

# CasaXPS Manual 2.3.15

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## **CasaXPS Processing Software for XPS Spectra**

***Casa Software Ltd.***

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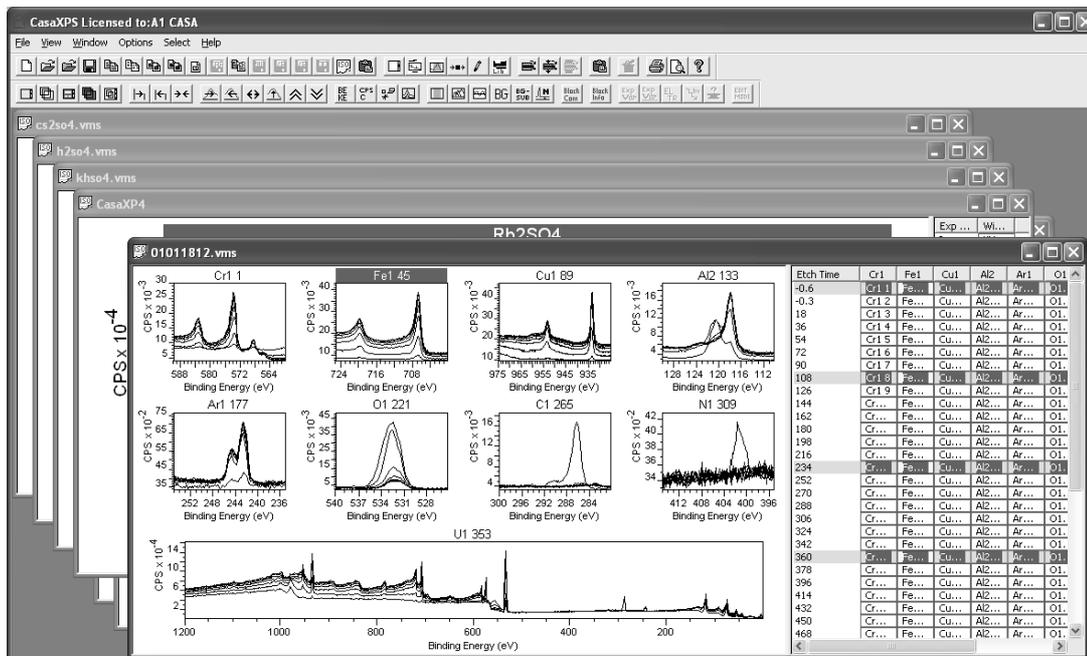
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## Basics of CasaXPS

The following is an introduction to the basics of CasaXPS. The intention is to provide an overview of the software in terms of displaying and quantifying XPS spectra.

### CasaXPS Main Window

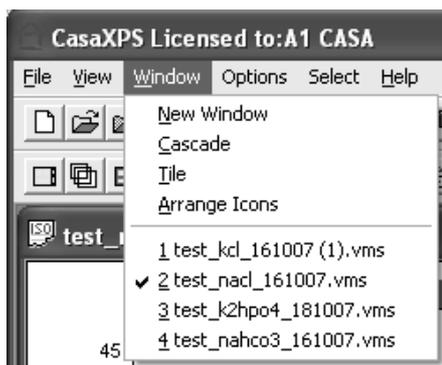


The Main Window of CasaXPS is a multiple document interface capable of managing large numbers of files all open at the same time.

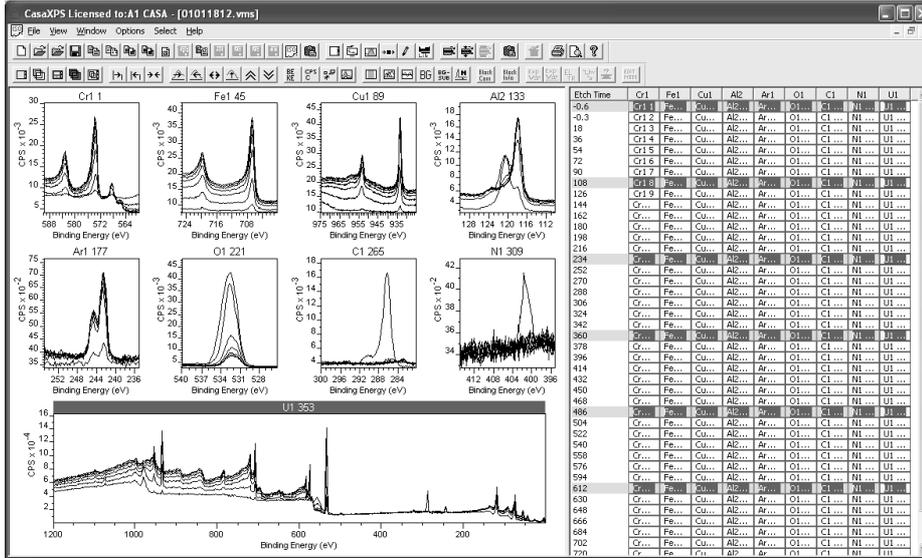
Key points:

- Each file opened in CasaXPS appears in an experiment frame.
- The top-most experiment frame has mouse focus.
- An experiment frame is divided into two panes; the left-hand pane displays the data in graphical form, while the right-hand pane displays the logical structure of the VAMAS file opened in CasaXPS.

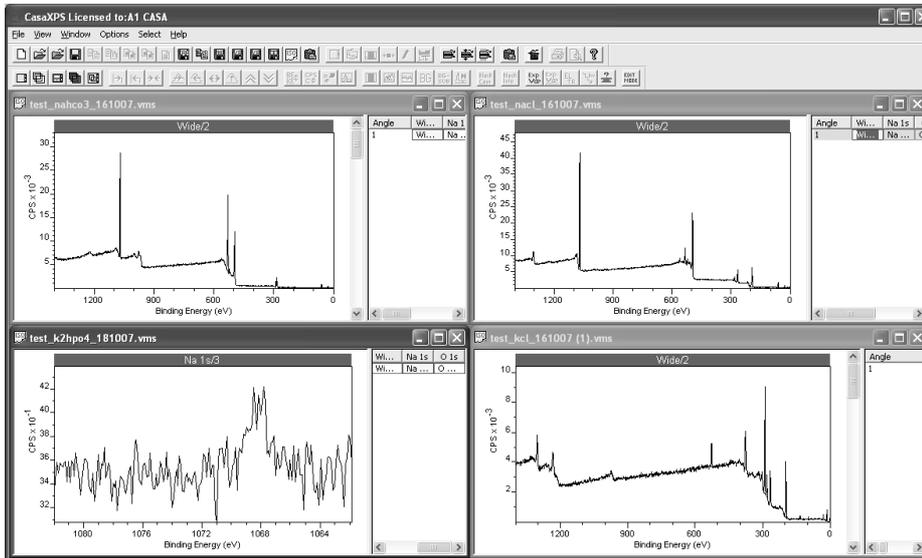
Management of experiment frames is performed using the Window menu on the CasaXPS main window.



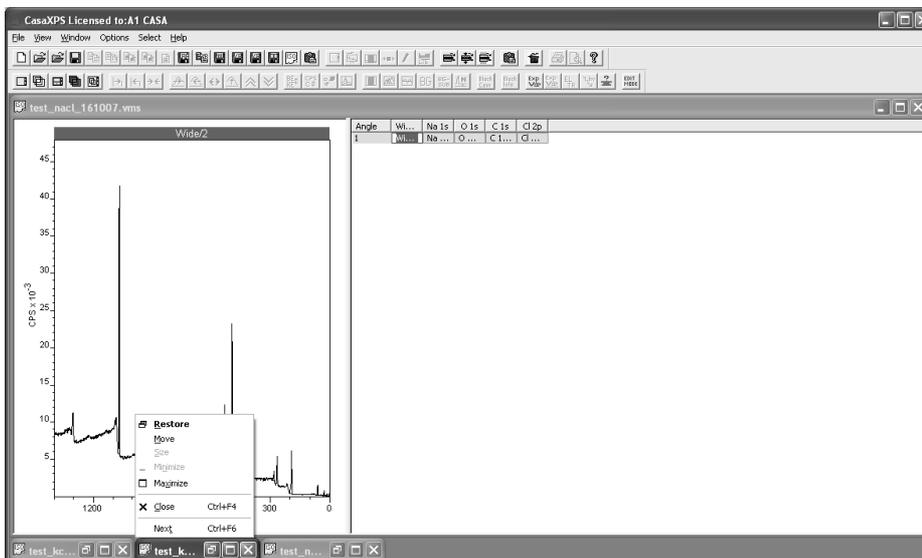
- Experiment frames may appear full sized.



- Experiment frames may be tiled.

