Quantification Parameters Dialog Window

Components Property Page

Photoemission resulting in spectra with overlapping signal from multiple emission lines is analysed using peak models constructed from sets of components. Each component to a peak model defines photoemission in terms of line shapes, fitting parameters (area, FWHM and position) and a set of constraints to fitting parameters. These aspects of a peak model are entered via fields in a table of components, together with additional fields that are used to guide a definition for components in a peak model, quantification derived from components and display of components. The Components property page (Figure COMP1) also includes a number of pushbuttons that are designed to aid the construction of peak models.

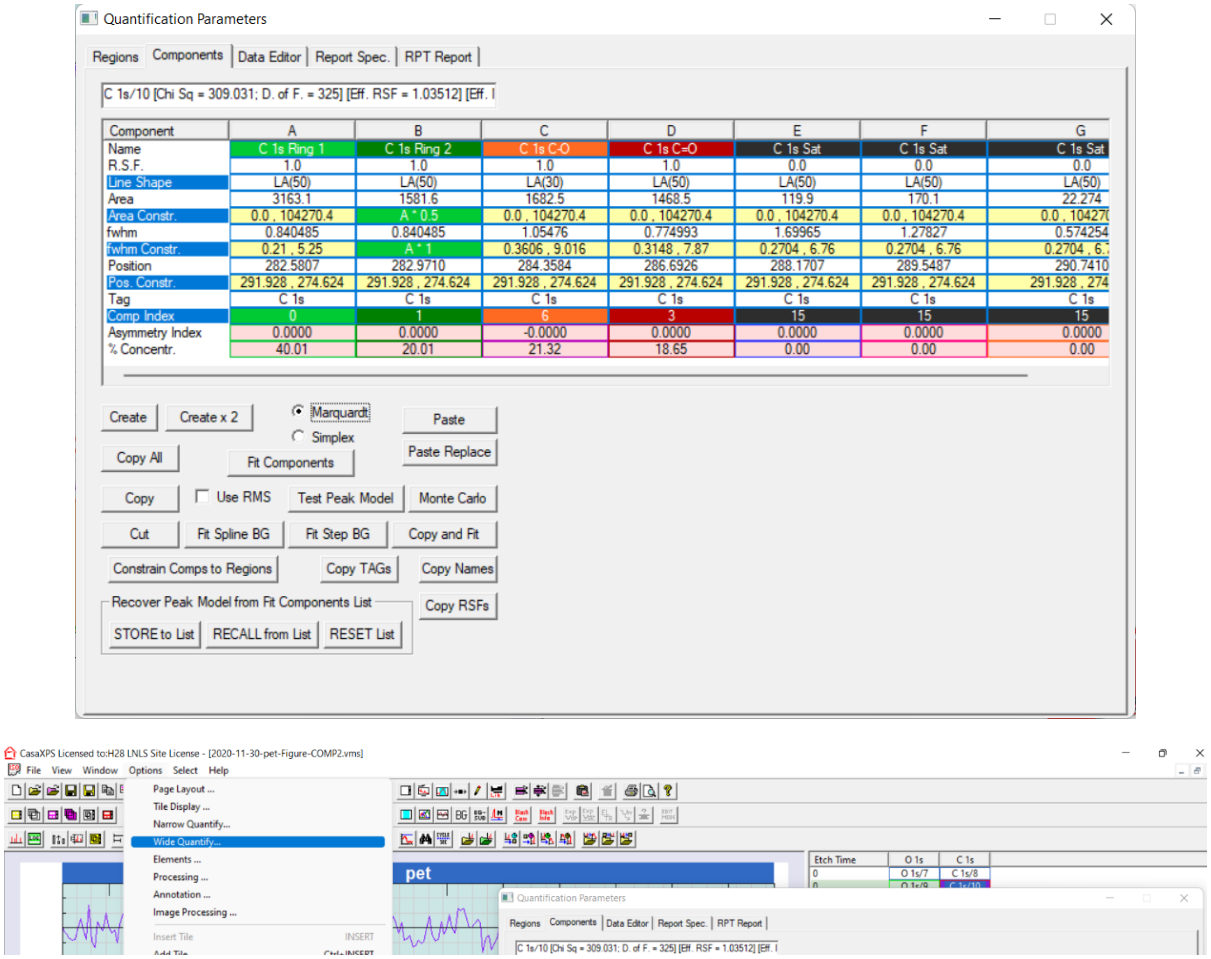


Figure COMP1. Quantification Parameters Dialog Window invoked from the Options menu via the menu item *Wide Quantify*.

The Components property page is one of five property pages on the Quantification Parameters dialog window. Peak models are defined using the first two property pages, namely, the Regions property page and the Components property page. Components to a peak model are predominantly used to represent photoemission signal associated with a specific chemical state for an atom. The Regions property page is used to create curves that are intended to model inelastic scattered photoemission signal which represent background signal not associated with specific photoemission events. The narrow form of the Quantification Parameters dialog window, which is invoked via the Options menu via the menu item *Narrow Quantify* is illustrated in Figure COMP2.

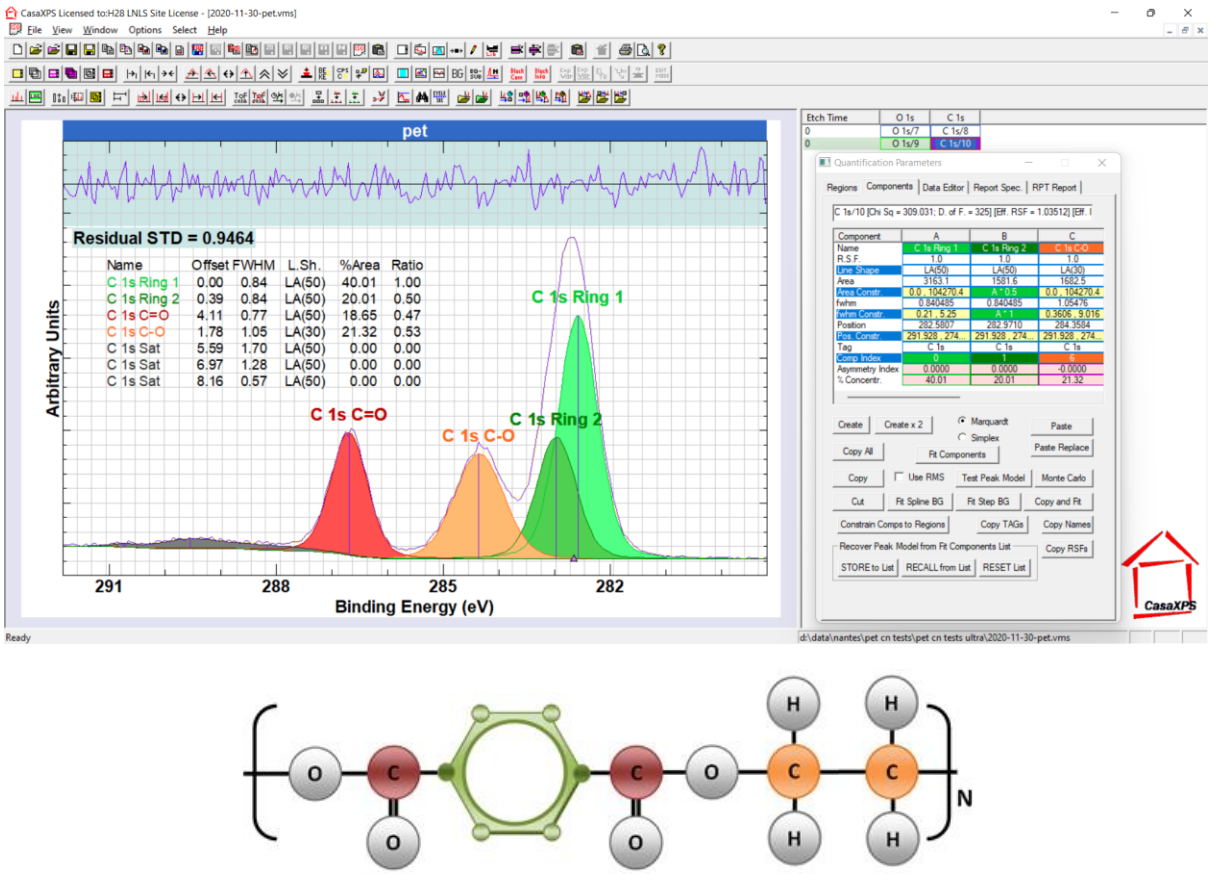


Figure COMP2. Peak model defined for C 1s photoemission from atoms in chemical states recorded from the polymer poly (ethylene phthalate) PET.

Component Property Page Pushbuttons

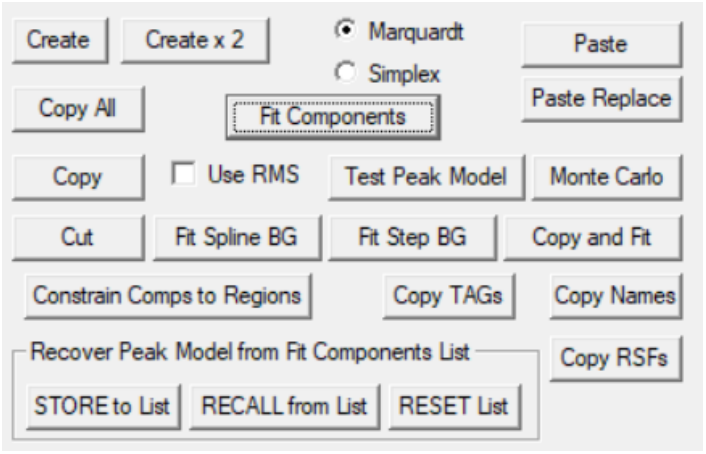
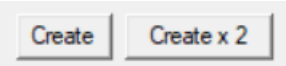


Figure COMP3. Buttons on the Components property page used to create and manage components to peak models.

Creating a Component



Before a peak model exists for a spectrum, the table of components defining a peak model is empty (Figure COMP4). To create the first component for a peak model, the *Create* or *Create x 2* pushbutton is pressed (Figure COMP5). Depending on which of these buttons is pressed one or two components are added to the table of components on the Components property page. Default component parameters are used which may be augmented by element library information, if possible. The element library can update component parameters provided VAMAS blocks contain appropriate information. When a component is created for a VAMAS block, the element and transition fields defined for the VAMAS block are used to form a string which is used to search the element library for information that can be used to create appropriate component parameters for the given spectrum. Examples of concatenated element and transition field typical for VAMAS block data associated with spectra include O 1s, Ti 2p, Fe 2p3/2. If a match occurs between these strings and the Name entry for a photoemission line within the element library, then RSF and line shape component fields are updated from the element library. If the *Create x 2* button is pressed and the element library includes entries with information about doublet photoemission, then two components are created with constraints for doublets as defined by the element library. If no corresponding doublet entry is found in the element library, then two peaks are created making use of basic theoretical relationships between doublet component peaks.

