

Working with Multiple Samples: Tricks to Save Time

The purpose of this article is to review the features in CasaXPS for aiding those working with large sets of samples, where the data are not necessarily identical in nature but nevertheless have a common theme. For example, a series of measurements might be made on a set of stainless steel samples, where each experiment includes a survey plus a set of high resolution spectra; however, while the spectra always include data from the C 1s, O 1s and N 1s energy intervals, other intervals such as Cr 2p or Fe 2p may also be included in the data files. If the data were identical in terms of the number of spectral regions and order of acquisition, and such samples were routinely analysed over an extended period of time, then it would be worth investing the time to setup the required batch processing files. The fact that the data includes variations on a theme means that batch processing is not an option. Fortunately, all is not lost. Version 2.3.12 offers many features for manipulating multiple samples and by applying some of the tricks-of-the-trade, large sets of data files can be processed with relative ease. The tricks on offer are the subject of this article.

The topics covered are:

- Opening multiple files
- Selection mechanism for VAMAS blocks
- One shot energy calibration for multiple files
- Propagation based on matching species/transition to multiple files
- Tile display format and printing the results.

Opening the Files

When manipulating multiple samples, it is sometimes convenient to merge the data into a single Experiment Frame. Other times, the data is best maintained as individual files. In either case the files can be opened in one action. Both the **Open and Merge** and **Open** options on the File menu (Figure 1) offer a File Dialog window and by selecting a range of files, the action associated with the window will be applied to the selected files when the **Open** button on the dialog window (Figure 2) is pressed.

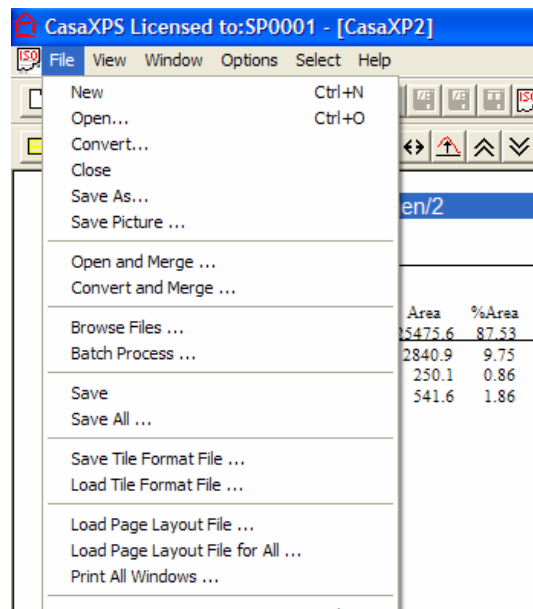


Figure 1

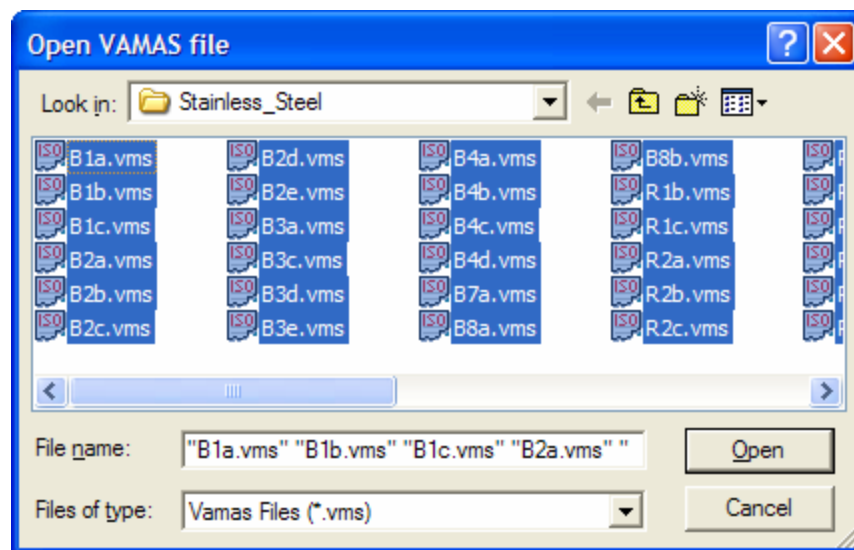


Figure 2

Opening sets of files into separate Experiment Frames

Once the **Open** File menu item has been selected and the Open VAMAS File dialog is active, the normal operations for making selections in Windows programs are available for choosing the files to be opened. A single file is selected with a left-click of the mouse, which can be followed by holding the Shift or Control keyboard keys down and left-clicking the mouse over a different file. The Shift modifies the left-click action and

