A1A1	161	161	161
325	grey64	#A3A3A3	163	163	163
326	grey65	#A6A6A6	166	166	166
327	grey66	#A8A8A8	168	168	168
328	grey67	#ABABAB	171	171	171
329	grey68	#ADADAD	173	173	173
330	grey69	#B0B0B0	176	176	176
331	grey70	#B3B3B3	179	179	179
332	grey71	#B5B5B5	181	181	181
333	grey72	#B8B8B8	184	184	184
334	grey73	#BABABA	186	186	186
335	grey74	#BDBDBD	189	189	189
336	grey75	#BFBFBF	191	191	191
337	grey76	#C2C2C2	194	194	194
338	grey77	#C4C4C4	196	196	196
339	grey78	#C7C7C7	199	199	199
340	grey79	#C9C9C9	201	201	201
341	grey80	#CCCCCC	204	204	204
342	grey81	#CFCFCF	207	207	207
343	grey82	#D1D1D1	209	209	209
344	grey83	#D4D4D4	212	212	212
345	grey84	#D6D6D6	214	214	214
346	grey85	#D9D9D9	217	217	217
347	grey86	#DBDBDB	219	219	219
348	grey87	#DEDEDE	222	222	222
349	grey88	#E0E0E0	224	224	224
350	grey89	#E3E3E3	227	227	227
351	grey90	#E5E5E5	229	229	229
352	grey91	#E8E8E8	232	232	232
353	grey92	#EBEBEB	235	235	235
354	grey93	#EDEDED	237	237	237
355	grey94	#F0F0F0	240	240	240
356	grey95	#F2F2F2	242	242	242
357	grey96	#F5F5F5	245	245	245
358	grey97	#F7F7F7	247	247	247
359	grey98	#FAFAFA	250	250	250
360	grey99	#FCFCFC	252	252	252
361	grey100	#FFFFFF	255	255	255
362	honeydew	#FOFFF0	240	255	240
363	honeydew1	#FOFFF0	240	255	240
364	honeydew2	#E0EEE0	224	238	224
365	honeydew3	#C1CDC1	193	205	193
366	honeydew4	#83B83	131	139	131
367	hotpink	#FF69B4	255	105	180
368	hotpink1	#FF6EB4	255	110	180
369	hotpink2	#EE6AA7	238	106	167
370	hotpink3	#CD6090	205	96	144
371	hotpink4	#8B3A62	139	58	98
372	indianred	#CD5C5C	205	92	92
373	indianred1	#FF6A6A	255	106	106
374	indianred2	#EE6363	238	99	99
375	indianred3	#CD5555	205	85	85
376	indianred4	#8B3A3A	139	58	58
377	ivory	#FFFFFF0	255	255	240
378	ivory1	#FFFFFF0	255	255	240
379	ivory2	#EEEEEE0	238	238	224
380	ivory3	#CDCDC1	205	205	193
381	ivory4	#8B8B83	139	139	131
382	khaki	#F0E68C	240	230	140
383	khaki1	#FFF68F	255	246	143
384	khaki2	#EEE685	238	230	133
385	khaki3	#CDC673	205	198	115
386	khaki4	#8B864E	139	134	78
387	lavender	#E6E6FA	230	230	250
388	lavenderblush	#FFF0F5	255	240	245
389	lavenderblush1	#FFF0F5	255	240	245
390	lavenderblush2	#EEE0E5	238	224	229
391	lavenderblush3	#CDC1C5	205	193	197
392	lavenderblush4	#8B8386	139	131	134
393	lawngreen	#7CFC00	124	252	0
394	lemonchiffon	#FFFACD	255	250	205
395	lemonchiffon1	#FFFACD	255	250	205
396	lemonchiffon2	#EEE9BF	238	233	191
397	lemonchiffon3	#CDC9A5	205	201	165
398	lemonchiffon4	#8B8970	139	137	112
399	lightblue	#ADD8E6	173	216	230
400	lightblue1	#BFEFFF	191	239	255