Figure COMP4 and Figure COMP5 illustrate a VAMAS block with element transition fields identifying data as O 1s photoemission. Figure COMP4 shows the Components property page prior to the creation of any components. A region defining the background curve is already available for the VAMAS block when shown in Figure COMP4. Figure COMP5 illustrates the consequence of pressing the *Create* button. A component is added to the table of components for a peak model and three parameters for the newly created component are extracted from the element library (indicated by arrows in Figure COMP5).

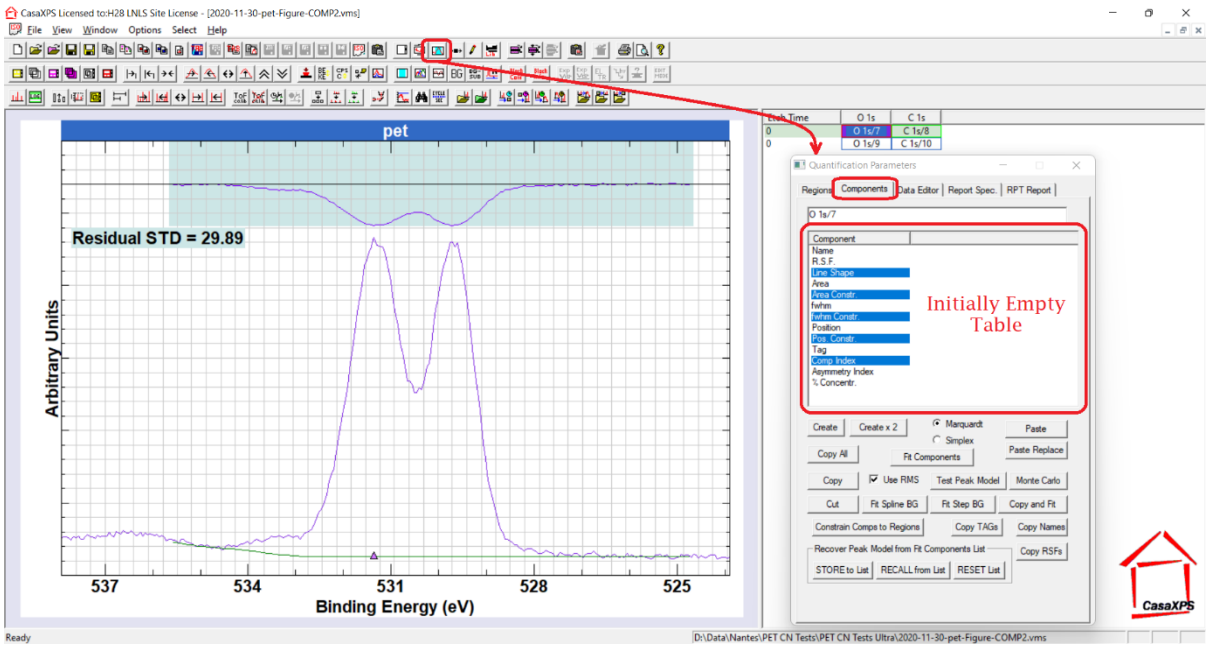


Figure COMP4. VAMAS block with element/transition fields set to O 1s prior to creating the first component on these data.

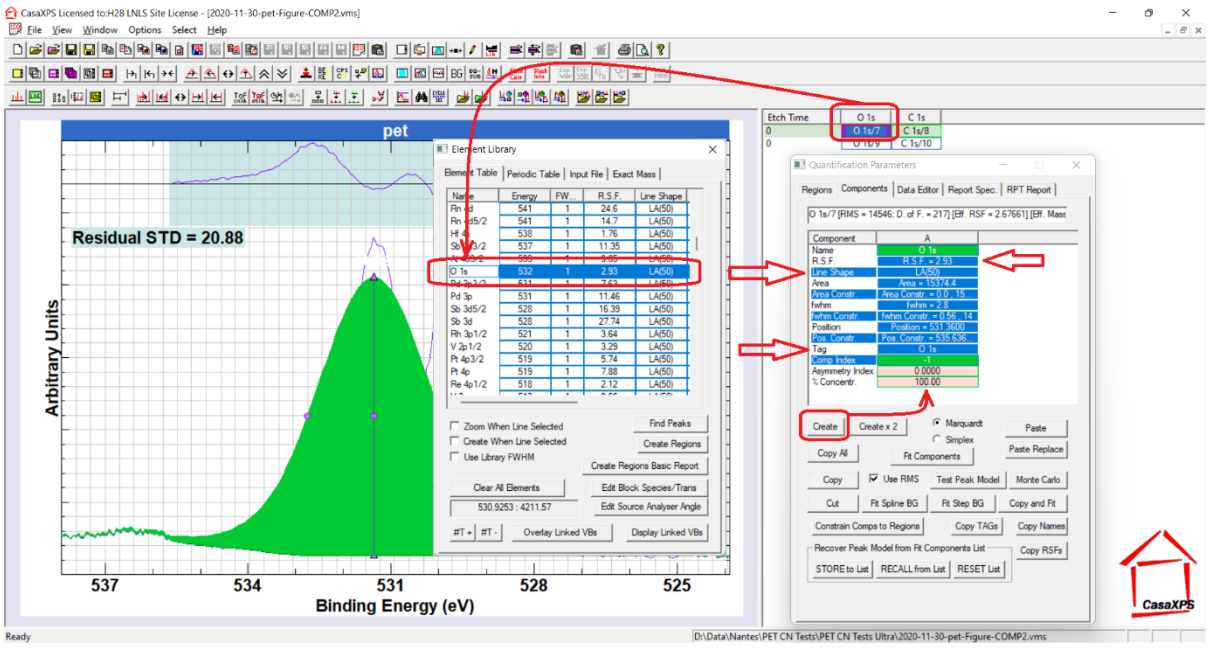
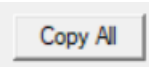


Figure COMP5. VAMAS block state after the *Create* button is pressed. The element transition VAMAS block strings allow a match to an entry in the element library. Therefore, when a new component is created, component parameters RSF, Line Shape and TAG are updated from the element library.

Copying Existing Components – Component-Clipboard Actions

Once at least one component is created, copy and paste operations can be used to add components to a peak model. One or more components can be copied onto a components clipboard and then inserted into the table of components for the same peak model or peak models under construction on other VAMAS blocks.



A peak model in its entirety of components from the VAMAS block displayed in the active tile are added to the component clipboard.

The Copy button adds one or more components to the component clipboard depending on the selected component and relational constraints between other components in a peak model and the selected component.

Components listed on the Components property page are displayed as columns of parameters. One column of parameters is selected at a time, which is indicated by the use of a highlight colour for background to text-fields and the colour of text display in the selected component compared to components that are not selected. Left-clicking the mouse with the cursor over a column of component parameters deselects the previously selected component and selects the component indicated by the action of the mouse. Figure COMP5 is an example of a component that is currently selected. Figure COMP1 is an example of a table of components for which none of the components are selected. When the *Copy* button is pressed for the scenario in Figure COMP5, the selected O 1s component is added to the clipboard and is then available for the *Paste* or *Paste Replace* actions.

If relational constraints of the form A*1 exist between the selected component and other components in a peak model, then the *Copy* button copies the selected component and any other component for which a relational constraint makes use of the selected component. For example, the peak model for C 1s signal from PET in Figure COMP6 includes a pair of components in columns A and B representing signal from a carbon ring. The ring of carbon is attached in two atoms to carbon bonded to oxygen, hence the ring signal is divided into four carbon atoms that are less influenced by oxygen atoms and two that are more influenced by oxygen in PET. The intensity for ring signal is therefore divided between two components with area in the ratio 4:2, which is implemented in the peak model using area relational constraint between component in the column B and the component in column A of the form A * 0.5. Thus, selecting column A as shown in Figure COMP6 then pressing the *Copy* button places both component A and component B onto the component-clipboard. Figure COMP7 illustrates the outcome when the steps pictured in Figure COMP6 are followed then applied to a different VAMAS block via a paste operation. Displaying the second VAMAS block (region already defined) in the active tile and pressing the *Paste Replace* button results in two components which were placed on the component-clipboard being used to initialise the VAMAS block peak model.

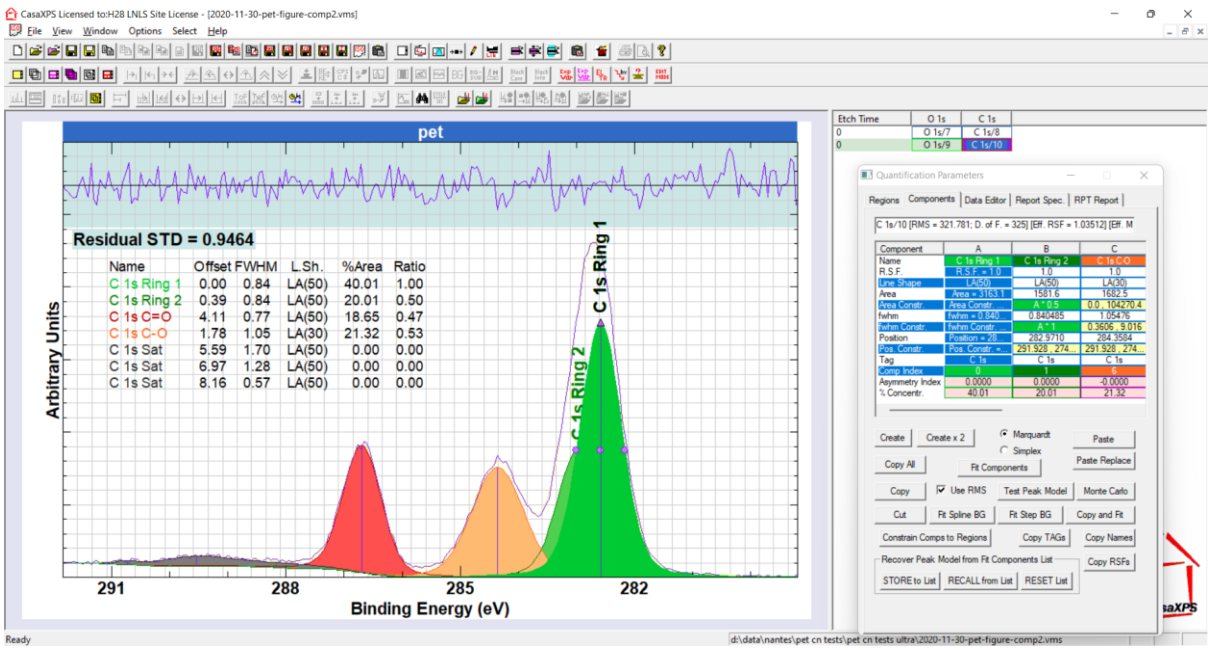


Figure COMP6. C 1s peak model in which the component in column A is selected. In addition, the component in Column B has relational constraints of the form area constraint A*0.5 and FWHM constraint A*1. Pressing the Copy button will add to the component clipboard the component in column A and, because of the relational constraints between column B and column A, the component in column B.