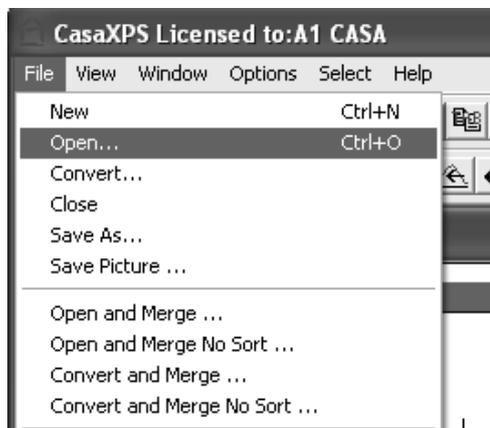


- Or as icons within the CasaXPS Main Window.

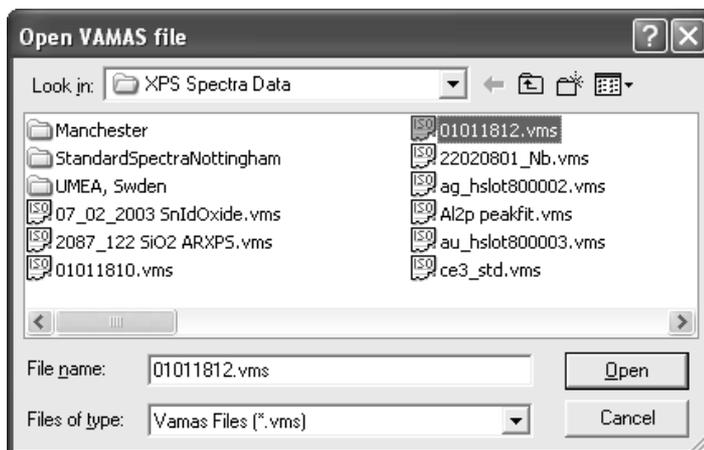


## Loading Data into CasaXPS

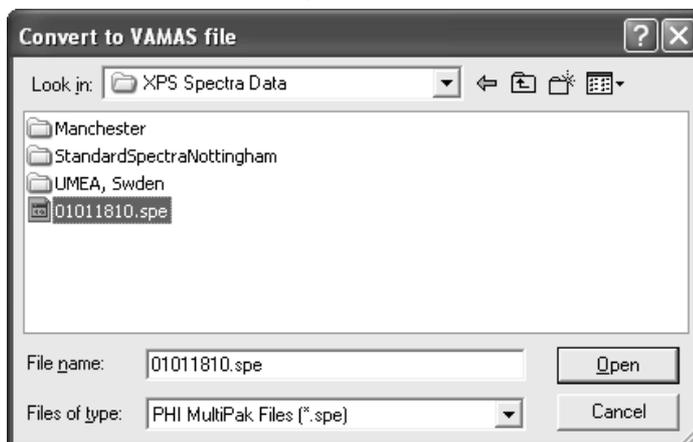
CasaXPS converts other data formats to ASCII ISO 14976 (VAMAS) format. Data in VAMAS format are opened as experiment frames by selecting the VAMAS file via the Open option on the File menu.



A file dialog window allows data to be selected from disk.



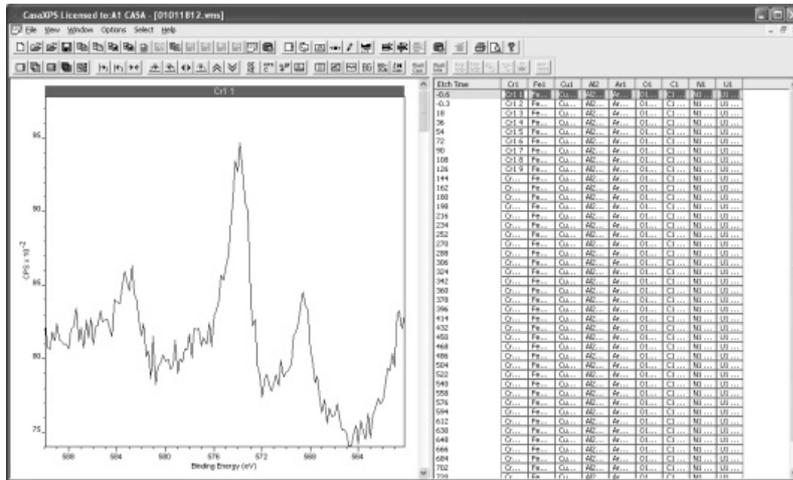
Data not in VAMAS format is converted through CasaXPS via the Convert option on the File menu. A Convert to VAMAS file dialog window offers a means of selecting a file type for conversion. The file extension is typically used to determine the file format, for example, the file extension spe is allocated to data saved in PHI Multipak format.