R colors

401	lightblue2	#B2DFEE	178	223	238
402	lightblue3	#9AC0CD	154	192	205
403	lightblue4	#68838B	104	131	139
404	lightcoral	#F08080	240	128	128
405	lightcyan	#E0FFFF	224	255	255
406	lightcyan1	#E0FFFF	224	255	255
407	lightcyan2	#D1EEEE	209	238	238
408	lightcyan3	#B4CDCD	180	205	205
409	lightcyan4	#7A8B8B	122	139	139
410	lightgoldenrod	#EEDD82	238	221	130
411	lightgoldenrod1	#FFEC8B	255	236	139
412	lightgoldenrod2	#EEDC82	238	220	130
413	lightgoldenrod3	#CDBE70	205	190	112
414	lightgoldenrod4	#8B814C	139	129	76
415	lightgoldenrodyellow	#FAFAD2	250	250	210
416	lightgray	#D3D3D3	211	211	211
417	lightgreen	#90EE90	144	238	144
418	lightgrey	#D3D3D3	211	211	211
419	lightpink	#FFB6C1	255	182	193
420	lightpink1	#FFAEB9	255	174	185
421	lightpink2	#EEA2AD	238	162	173
422	lightpink3	#CD8C95	205	140	149
423	lightpink4	#BB5F65	139	95	101
424	lightsalmon	#FFA07A	255	160	122
425	lightsalmon1	#FFA07A	255	160	122
426	lightsalmon2	#EE9572	238	149	114
427	lightsalmon3	#CD8162	205	129	98
428	lightsalmon4	#8B5742	139	87	66
429	lightseagreen	#20B2AA	32	178	170
430	lightskyblue	#87CEFA	135	206	250
431	lightskyblue1	#B0E2FF	176	226	255
432	lightskyblue2	#A4D3EE	164	211	238
433	lightskyblue3	#8DB6CD	141	182	205
434	lightskyblue4	#607B8B	96	123	139
435	lightslateblue	#8470FF	132	112	255
436	lightslategray	#778899	119	136	153
437	lightslategrey	#778899	119	136	153
438	lightsteelblue	#B0C4DE	176	196	222
439	lightsteelblue1	#CAE1FF	202	225	255
440	lightsteelblue2	#BCD2EE	188	210	238
441	lightsteelblue3	#A2B5CD	162	181	205
442	lightsteelblue4	#6E7B8B	110	123	139
443	lightyellow	#FFFFE0	255	255	224
444	lightyellow1	#FFFFE0	255	255	224
445	lightyellow2	#EEDDE1	238	238	209
446	lightyellow3	#CDCDB4	205	205	180
447	lightyellow4	#8B8B7A	139	139	122
448	limegreen	#32CD32	50	205	50
449	linen	#FAF0E6	250	240	230
450	magenta	#FF00FF	255	0	255
451	magenta1	#FF00FF	255	0	255
452	magenta2	#EE00EE	238	0	238
453	magenta3	#CD00CD	205	0	205
454	magenta4	#8B008B	139	0	139
455	maroon	#B03060	176	48	96
456	maroon1	#FF34B3	255	52	179
457	maroon2	#EE30A7	238	48	167
458	maroon3	#CD2990	205	41	144
459	maroon4	#8B1C62	139	28	98
460	mediumaquamarine	#66CDAA	102	205	170
461	mediumblue	#0000CD	0	0	205
462	mediumorchid	#BA55D3	186	85	211
463	mediumorchid1	#E066FF	224	102	255
464	mediumorchid2	#D15FEE	209	95	238
465	mediumorchid3	#B452CD	180	82	205
466	mediumorchid4	#7A378B	122	55	139
467	mediumpurple	#9370DB	147	112	219
468	mediumpurple1	#AB82FF	171	130	255
469	mediumpurple2	#9F79EE	159	121	238
470	mediumpurple3	#8968CD	137	104	205
471	mediumpurple4	#5D478B	93	71	139
472	mediumseagreen	#3CB371	60	179	113
473	mediumslateblue	#7B68EE	123	104	238
474	mediumspringgreen	#00FA9A	0	250	154
475	mediumturquoise	#48D1CC	72	209	204
476	mediumvioletred	#C71585	199	21	133
477	midnightblue	#191970	25	25	112
478	mintcream	#F5FFFA	245	255	250
479	mistyrose	#FFE4E1	255	228	225
480	mistyrose1	#FFE4E1	255	228	225
481	mistyrose2	#EED5D2	238	213	210
482	mistyrose3	#CDB7B5	205	183	181
483	mistyrose4	#8B7D7B	139	125	123
484	moccasin	#FFE4B5	255	228	181
485	navajowhite	#FFDEAD	255	222	173
486	navajowhite1	#FFDEAD	255	222	173
487	navajowhite2	#EECFA1	238	207	161
488	navajowhite3	#CDB38B	205	179	139
489	navajowhite4	#8B795E	139	121	94
490	navy	#000080	0	0	128
491	navyblue	#000080	0	0	128
492	oldlace	#FDF5E6	253	245	230
493	olivedrab	#6B8E23	107	142	35
494	olivedrab1	#C0FF3E	192	255	62
495	olivedrab2	#B3EE3A	179	238	58
496	olivedrab3	#9ACD32	154	205	50
497	olivedrab4	#69B22	105	139	34
498	orange	#FFA500	255	165	0
499	orange1	#FFA500	255	165	0
500	orange2	#EE9A00	238	154	0