causes a range-selection to occur, where all the file names between the first and second left-clicked file names become selected. The Control key causes files to be added to the current selection. The selection in Figure 2, in which all the files in the current directory are required, is achieved by first, left-clicking on a file name to ensure the list of files is the active item on the dialog window, then pressing Ctrl-A. All the files in the current directory, subject to the “Files of type” filter, become selected. On pressing the Open button on the dialog in Figure 2 an Experiment Frame, one for each file selected, appears in the CasaXPS main window.

Selection Mechanisms in CasaXPS

With large sets of similar data, the intension is typically to apply the same set of processing operations to each file, prepare the display and print the results. The problem is therefore to manipulate the data such that these operations are as painless as possible. The basis for any operation in CasaXPS is the selection of one or more VAMAS blocks, so before describing the operations, the new selection mechanism for multiple files are described first.

An Experiment Frame offers two views into a VAMAS file, namely, the left-hand-side in which spectra are displayed in graphical format and the right-hand-side browser. Both play a role in defining the target and source for various operations such as processing and propagating the results of processing to other data blocks.

The logic governing the use of these two selection mechanisms requires some explanation. In general, a single target for a processing operation is defined as the *active VAMAS block* in the *active display tile* of the Experiment Frame with input focus. The *active display tile* is the tile displaying data in the left-hand-side of the Experiment Frame for which the title to the data is marked as highlighted text. The *active VAMAS block* is the block selected first using the mouse and the browser at the time the data are displayed in the *active display tile*. Property pages such as those on the Spectrum Processing dialog window and the Annotation dialog window act on a single target data block and therefore the concept of the *active VAMAS block* is central to understand the cause and effect mechanism within CasaXPS. Once a block has been manipulated using the *active VAMAS block*, the progression is to transfer these processing operations to other blocks requiring the same manipulations. Hence the requirement to specify a source block and a set of target blocks. The source for a propagation action is specified using the *active VAMAS block* mechanism, while the target blocks are defined using the selection in the Experiment Frame browser. Anyone processing XPS depth profiles (see The Casa Cookbook page 121) would routinely use these concepts, where all the selections in terms of *active display tiles* and the browser are made within a single Experiment Frame. When multiple files are involved, the definition for the source and target blocks extends to cover selections over many different Experiment Frames.

The method for selecting data blocks in the browser of an Experiment Frame is not limited to a single Experiment Frame. Provided the Control key is held down, any

subsequent selections made by left-clicking the mouse adds to the set of currently selected data block. Figure 3 shows a set of six files where a survey spectrum from each file is displayed in the active tile and are also the current selection in the Experiment Frame browsers. While these data blocks could have been individually selected using the mouse, for larger sets of files, relying on the mouse and the Control key to make such selections is not very time efficient. To improve the ability to select related data blocks across Experiment Frames, the Select menu (Figure 3) of the CasaXPS main window offers options for selecting blocks throughout a set of Experiment Frames. Function keys have been associated with these menu options so that the selections can be made without excessive mouse movements, if desired.