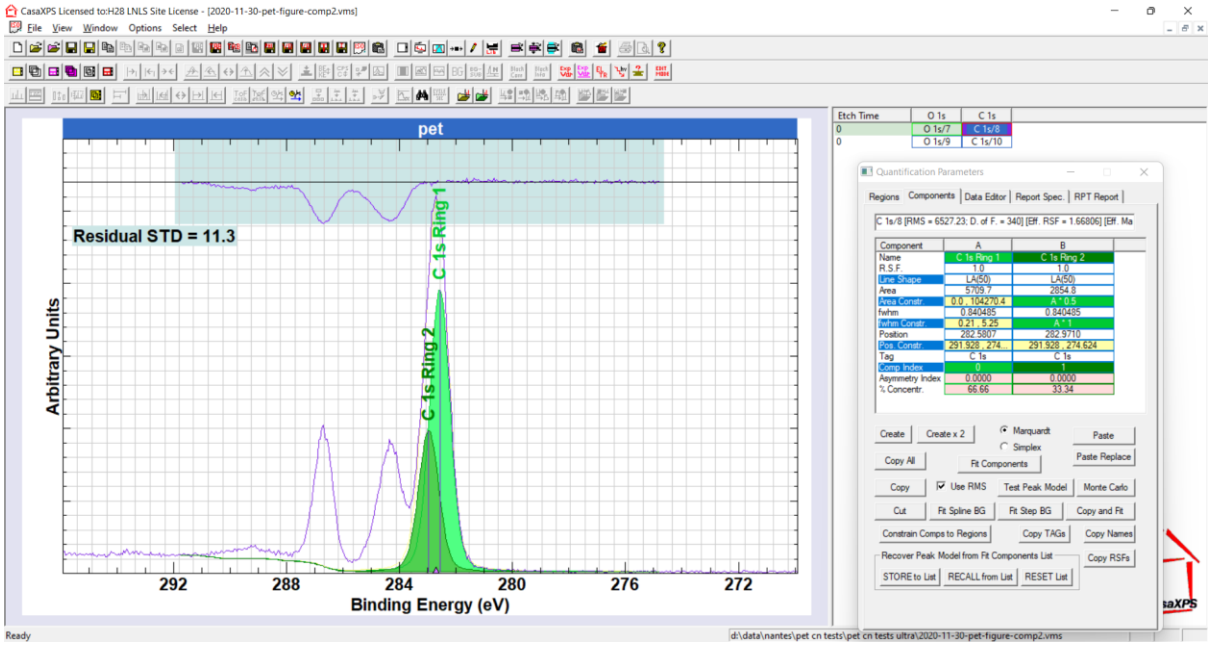
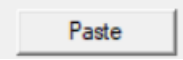


Figure COMP7. Components added to the component-clipboard in Figure COMP6 are added to the VAMAS block shown selected in the right-hand pane and displayed in the active tile in the left-hand pane by means of the *Paste Replace* button.

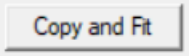
Removing and saving the removed component to the component clipboard is performed using the *Cut* button. A component can be removed via the *Cut* button provided the selected component is without any other components with relational constraints to the selected component.



The *Paste* button adds to the current peak model any components previously placed in the component-clipboard.

Components on the component-clipboard are used to reinitialise the peak model for the VAMAS block displayed in the active display tile. The set of components on the component-clipboard are rescaled with respect to the data onto which the paste action applies and any existing components in a peak model are overwritten by the component-clipboard components. The actions illustrated in Figure COMP6 and Figure COMP7 are a typical use of *Copy* and *Paste Replace* buttons.

Copying Existing Components – Non-Component-Clipboard Operation



Copy and Fit button uses components in a peak model (from the VAMAS block in the active display tile) as the template for transferring components to a set of spectra displayed in tiles in the left-hand pane scrolled-list of display tiles. The components in a peak model are transferred to other VAMAS blocks displayed in the left-hand pane before fitting the peak model to each spectrum in the scrolled

list of display tiles. Since the display tiles can only be constructed from VAMAS blocks in the same VAMAS file, the *Copy and Fit* button is only capable of transferring components in a peak model to VAMAS blocks in the same VAMAS file. The *Copy and Fit* button action requires a background appropriately defined for each spectrum that will receive the copied components. An option on the Regions property page of the Quantification Parameters dialog window performs the equivalent task via the button labelled *Copy and Paste*, where regions are copied from the active display tile to all spectra displayed in the scrolled list of display tiles (Figure COMP8 and Figure COMP9).

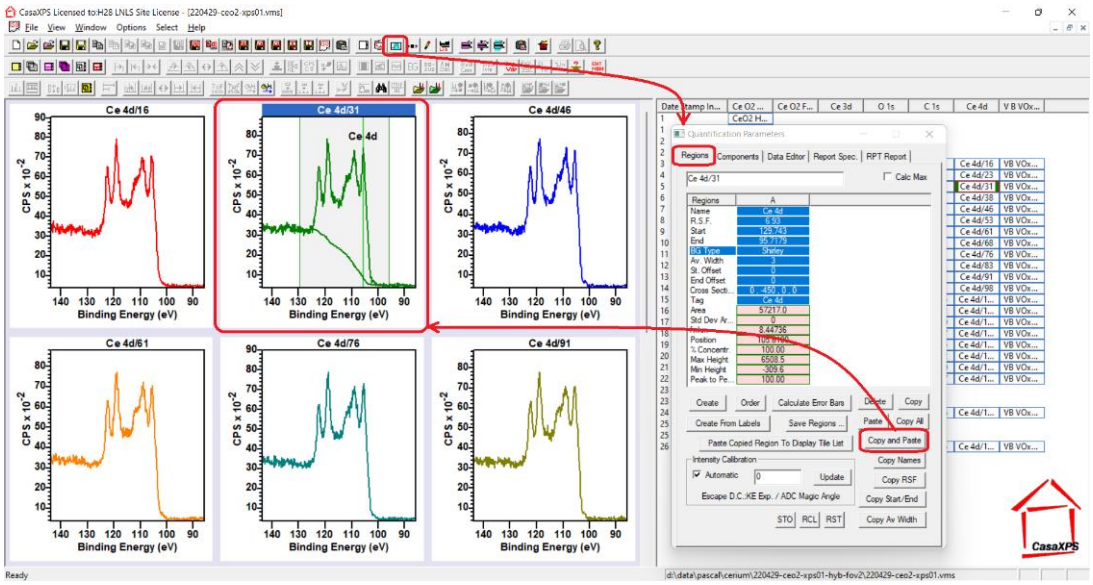


Figure COMP8. Arrangement of display tiles with data displayed in each tile corresponding to spectra for which the region shown in the active display tile can be transferred via the action of the *Copy and Paste* button.

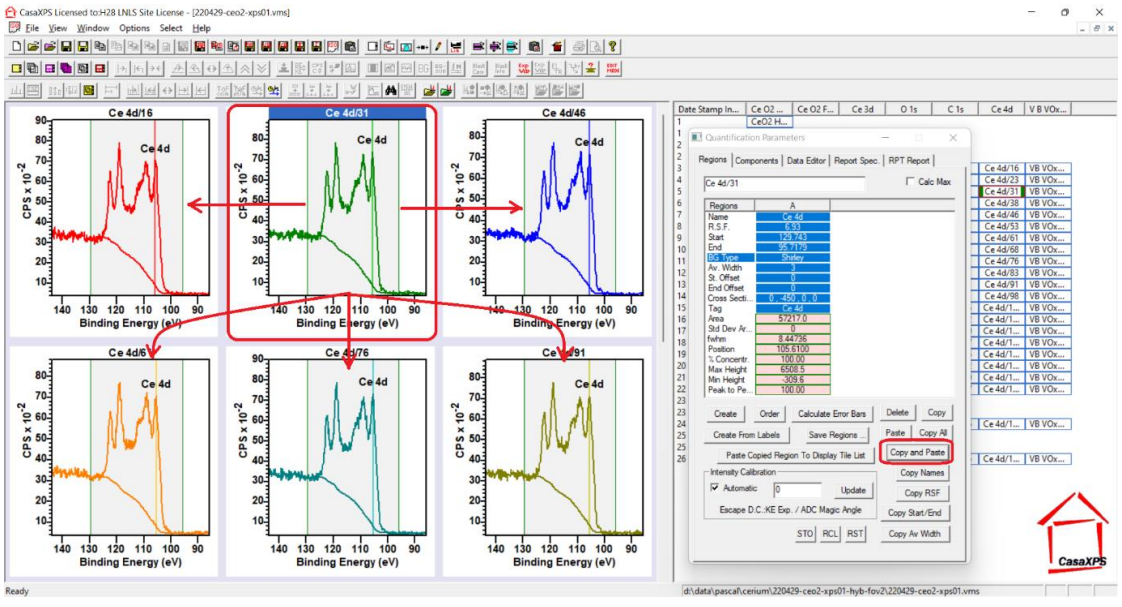


Figure COMP9. Regions property page *Copy and Paste* button action. Regions defined on the VAMAS block displayed in the active display tile are copied and then pasted to all VAMAS blocks for which their data are currently displayed in the scrolled list of display tiles. Six display tiles are visible in the left-hand pane but the scrollbar indicates that the *Copy and Paste* action will applied to VAMAS blocks not visible but nevertheless present in the scrolled-list of display tiles.

The Browser Operations dialog window available from the main toolbar of CasaXPS is used to propagate peak models from one VAMAS block to VAMAS blocks spread over many VAMAS files. The *Copy and Fit* button option on the Components property page is designed to permit transfer of components within a file only.