R colors

501	orange3	#CD8500	205	133	0
502	orange4	#8B5A00	139	90	0
503	orangered	#FF4500	255	69	0
504	orangered1	#FF4500	255	69	0
505	orangered2	#EE4000	238	64	0
506	orangered3	#CD3700	205	55	0
507	orangered4	#8B2500	139	37	0
508	orchid	#DA70D6	218	112	214
509	orchid1	#FF83FA	255	131	250
510	orchid2	#EE7AE9	238	122	233
511	orchid3	#CD69C9	205	105	201
512	orchid4	#8B4789	139	71	137
513	palegoldenrod	#EEE8AA	238	232	170
514	palegreen	#98FB98	152	251	152
515	palegreen1	#9AFF9A	154	255	154
516	palegreen2	#90EE90	144	238	144
517	palegreen3	#7CCD7C	124	205	124
518	palegreen4	#548B54	84	139	84
519	paleturquoise	#AFEEEE	175	238	238
520	paleturquoise1	#BBFFFF	187	255	255
521	paleturquoise2	#AEEEEEE	174	238	238
522	paleturquoise3	#96CDCD	150	205	205
523	paleturquoise4	#668888	102	139	139
524	palevioletred	#DB7093	219	112	147
525	palevioletred1	#FF82AB	255	130	171
526	palevioletred2	#EE799F	238	121	159
527	palevioletred3	#CD6889	205	104	137
528	palevioletred4	#8B475D	139	71	93
529	papayawhip	#FFEFD5	255	239	213
530	peachpuff	#FFDAB9	255	218	185
531	peachpuff1	#FFDAB9	255	218	185
532	peachpuff2	#EECBAD	238	203	173
533	peachpuff3	#CDAF95	205	175	149
534	peachpuff4	#8B7765	139	119	101
535	peru	#CD853F	205	133	63
536	pink	#FFC0CB	255	192	203
537	pink1	#FFB5C5	255	181	197
538	pink2	#EEA9B8	238	169	184
539	pink3	#CD919E	205	145	158
540	pink4	#8B636C	139	99	108
541	plum	#DDA0DD	221	160	221
542	plum1	#FFBBFF	255	187	255
543	plum2	#EEAEEE	238	174	238
544	plum3	#CD96CD	205	150	205
545	plum4	#8B66BB	139	102	139
546	powderblue	#B0E0E6	176	224	230
547	purple	#A020F0	160	32	240
548	purple1	#9B30FF	155	48	255
549	purple2	#912CEE	145	44	238
550	purple3	#7D26CD	125	38	205
551	purple4	#551A8B	85	26	139
552	red	#FF0000	255	0	0
553	red1	#FF0000	255	0	0
554	red2	#EB0000	238	0	0
555	red3	#CD0000	205	0	0
556	red4	#8B0000	139	0	0
557	rosybrown	#BC8F8F	188	143	143
558	rosybrown1	#FFC1C1	255	193	193
559	rosybrown2	#EEB4B4	238	180	180
560	rosybrown3	#CD9B9B	205	155	155
561	rosybrown4	#8B6969	139	105	105
562	royalblue	#4169E1	65	105	225
563	royalblue1	#4876FF	72	118	255
564	royalblue2	#436EEE	67	110	238
565	royalblue3	#3A5FCD	58	95	205
566	royalblue4	#27408B	39	64	139
567	saddlebrown	#8B4513	139	69	19
568	salmon	#FA8072	250	128	114
569	salmon1	#FF8C69	255	140	105
570	salmon2	#EE8262	238	130	98
571	salmon3	#CD7054	205	112	84
572	salmon4	#8B4C39	139	76	57
573	sandybrown	#F4A460	244	164	96
574	seagreen	#2E8B57	46	139	87
575	seagreen1	#54FF9F	84	255	159
576	seagreen2	#4EEE94	78	238	148
577	seagreen3	#43CD80	67	205	128
578	seagreen4	#2E8B57	46	139	87
579	seashell	#FFF5EE	255	245	238
580	seashell1	#FFF5EE	255	245	238
581	seashell2	#EEE5DE	238	229	222
582	seashell3	#CDC5BF	205	197	191
583	seashell4	#8B8682	139	134	130
584	sienna	#A0522D	160	82	45
585	sienna1	#FF8247	255	130	71
586	sienna2	#EE7942	238	121	66
587	sienna3	#CD6839	205	104	57
588	sienna4	#8B4726	139	71	38
589	skyblue	#87CEEB	135	206	235
590	skyblue1	#87CEFF	135	206	255
591	skyblue2	#7EC0EE	126	192	238
592	skyblue3	#6CA6CD	108	166	205
593	skyblue4	#4A708B	74	112	139
594	slateblue	#6A5ACD	106	90	205
595	slateblue1	#836FFF	131	111	255
596	slateblue2	#7A67EE	122	103	238
597	slateblue3	#6959CD	105	89	205
598	slateblue4	#473C8B	71	60	139
599	slategray	#708090	112	128	144
600	slategray1	#C6E2FF	198	226	255