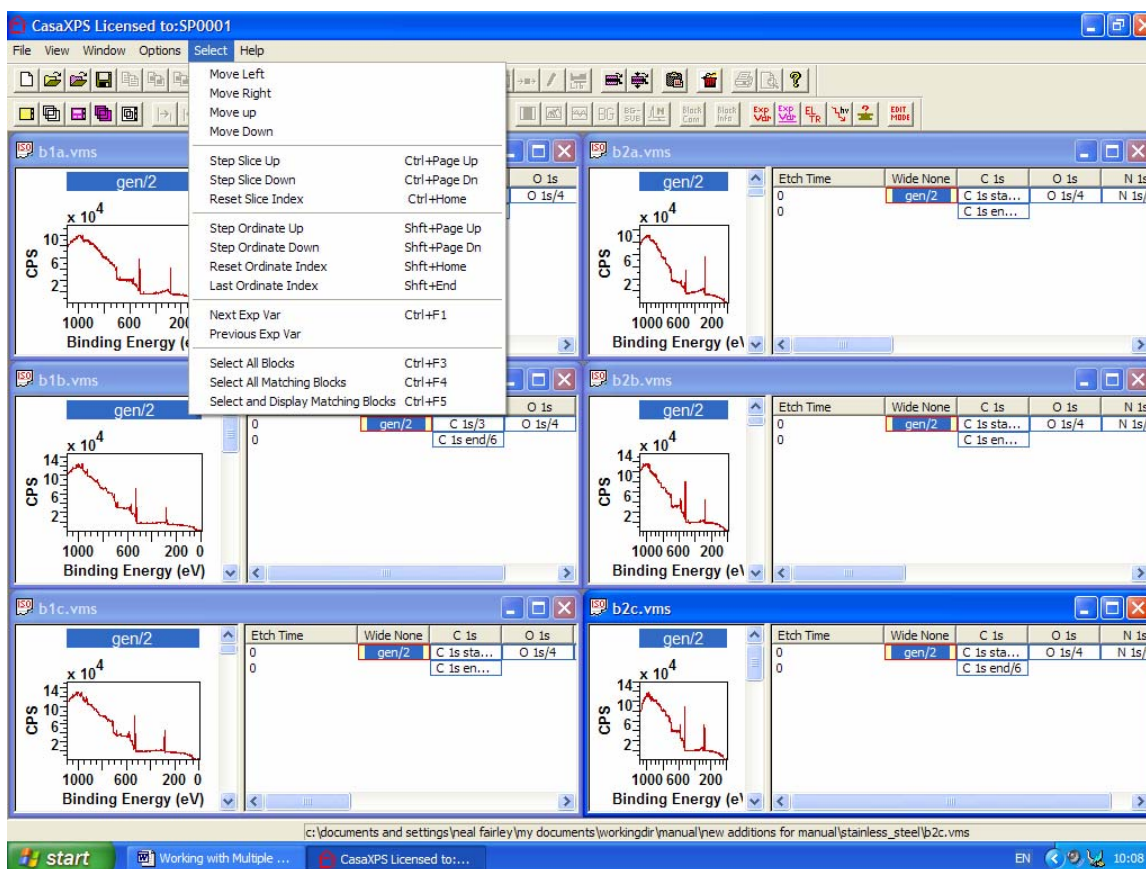


Figure 3

Select All Blocks (Ctrl F3): All data blocks in each Experiment Frame are selected via the menu option or alternatively hold the Control key down and press the F3 function key on the keyboard.

Select All Matching Blocks (Ctrl F4): The selected blocks in the Experiment Frame with input focus define the species/transition fields used to match against all the data blocks in the current set of Experiment Frames. The result of pressing the **Select All Matching**

Blocks menu option is all data blocks from the current set of Experiment Frames with identical species/transition fields are added to the current set of selected data blocks. For example, to add the set of O 1s data blocks to the selection shown in Figure 3, the Control key must be held down and one O 1s data block from any file selected. The Control key must be held down to prevent the survey spectra from becoming deselected. While input focus is still on the Experiment Frame with both the survey and the O 1s selected, holding the Control key down and pressing the F4 function key results in the selection of both the survey and the O 1s in every Experiment Frame. The data displayed in the scrolled list of tiles in each Experiment Frame are unaffected by the action of the menu option.

Select and Display Matching Blocks (Ctrl F5): The data displayed in the active tile is affected by the **Select and Display Matching Blocks** menu option. The intention is to change the active VAMAS block in each and every Experiment Frame using the same selection mechanism as **Select Matching Blocks**. The need to adjust the active VAMAS block is motivated by the new energy calibration option which performs a calibration across files (see below).