The actions associated with *Copy and Fit* button make use of the current arrangement of display tiles in the left-hand pane (Figure COMP10). Components to the peak model prepared for a spectrum displayed in the active tile is the source from which the component-copy operation is performed. The set of spectra displayed one-per-tile in the list of display tiles, which includes all display tiles contributing to the scrolled list of display tiles in the left-hand pane, are the target for the component-paste and then fit operation. The *Copy and Fit* button copies components only and therefore each spectrum for which the paste action is performed must have a region defined with suitable background to allow the fit operation to occur (Figure COMP10). On pressing the *Copy and Fit* button, a dialog window indicates the number of display tiles within the scrolled list which will be affected by the paste and fit operation. The example in Figure COMP10 shows a scenario where components defined for the spectrum in the active display tile are about to be copied then pasted and fit to data corresponding to eleven display tiles, six of which are visible via the current page setting that displays six tiles per page. Proceeding with the *Copy and Fit* operation results in the outcome as illustrated in Figure COMP11. While Figure COMP11 provides visual verification that components are copied and the resulting fit to data of the peak model has occurred for the first six spectra, all eleven display tiles currently loaded into the scrolled list are similarly processed.

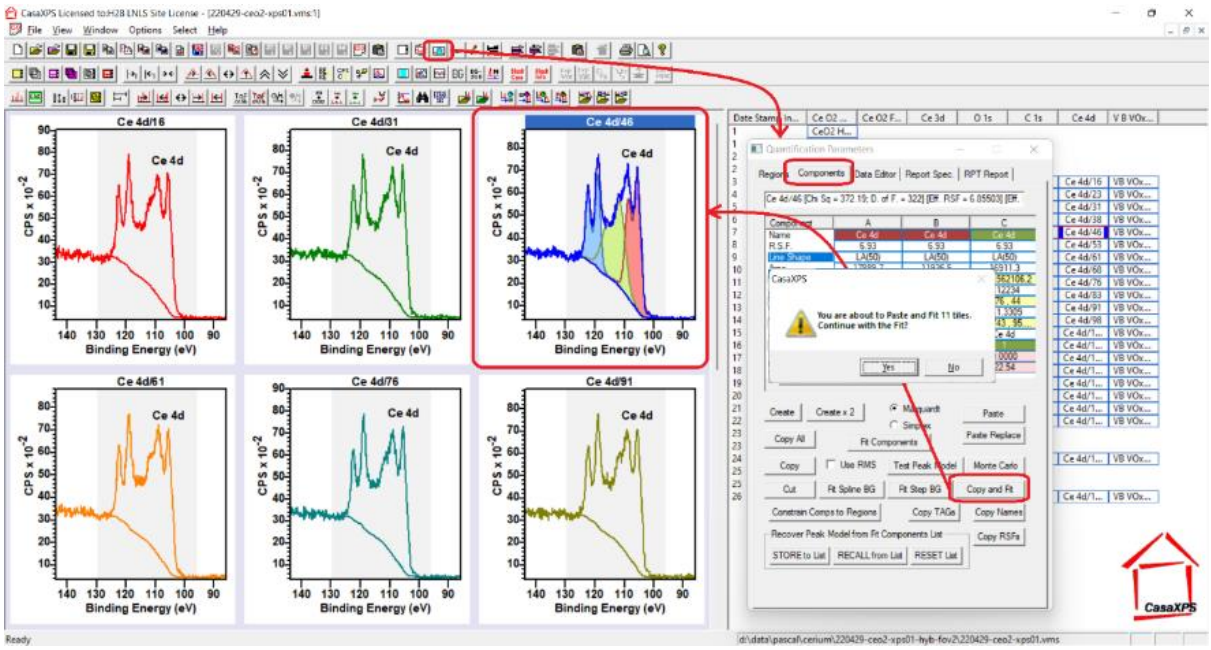


Figure COMP10. Arrangement of display tiles prior to application of the *Copy and Fit* button.

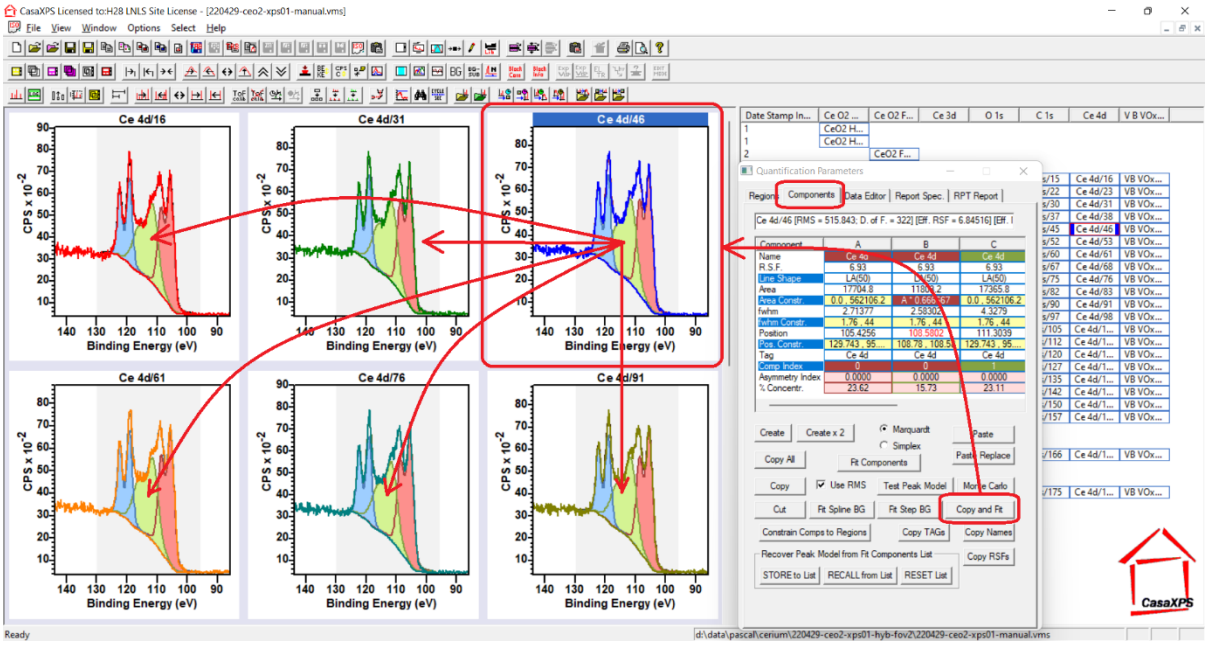
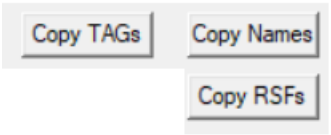


Figure COMP11. Result of applying the Copy and Fit button to the display arrangement in Figure COMP10.

After-Thought Adjustments to Components

A set of buttons on the Components property page are designed to permit adjustments to component parameters such as name fields and RSF values without altering component parameters that are used to fit data with a given peak model.



Component parameters that influence quantification and other uses are on occasion given proper attention only following the fine-tuning of peak models applied to many spectra in an experiment. Fine tuning of fits to data are sometimes necessary to allow for changes to background signal or other tweaks that allow the application of a peak model to data which differs from the general form. Specific adjustments to peak models would be lost if components for one peak model are adjusted and then copied a further time to other spectra. To preserve subtle differences created by these adjustments, options are available to copy specific component fields rather than copying an entire component parameter-set between spectra. For example, the names used for components in a peak model are used to identify signal from different photoemission sources and are used in the construction of quantification results gathered from peak models. A button labelled *Copy Names* is used to copy from the peak model in the active tile the component names from that peak model to a set of VAMAS blocks under the control of the selection in the right-hand pane. Copying specific component parameter fields between peak models does, however, require the essential construction of the peak model in the source VAMAS block to match the peak model in a destination VAMAS block. The set of components to all peak models in Figure COMP11, by virtue of the copy and fit operation, are all essentially the same for each VAMAS block. The peak model is constructed from six component peaks that can be associated with three spin-orbital split doublet pairs. However, the copy and fit operation was applied making use of the same name field for all six components, so as these peak models stand in Figure COMP11 there is no means to separate doublet signal by name.

The scenario in Figure COMP11 is precisely the situation where the button labelled *Copy Names* would be used to update the name field for all VAMAS blocks involved in Figure COMP11 without altering the fitting parameters from their current values.

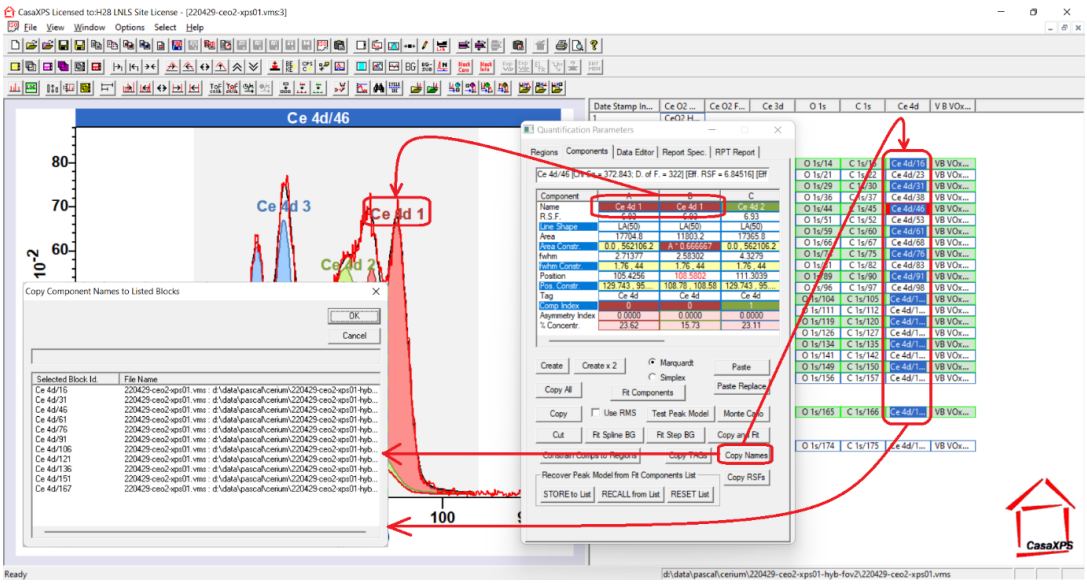
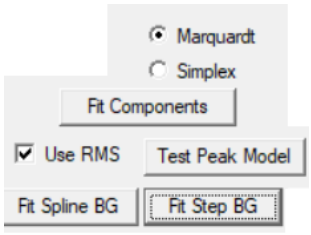
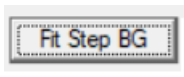


Figure COMP12. *Copy Names*, *Copy TAGs* and *Copy RSFs* all transfer component fields from the peak model displayed in the active tile to peak models defined on VAMAS blocks selected in the right-hand pane. Each button assumes the set of components defined by the active tile VAMAS block are the same structure and order as components in the destination VAMAS blocks.