R colors

601	slategray2	#B9D3EE	185	211	238
602	slategray3	#9FB6CD	159	182	205
603	slategray4	#6C7B8B	108	123	139
604	slategrey	#708090	112	128	144
605	snow	#FFFafa	255	250	250
606	snow1	#FFFafa	255	250	250
607	snow2	#EEE9E9	238	233	233
608	snow3	#CDC9C9	205	201	201
609	snow4	#8B8989	139	137	137
610	springgreen	#00FF7F	0	255	127
611	springgreen1	#00FF7F	0	255	127
612	springgreen2	#00EB76	0	238	118
613	springgreen3	#00CD66	0	205	102
614	springgreen4	#008B45	0	139	69
615	steelblue	#4682B4	70	130	180
616	steelblue1	#63B8FF	99	184	255
617	steelblue2	#5CACEE	92	172	238
618	steelblue3	#4F94CD	79	148	205
619	steelblue4	#36648B	54	100	139
620	tan	#D2B48C	210	180	140
621	tan1	#FFA54F	255	165	79
622	tan2	#EE9A49	238	154	73
623	tan3	#CD853F	205	133	63
624	tan4	#8B5A2B	139	90	43
625	thistle	#D8BFD8	216	191	216
626	thistle1	#FFE1FF	255	225	255
627	thistle2	#EED2EE	238	210	238
628	thistle3	#CDB5CD	205	181	205
629	thistle4	#8B7B8B	139	123	139
630	tomato	#FF6347	255	99	71
631	tomato1	#FF6347	255	99	71
632	tomato2	#EE5C42	238	92	66
633	tomato3	#CD4F39	205	79	57
634	tomato4	#8B3626	139	54	38
635	turquoise	#40E0D0	64	224	208
636	turquoise1	#00F5FF	0	245	255
637	turquoise2	#00ESEE	0	229	238
638	turquoise3	#00C5CD	0	197	205
639	turquoise4	#00868B	0	134	139
640	violet	#EE82EE	238	130	238
641	violetred	#D02090	208	32	144
642	violetred1	#FF3E96	255	62	150
643	violetred2	#EE3A8C	238	58	140
644	violetred3	#CD3278	205	50	120
645	violetred4	#8B2252	139	34	82
646	wheat	#F5DEB3	245	222	179
647	wheat1	#FFE7BA	255	231	186
648	wheat2	#EED8AE	238	216	174
649	wheat3	#CDBA96	205	186	150
650	wheat4	#8B7E66	139	126	102
651	whitesmoke	#F5F5F5	245	245	245
652	yellow	#FFFF00	255	255	0
653	yellow1	#FFFF00	255	255	0
654	yellow2	#EEEE00	238	238	0
655	yellow3	#CDCD00	205	205	0
656	yellow4	#8B8B00	139	139	0
657	yellowgreen	#9ACD32	154	205	50

Plot symbols in R;
col = " red3 ", bg= " slateblue3 "