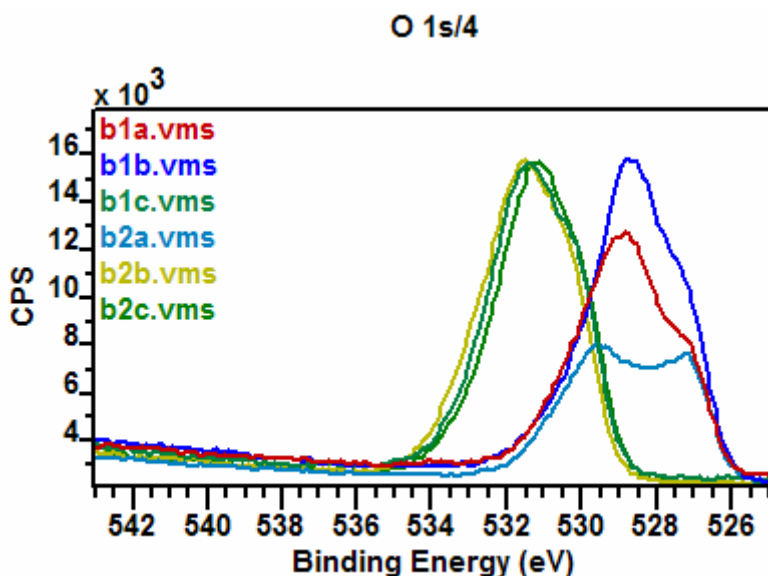


Figure 4

Energy Calibration and Multiple Files

Charge compensation issues often cause photoelectric lines to appear shifted on a sample-by-sample basis. Figure 4 illustrates the problem for the set of six samples displayed in separate Experiment Frames in Figure 3. Each set of data is shifted in energy by potentially a different amount and as a result, simply creating a region for one spectrum

then propagating the region to the set of spectra in Figure 4 would typically fail to define the background in an ideal fashion. It is therefore advisable to energy calibrate the spectra from each file before performing the propagation of regions and/or components. As a result, two new options (Figure 5) on the Calibration property page of the Spectrum Processing dialog window offers a means of calibrating sets of spectra in different Experiment Frames as a single operation.