Fitting Curves to Data



There are three buttons on the Components property page that when pressed fit curves to data. The most commonly used button labelled *Fit Components* adjusts fitting parameters for components to a peak model (area, FWHM and position) to achieve the best data reproduction. Two buttons, namely, *Fit Spline BG* and *Fit Step BG* are used to fit specific curves with respect to data where the parameters optimised are defined in the Cross-section field defined on the Regions property page. One further button provides a means of systematically adjusting parameters relating to peak models and creating visual feedback that helps to assess the consequences of adjusting peak model parameters when fitting curves to data. The button labelled *Test Peak Model* creates a new VAMAS file containing copies of the VAMAS block analysed in which peak model parameters, such as line shape, can be incremented before fitting these modified peak models to data. The output from *Test Peak Model* button is a list of VAMAS blocks all of which are copies of the original data including the fit of modified peak models to data and one VAMAS block in which the figure of merit is plotted against the parameter representing a modification to the original peak model.



Background types Step Down, Step Up, Edge Down and Edge Up are defined on the Regions property page with parameters that can be optimised with respect to a figure-of-merit. These optimisation parameters are listed in the Cross-section field for a region and are adjusted to achieve best fit to data using either the Regions button indicated by the arrow in Figure COMP13 or the *Fit Step BG* button illustrated in Figure COMP14.

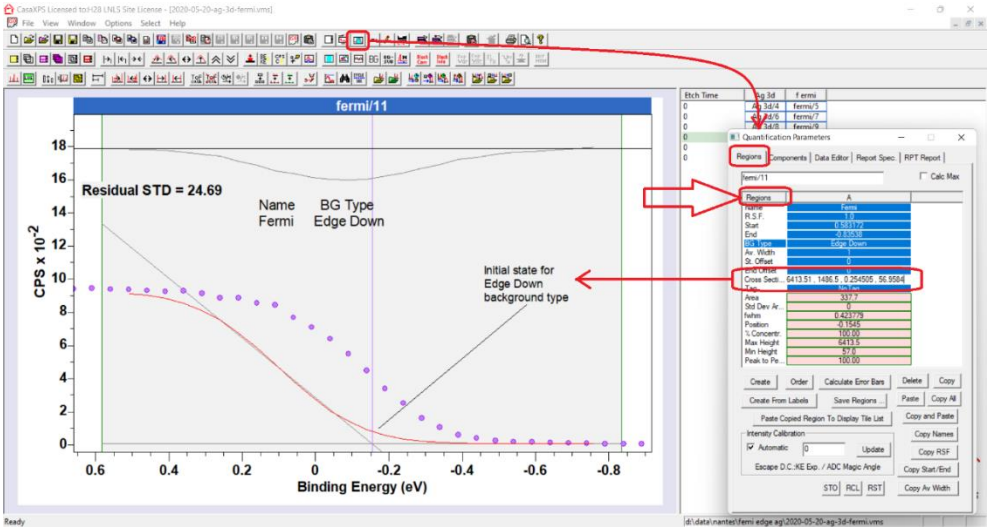


Figure COMP13. An example of data defined with a region for which the background type is Edge Down. The background is specified through parameters listed in the Cross Section field and represent values for which the background shown is yet to be fitted to data. The *Fit Step BG* button on the Components property page shown in Figure COMP14 is used to fit the Edge Down background to data.

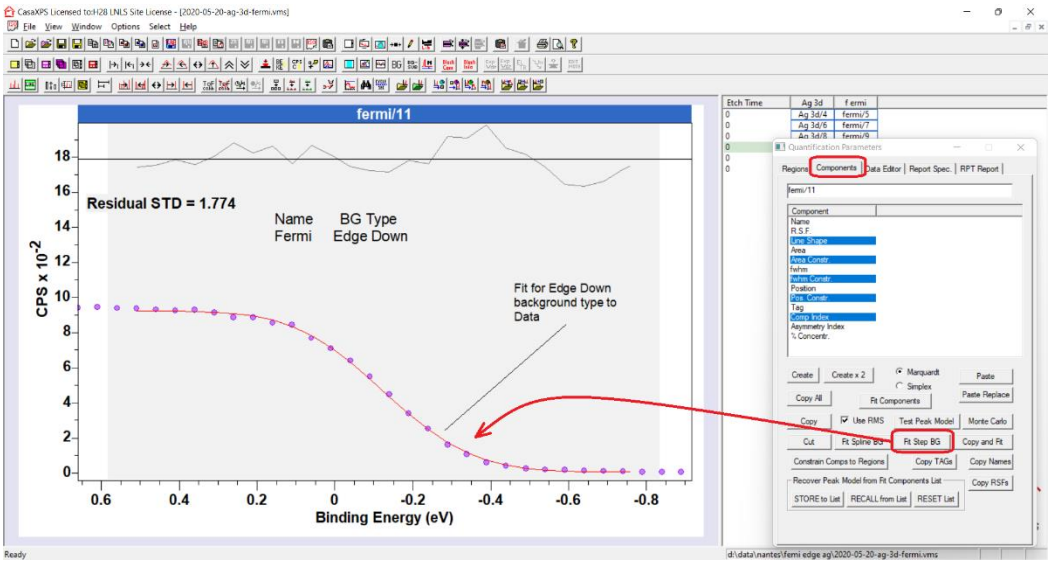
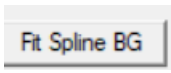


Figure COMP14. The result of pressing the *Fit Step BG* button for an Edge Down background initially defined as shown in Figure COMP13.



Background types based on cubic splines are available via *Spline Linear*, *Spline Shirley* and *Spline Tougaard* initialisation for cubic spline functions with five cubic polynomial sections. The cubic spline background is defined by parameters listed in the Cross-section field on the Regions property page.

These Cross-section values are optimised for a given region by pressing the *Fit Spline BG* button. There is no physical meaning for spline backgrounds with respect to XPS data. The background defined by a spline function is only offered as a means of fitting smooth curves to low curvature data. The example in Figure COMP15 and Figure COMP16 illustrates how the broad feature measured using low energy resolution data spanning the Fermi edge can be approximated by a spline function. The spline function in Figure COMP15 is initialised to be a straight line, which is subsequently fitted to data by pressing the *Fit Spline BG* button on the Components property page (Figure COMP16).

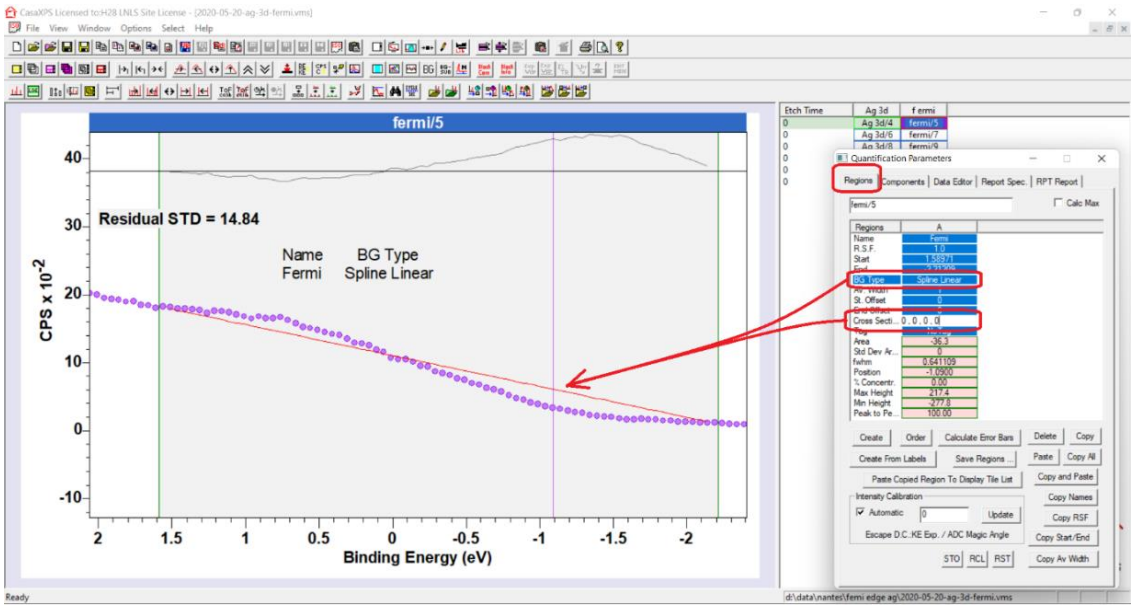


Figure COMP15. Cubic spline background initialised using the background option *Spline Linear*. Parameters that permit the fitting of a spline background to data are optimised via the button shown in Figure COMP16.

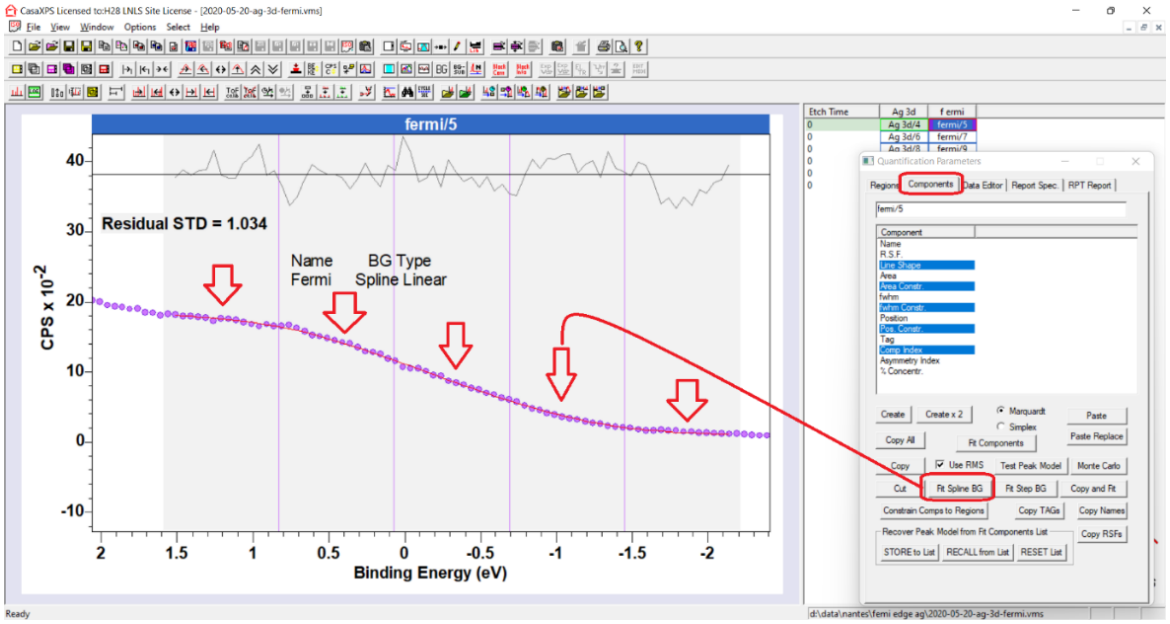
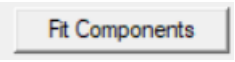
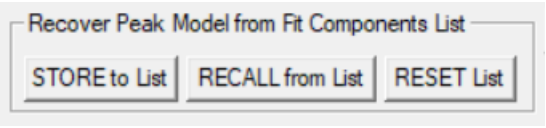


Figure COMP16. The initial parameters to a cubic spline background shown in Figure COMP15 are adjusted by optimisation yielding a fit to data by pressing the *Fit Spline BG* button.



Ctrl+G

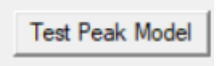
Once a peak model is defined for the spectrum displayed in the active display tile, pressing the *Fit Components* button initiates automatic fitting for the components to the peak model using non-linear optimisation to improve the figure-of-merit indicated by the *Use RMS* tick-box. The figure-of-merit is calculated from the data and the curve calculated from the sum of all curves (bell-shaped or otherwise plus background curves). If the *RMS* tick-box is ticked then the figure-of-merit is calculated directly from the differences between the sum of all curves and the data. If *RMS* tick-box is unticked then the figure-of-merit is calculated from these differences after normalisation to the uncertainty expected for each data bin. *RMS* tick-box unticked allows optimisation which fits data bins with high counts with equal weight to data bins with low count rates.



When the *Fit Components* button is pressed the current state for a peak model (components and background) are saved to a list of peak models for a given VAMAS block. The list of peak models for a VAMAS block can be recovered using the button labelled *RECALL from List*. Each time the *RECALL from List* button is pressed the peak model for the active tile is replaced by the previous state of the peak model as saved each time *Fit Components* button was pressed. The list of peak models will cycle through all previous states of the peak model.

The list of peak models can be added to at will by at any time pressing the *SAVE to List* button. In the event the list of saved peak models becomes too numerous to manage, a further button can be used to reinitialise the list. Pressing the *RESET List* button empties the list of peak models.

Checking Peak Models and Fits to Data are Meaningful



Fitting a peak model to data is achieved by non-linear optimisation algorithms which search for a best fit through a sequence of mathematical steps that move from the current set of optimisation parameters to a new set of these parameters by an algorithm-dependent prescription. The suitability of any one of these steps is determined by reducing the magnitude for a figure-of-merit. Thus, physically significant parameters such as intensity, binding energy or FWHM are chosen by either of two optimisation algorithms used in CasaXPS (Marquardt or Simplex) based on a single value (Chi-square or RMS) which in the absence of physical guidance yield a mathematical solution that may be difficult to justify on scientific grounds. Further, non-linear optimisation does not have a well-defined termination test and therefore knowing that optimisation has terminated with the best outcome for a figure-of-merit is not always clear either. It is therefore important to test peak models by exploring how the outcomes for optimisation are changed by varying or fixing optimisation parameters for a given peak model when fitted to the original data or data similar to the original data.

Testing Line Shapes

There are a number of tests one might perform for a peak model that can be explored via the *Test Peak Model* button. The action taken by the *Test Peak Model* button depends on the component parameter selected in the table of components prior to pressing the *Test Peak Model* button. For example, if a line shape parameter is selected before pressing the *Test Peak Model* button, then a

dialog window appears (Figure COMP17) which allows tests aimed at the line shape parameter used for one or more components in the peak model corresponding to data displayed in the active tile. The result of performing *Test Peak Model* applied to line shape parameters is a new file (Figure COMP18) in which the same VAMAS block data is used with incremental changes to a line shape parameter to introduce changes to the peak model that are tested by fitting these new peak models to the same data. The outcome for these tests is a plot of figure of merit against the line shape parameter as well as a list of VAMAS blocks each representing the fit for each peak model to the data. These results allow the influence of line shape on outcomes to optimisation to be assessed and the consequences of line shape choices to be visually inspected.

Visual inspection of peak models after fitting to data are useful, however, extracting quantification information from the new file created by the *Test Peak Model* button offers a means to examine how fitting parameters and results of quantification change as a consequence of scanning component parameters. The results shown in Figure COMP19 is a plot of %area for each of the O 1s components used in Figure COMP18 which demonstrates that the relative intensity measured by fitting peak models to data depends on the choice of line shape. Further, the line shape and relative area measured by components is linked to some extent. While there is an obvious minimum in the figure-of-merit, there is no obvious choice for the line shape based on %area in this example. Tests for area, position and FWHM can be similarly performed using the results file shown in Figure COMP18 and making use of the Custom Report section of the Reports Spec property page of the Quantification Parameters dialog window. Quantification using keywords entered into TAG field allow reports and plots similar to Figure COMP19 to be compiled for area, position and FWHM. The problem of choosing the most appropriate line shape for data should be coupled to observing the response of physically meaningful outputs from peak models formed by line shapes.

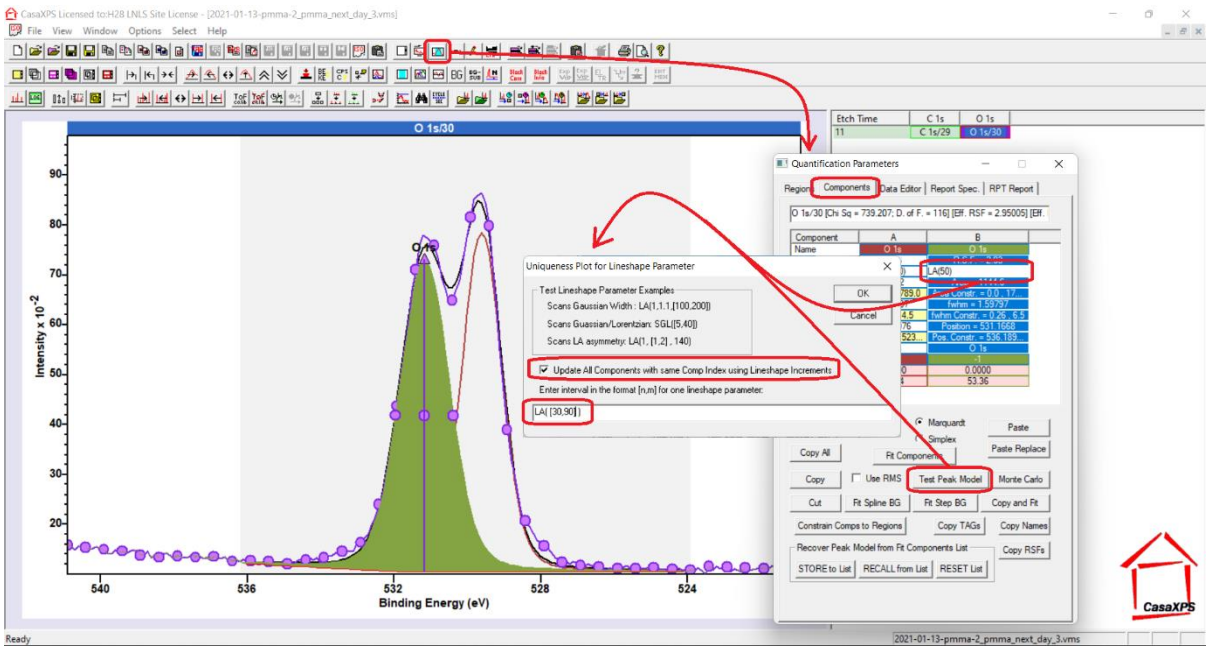


Figure COMP17. Applying *Test Peak Model* button to a peak model in the active tile, where the component field selected is the Line Shape field for the component in column B of the components table. As a consequence of selecting the Line Shape field a dialog window is invoked that allows a specification for a scan of line shape parameter LA(m), m between 30 and 90 to be initiated. A line shape parameter entered in the format [a,b] (in this example LA([30,90]) results in 31 VAMAS blocks entered into a new VAMAS file (Figure COMP18) where optimisation fits 31 different peak models to

the same data shown here. The tick-box *Update All Components with same Comp Index using Line Shape Increments* when ticked causes a common line shape to be applied where appropriate.

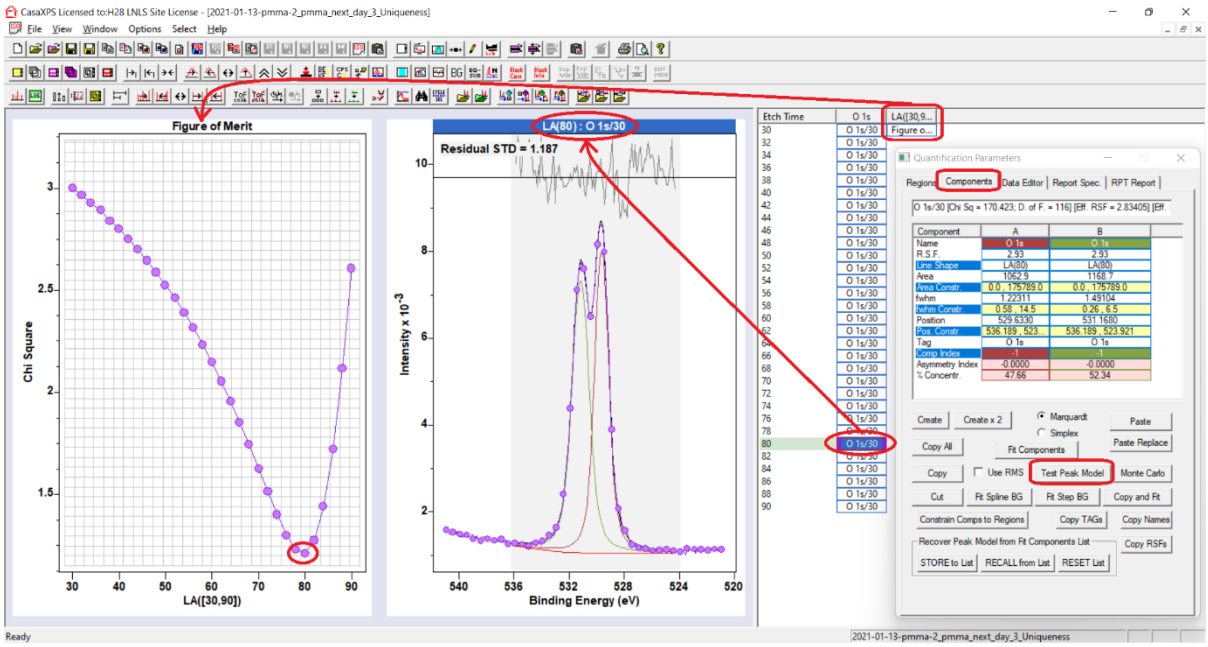


Figure COMP18. Results of *Test Peak Model* button initiated as shown in Figure COMP17. Both O 1s components are assigned the same Comp Index value and by virtue of the options enabled in Figure COMP17, both component line shapes are adjusted before fitting peak models to data. The figure-of-merit plot shows a minimum for the line shape LA(80). The peak model with line shape LA(80) is shown fitted to the data from the active tile in Figure COMP17.