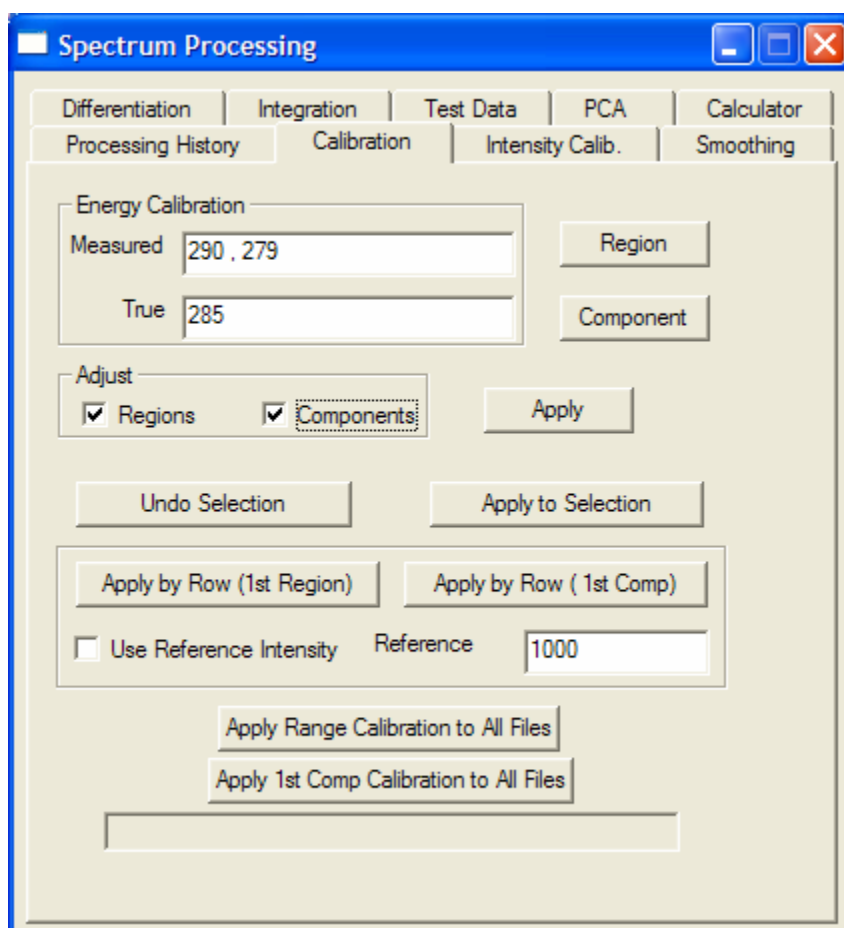


Figure 5

Energy calibration is often performed to ensure the saturated carbon peak appears at binding energy 285.0 eV. The implication is therefore that a peak-fit is required for the carbon data in order to establish the appropriate position for the saturated carbon transition. The problem with data such as that displayed in Figure 4 is that an energy calibration must exist before a peak model can be propagated to the data from the different files. Without an initial calibration, the location of the background region and synthetic peaks may be in error by several eV and therefore automatic peak fitting fails to produce appropriate results as exemplified in Figure 6. For this reason, the energy calibration is sometimes performed in two stages. First a calibration based on the maximum intensity in a range is performed. Although not perfect, often the range calibration is more than good enough for the application, but in the event that greater precision is required, a second calibration based on the position of a synthetic component

is available. The range calibration allows peak models to be copied and fitted to the data in the different files and once these peaks are fitted to the data, the second form of calibration is applied, where the position for one of the synthetic components define the fine adjustment needed to establish the precise energy calibration.

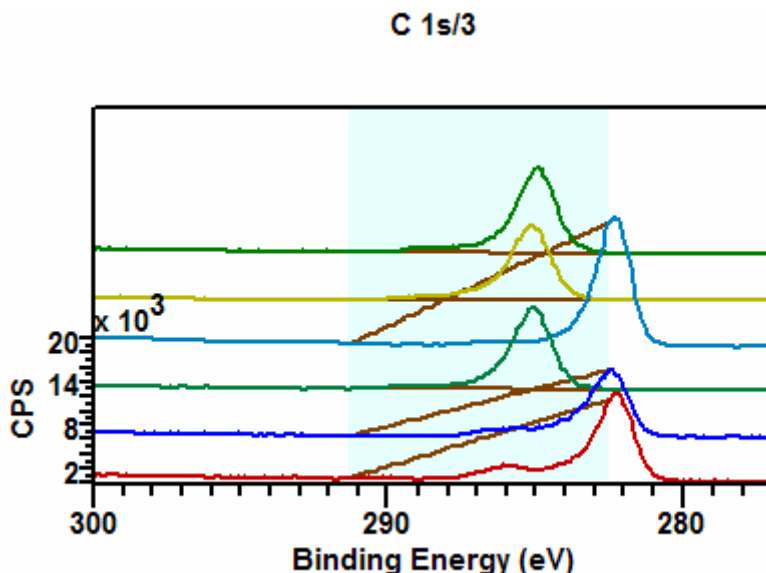


Figure 6

Both calibration buttons for energy-shifting data in multiple files require the use of the selection mechanism. The process of energy calibrating a file centres on identifying a spectrum from which the measured energy position of a peak is computed. Each Experiment Frame must define a single spectrum, from which the apparent location of a peak is determined and together with the known value, entered in the True field on the Calibration property page, are sufficient to calculate the shift required to correctly position the photoelectric lines in binding energy. The spectrum used in this calculation in each Experiment Frame is the *active VAMAS block* for that Experiment Frame. Hence the existence of the *Select and Display Matching Blocks* menu option described above. The display in each Experiment Frame can be set to a given species/transition at a click of a button. For example, the C 1s blocks can be used to calibrate the data in Figure 3, therefore in order to perform the calibration, each Experiment Frame must display the C 1s data in the active tile. Simply selecting a C 1s data block in any Experiment Frame then pressing the Ctrl+F5 key-sequence causes all the C 1s data blocks to highlight and at the same time display in the scrolled-list of tiles; thus, making the C 1s blocks the *active VAMAS block* in each Experiment Frame. By using the *active VAMAS block* to specify the spectrum from which the energy shift is computed, the browser selection is available for indicating those data block to which the calibration must also apply.