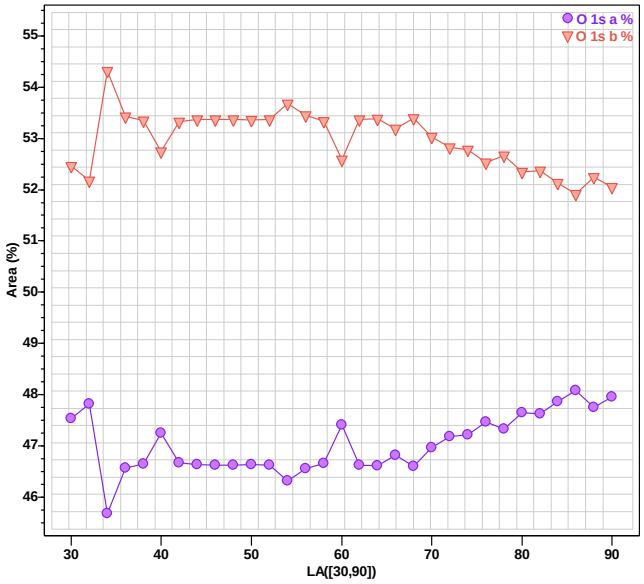


Figure COMP19. Profile of component percentage area for the two components shown in Figure COMP17 plotted as a function of the parameter m in LA(m) line shapes. Note how the line shape LA(80) offering a minimum in the figure-of-merit can be seen to belong to a set of LA(m) line shapes for which the %area diverges from the line shapes figure-of-merit that suggests a poorer quality fit to data.

Understanding Constraints to Optimisation Parameters

Similarly, relational or interval constraints may influence physically meaningful outputs from peak models when fitted to data. If the selected component field is a constraints field with an interval constraint, then the output file created by the *Test Peak Model* button is generated by a scan of a specific parameter corresponding to the selected constraint field. The constraint field selected provides an interval over which the corresponding parameter is scanned. Each value for the parameter is fixed within the peak model before fitting the peak model to data. The example illustrated in Figure COMP20 is a scan of component position for the O 1s component in column A. An energy interval is specified via the values in the interval constraint for position and the position constraint field is selected before pressing the *Test Peak Model* button. Results shown in Figure COMP21 are gathered from the data fitted using the peak model with the *O 1s a* component fixed at position values determined by the scan over the interval specified in the position constraint field. The top experiment window is a VAMAS file calculated from the set of VAMAS block entered into the newly created VAMAS file (bottom experiment window in Figure COMP21). The tools available on the Quantification Parameters dialog window via the Report Spec property page under the Custom Report section are used to create the profile in the top experiment frame.

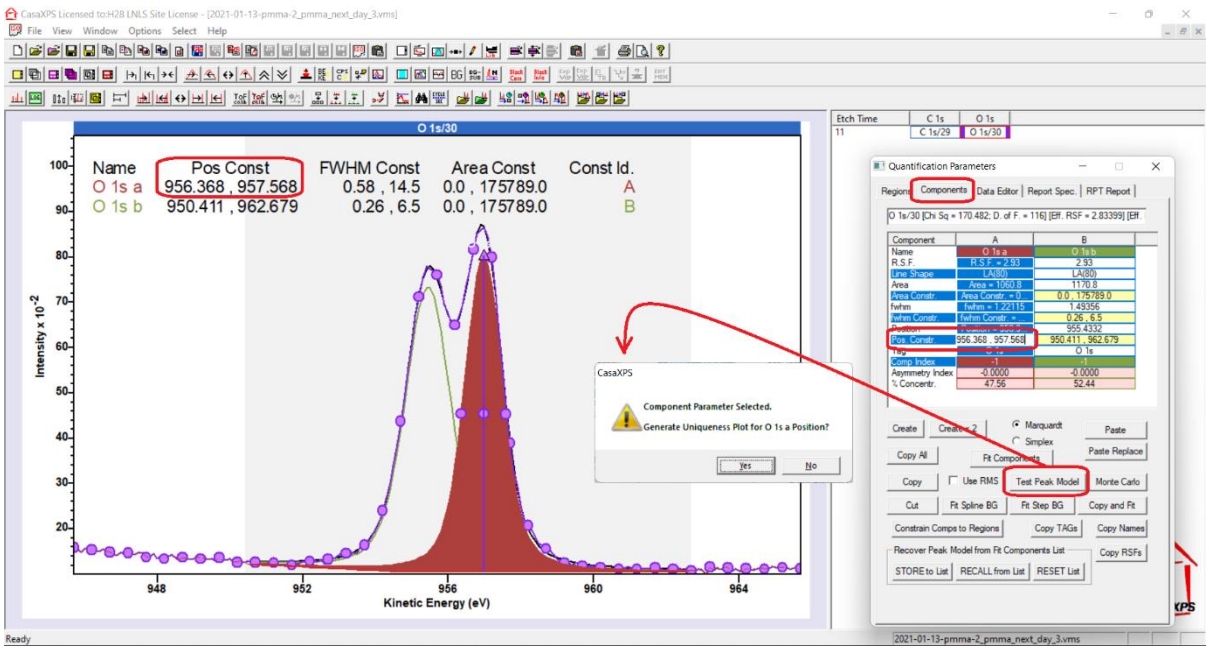


Figure COMP20. Preparation for performing a scan of position parameter for component in column A of the Components table. The Position Constraints field is selected and an interval constraint is entered to provide the range over which the position value is scanned. For each position value within the interval specified the position for component O 1s a is fixed at the scan value and the peak model is fitted to the data shown in the active tile. The result file generated by the position scan is shown in Figure COMP21.

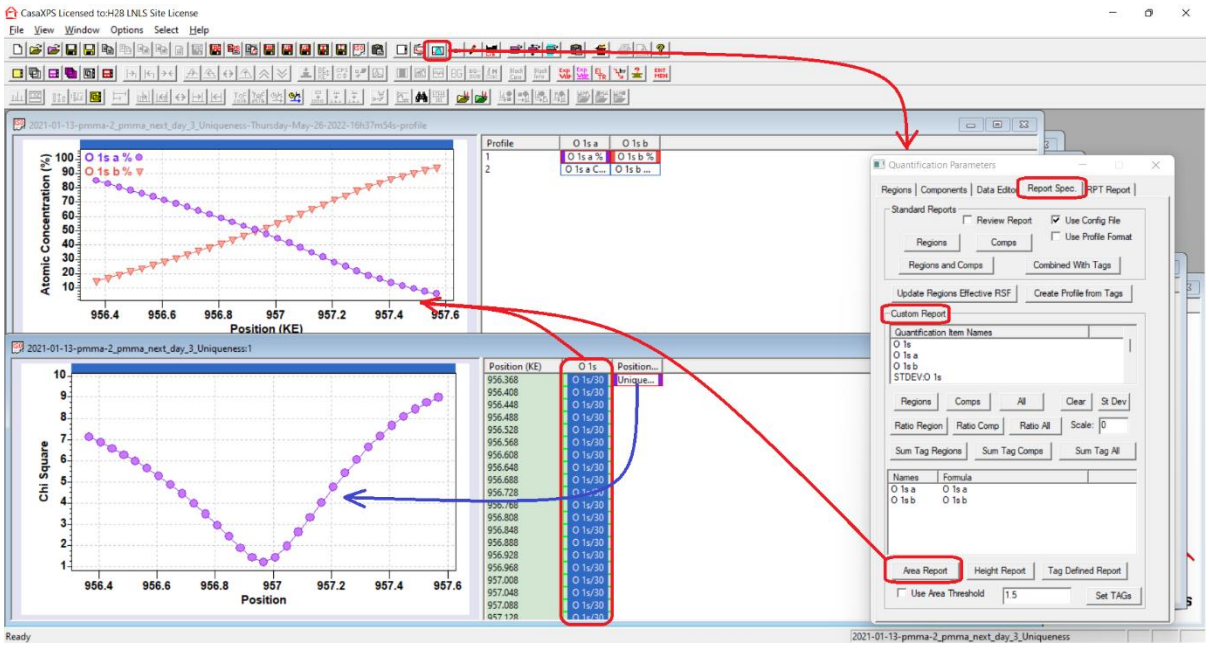


Figure COMP21. Bottom experiment window shows the result VAMAS file generated by the position scan defined as shown in Figure COMP20. The top experiment window is a profile generated by the Report Spec property page from the O 1s peak models after using a fixed position value and fitting to each spectrum the peak model so defined.