There is an underlying assumption about the nature of the data in the files under consideration. It is assumed that the spectrum used to perform the calibration is in the first row of the browser. The data in Figure 3 includes two C 1s regions, one acquired at the beginning of each measurement and one acquired after all the other spectra are recorded. As the data file stands, Ctrl+F5 would always make the first of these two C 1s spectra the *active VAMAS block*. If for any reason it is desired to calibrate using the second C 1s spectrum, it would be necessary to distinguish between the two C 1s spectra by changing the species/transition fields in the VAMAS block information so that these two spectra differ such that both appear on the first row in the browser.

In summary, the sequence of steps leading to an accurately calibrated set of files is as follows:

1. Perform an initial energy calibration based on locating the maximum intensity in a range of energies.
2. Propagate the regions and components to the spectra.
3. Recalibration using the option to calibrate using the first component defined on the spectrum in the active tile (the active VAMAS block).

The steps will now be described using the data in Figure 3.

Energy Calibration: An Example

The data in Figure 3 is a selection of files taken from a larger set all acquired from stainless steel samples at different stages of cleaning. The data are essentially the same in nature but not all experiments were performed in the same order nor were the high resolution spectra limited to the same number of acquisition intervals. Energy calibration for each file is achieved by positioning the largest C 1s component peak (Figure 7) at a binding energy of 285 eV and adjusting the remaining spectra using the energy shift computed from the C 1s data.

Processing of the survey spectrum in terms of quantification regions is dependent on calibrating the entire set of spectra using the C 1s peak-fit. The following steps are a guide to achieving this result.

1. Load the spectra into separate Experiment Frames. Select the Open button on the File menu and move the current directory displayed in the File Dialog window to the directory containing the stainless steel data. Press Ctrl+A to select all the files in the directory and press the Open button on the dialog window.
2. Create an initial calibration for the set of samples. Choose a representative file and open the Spectrum Processing dialog window, selecting the Calibration property page (Figure 5). Select and display the C 1s spectrum from the first row in the browser (Figure 7). Enter an appropriate range of energies in the *Measured* text-field (using “start-energy comma end-energy” e.g. 290 , 279) and the required position for the transition in the *True* text-field. It is important that the

- range of energies is valid for all C 1s in all of the open files. Ensure the Experiment Frame in which the chosen C 1s spectrum has input focus. If not left-click on the title bar of the Experiment Frame. Hold the Control Key down and press the F5 function key. All the C 1s spectra will be selected in the browser and the first C 1s spectrum will appear in the first tile as the active VAMAS block in each of the Experiment Frames open in CasaXPS. Confirmation of the action can be made by selecting the Cascade option on the Window menu and cycling through the open Experiment Frames by holding the Control Key down and repeatedly pressing the TAB key. Using the representative file, select all the blocks using the browser for which the energy calibration is to be performed and press the Ctrl+F4 key. In each Experiment Frame, all the blocks with identical species/transition fields as those selected in the representative file will become selected. In this example, the representative data set already contains regions and components, therefore the tick-boxes for adjusting the region limits and positions of components should be ticked. Finally, press the button labelled *Apply Range Calibration to All Files*. The processing history for each of the blocks affected by the calibration step will now display the values used to adjust the peak positions.
3. Propagate the processing information from the representative file. This action of propagating the processing from one file to others is covered below.
 4. Repeat the procedure described in step 2, but this time ensure the True text-field contains the correct energy for the peak in column A of the Components property page on the Quantification Dialog window and press the *Apply 1st Comp Calibration to All Files* button instead of the *Apply Range Calibration to All Files* button.