Testing Peak Models for Stability with respect to Noise

A peak model fitted to a specific spectrum may appear to have converged to a stable set of optimisation parameters. However, this apparent stability may be a peculiar case that depends to a greater extent on the characteristics of noise in data compared to the desired systematic physical information in spectra. In order to guard against excessive errors in outputs from fitting peak models to data, an approach based on Monte Carlo simulation is used to test a peak model's stability with respect to noise. The *Monte Carlo* button on the Components property page is used to calculate uncertainty in %area determined for the fit of a peak model to data which simulates spectra assuming noise in data bins is due to Poisson distributed random variations in signal. The results obtained by the *Monte Carlo* button can be added to quantification tables as numerical estimates for uncertainty in percentage atomic concentration. However, these uncertainties reported with quantification tables are not suitable to justify the uncertainty in a given physical quantity, but rather should be used to highlight the existence of errors in quantification results. An appreciation for these error estimates can be better visualised by one of the modes for the *Test Peak Model* button. If the component field selected prior to pressing the *Test Peak Model* button is the Name field for the component, then the *Test Peak Model* button creates a new VAMAS file in which the peak model (without modification) for data in the active display tile is used to create a set of VAMAS blocks containing spectra that differ from one another by simulated random noise. The peak model is then fitted to these simulated data. Overlaying these simulated spectra, each with peak model fitted to data, allows visual inspection of how responsive a peak model is to differences in spectra induced by noise (Figure COMP22). The example shown in Figure COMP22 should be compared against the example in Figure COMP23, where increased signal compared to noise for a similar spectrum to that in Figure COMP22 results in much improved stability for the same peak model.

One observation that is important when assessing the stability of a peak model with respect to noise is that the figure-of-merit tends to suggest the best fit is achieved for low signal spectra. This

however is in contrast to results from Monte Carlo simulation where the most stable peak fits are generally obtained for high signal low noise data. The message to accept from Monte Carlo tests for peak models is not to place too much reliance on the figure-of-merit used during optimisation as a measure for successful fitting of data by a particular peak model.

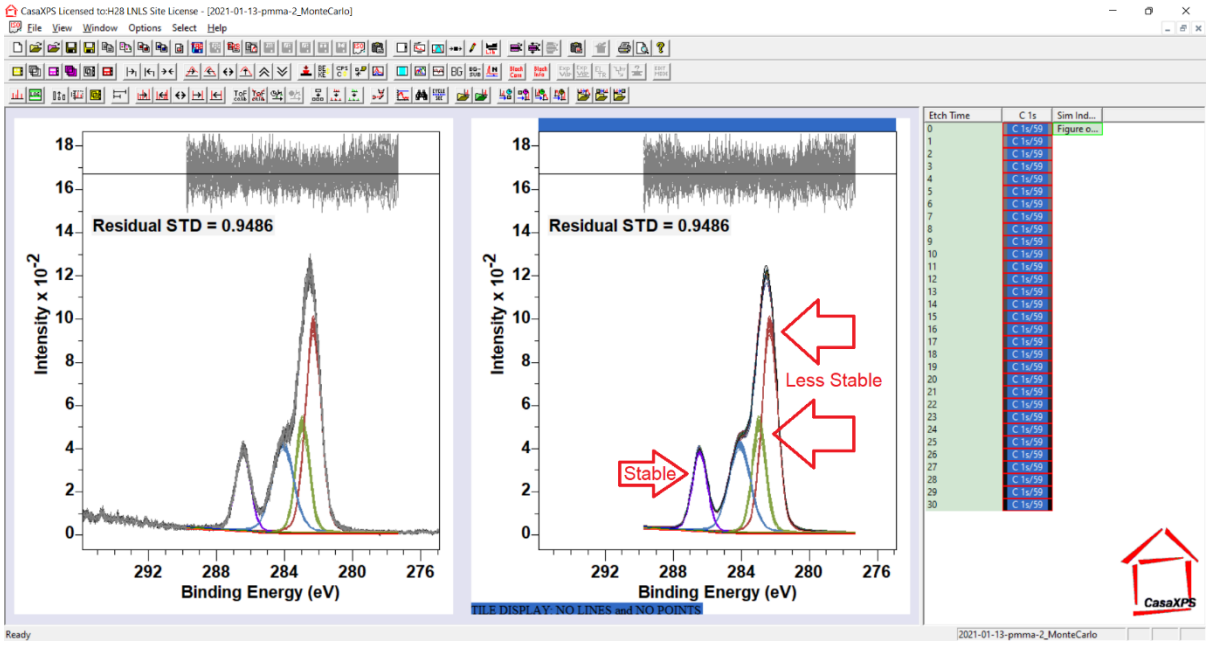


Figure COMP22. An example of a peak model that appears to have converged to a stable solution based on a fit to the original spectrum. However, simulating noise for the spectrum in question and fitting simulated spectra with the same peak model shows that the two correlated components with lowest binding energy are less stable with respect to noise than the highest binding energy component.

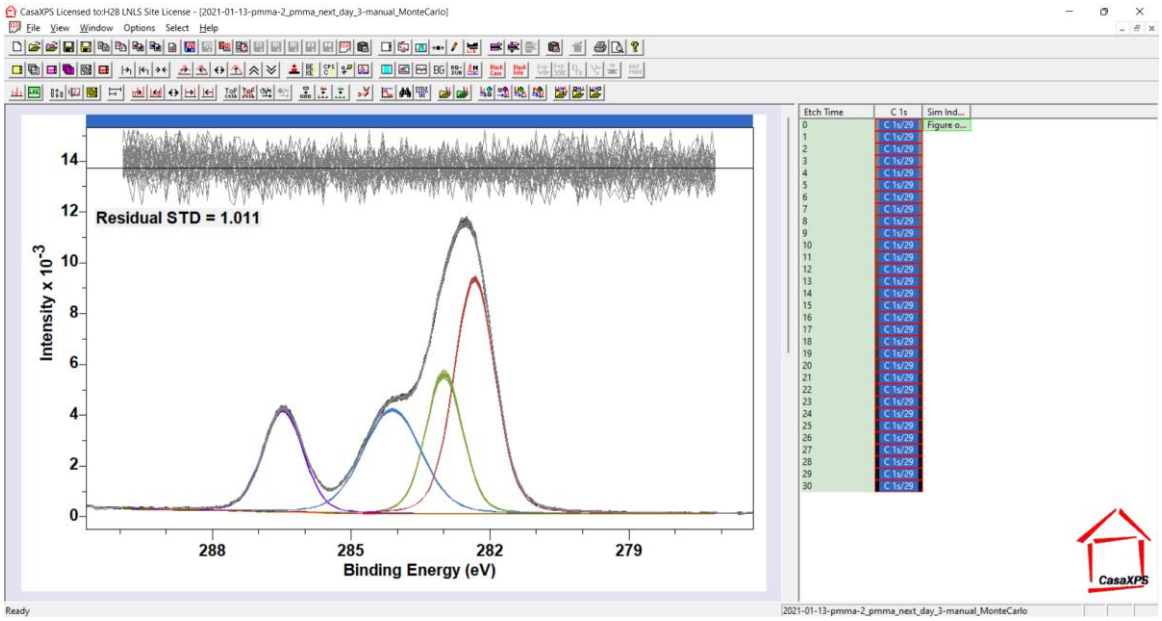
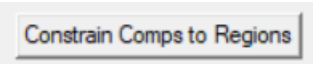


Figure COMP23. The same peak model used in Figure COMP22 applied to data with an order of magnitude more counts per bin. The *Test Peak Model* button invoked with a component name field selected creates a set of simulated data that shows the peak model responds to noise is far more stable than the result obtained for data in Figure COMP22.



Peak models are defined in terms of components representing zero-energy-loss photoemission signal and background curves representing inelastic scattered signal. For most situations components are defined within the same energy interval over which a background curve is defined. However, it is possible to define position constraints that allow the position for a component to be outside the energy interval defined by a region as shown in Figure COMP24. Optimisation for components is only performed using data within regions as defined for a spectrum. Components with positions outside of any region are without guidance during optimisation and therefore the outcome for a peak model as shown in Figure COMP24 is unpredictable and undefined. The button labelled *Constrain Components to Region* adjusts all components within a region that are governed by interval constraints to an energy interval that limits optimisation to the region. The position constraints for any component which prior to pressing the *Constrain Components to Region* button allow the component to be positioned outside a region are adjusted to ensure all components remain within the region.

Pressing the *Fit Components* button on the Components property page performs the same task of limiting the position for components performed by the *Constrain Components to Region* button before auto-fitting the peak model. The mechanism used to fit components in the active tile when fitting is invoked by Ctrl+G differs in that no adjustment to position constraints are performed for Ctrl+G. It is therefore possible to fit a component curve to data in a region where the component maximum is outside the region by means of Ctrl+G. This scenario is seldom encountered, but is useful in situations where a broad peak-like structure interferes with fitting of narrower photoemission peaks. An example of which might be Au $4p_{3/2}$ signal which is close to O 1s signal. Au $4p_{3/2}$ is broad in width and may influence higher binding energy background signal to O 1s, while O 1s is narrow and may contain structure for which peak fitting is necessary.

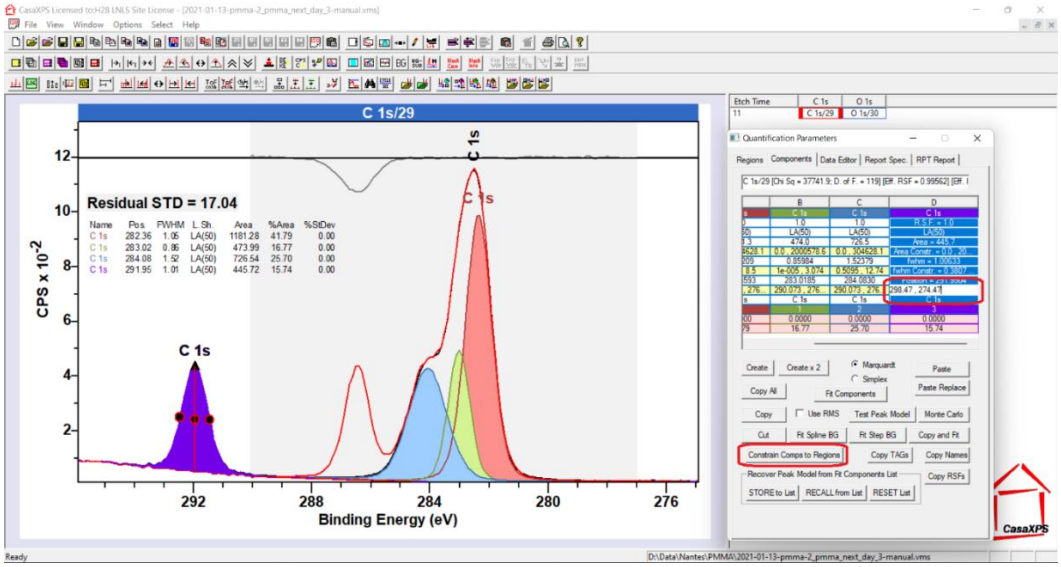


Figure COMP24. Example of a component for which the position constraints are such that the component is permitted to attain a position outside of the region interval in which a background curve is defined. A component outside of a region may during optimisation behave unpredictably.