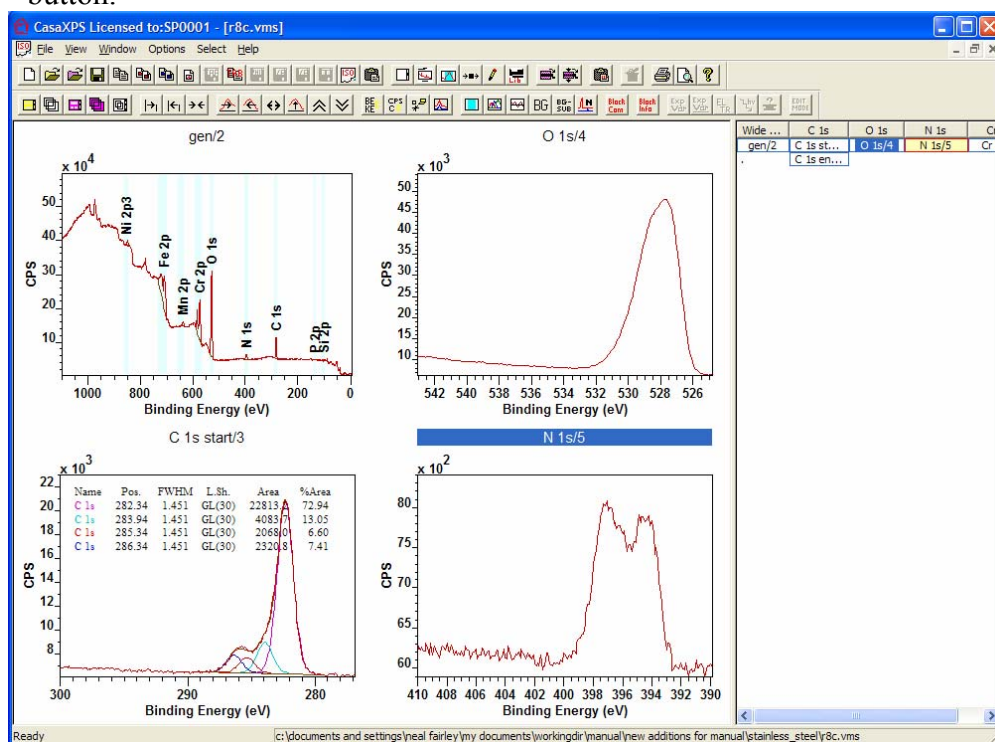


Figure 7

Propagating Processing to Similar Data Blocks

The Browser Actions dialog window (Figure 8) offers a means of transferring data reduction steps from the *active VAMAS block* to any block in any Experiment Frame. The concept used by the Browser Actions is that processing, regions, components etc. prepared on the *active VAMAS block* can be transferred to other blocks by simply selecting the blocks in the browser then right-clicking over the tile displaying the manipulated data. While still a means of propagating data reduction steps to other files, the Browser Actions dialog window is supplemented by a new option in version 2.3.12, which allows multiple blocks to be identified as the sources for the propagation, allowing at a stroke the entire processing performed on a file to be transferred to all the selected blocks in any Experiment Frame. The key feature is that the new form of propagation will match the species/transitions strings between the source blocks and the destination blocks. As a result the propagation procedure is less flexible about which blocks can receive the data reduction steps, but the transfer takes place with a minimum of fuss.

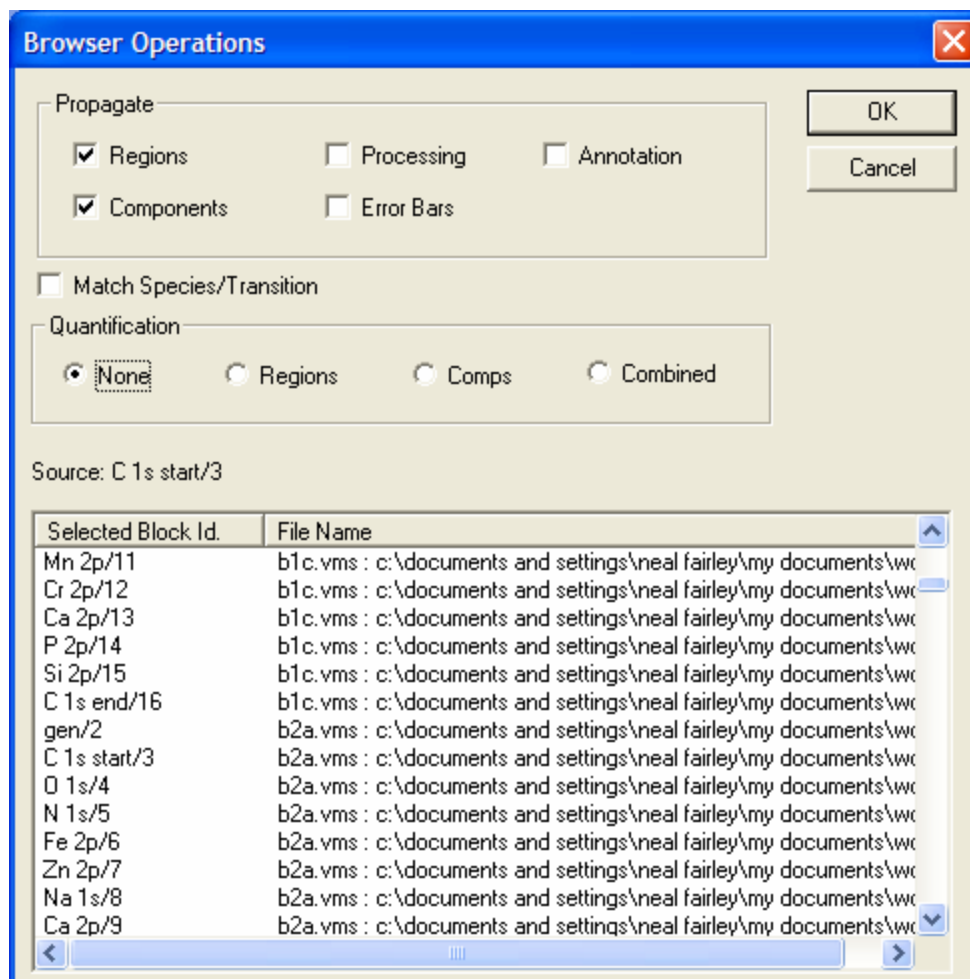



Figure 8

The source for the new propagation option  on the top toolbar is the set of blocks displayed in the *active tile*. Once the data for a set of blocks has been prepared, the blocks are overlaid in the *active tile*, while the target blocks are those blocks added to the selection prior to pressing the toolbar button. For example, if all the Experiment Frames are involved in the analysis, the Ctrl+F3 key action will select all the blocks in every Experiment Frame. When the toolbar button is pressed, a dialog window appears showing both the set of source blocks, identified by their Block Id strings, and the set of target blocks together with the file names for each of the blocks. When the OK button is pressed on the dialog window, the propagation operation is performed once for each species/transition type loaded into the *active tile*. The Progress dialog window will also appear and disappear for each block overlaid in the active tile.

Quantification reports generated from the set of selected blocks from multiple Experiment Frames are possible using the option on the Browser Operations dialog window. The section labelled Quantification offers a set of radio buttons (Figure 8) and if any option for Quantification other than the radio button labelled *None* is active, then a default quantification report is generated following the propagation action.

A further option for quantification exists via the Quantification property page on the Annotation dialog window (see page 121 in *The Casa Cookbook*). A quantification table added to the display for a spectrum requires the appropriate selection of the blocks in the browser; therefore the tile display and browser selection must be prepared before printing the results.

Formatting the Tiles and Printing

Tile format files saved using the File menu can be prepared and saved to the directory CasaXPS.PTF to act as a template for displaying the data from multiple samples. These templates are applied to the set of open Experiment Frames, again via the options on the File menu (Figure 1).