A new VAMAS file is created for each file selected via the dialog window and is written into the same directory as the original file.

## Displaying Data in CasaXPS

One or more files may be selected via the file dialog. On pressing the Open button, a new experiment frame appears in the CasaXPS main window.

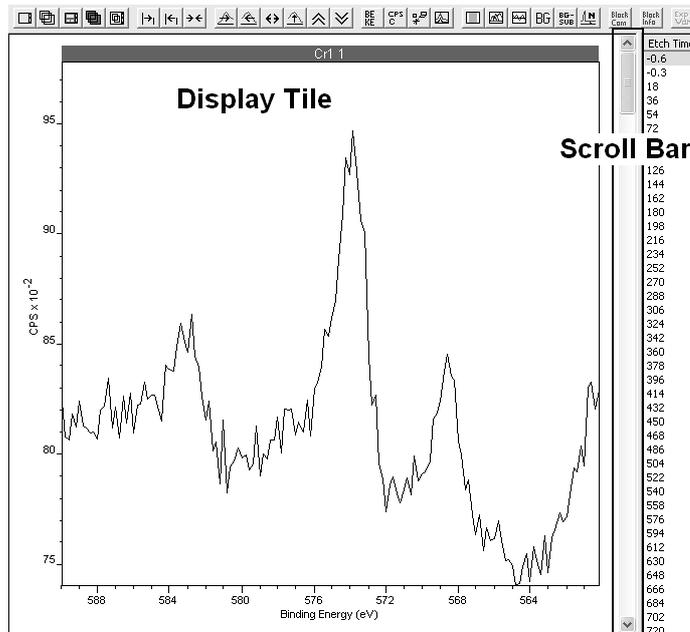


Initially, the first row of data blocks are selected in the right-hand pane

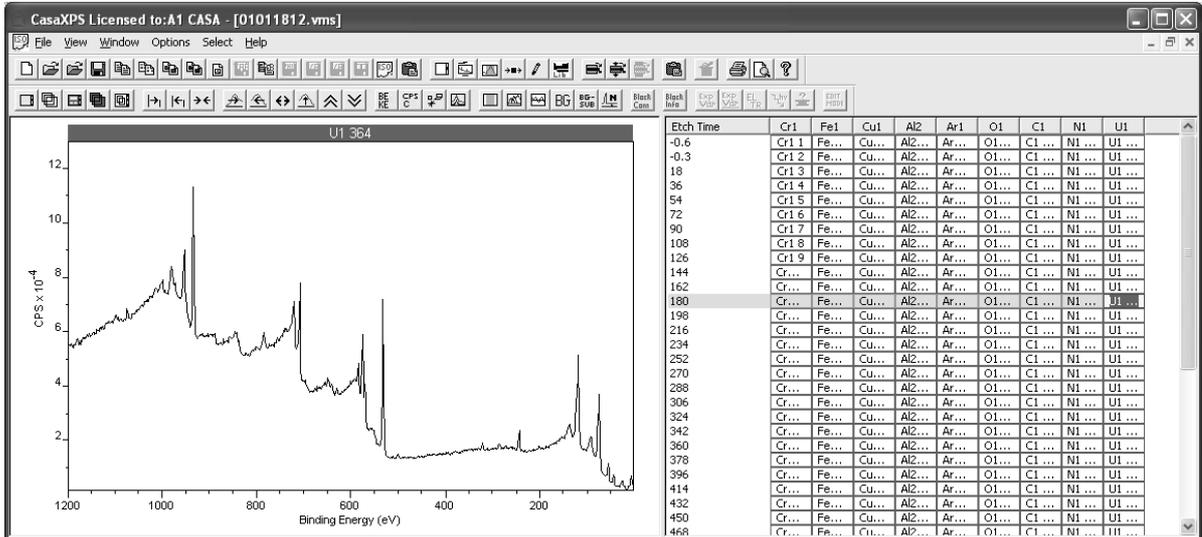
Etch Time	Cr1	Fe1	Cu1	Al2	Ar1	O1	C1	N1	U1
-0.6	Cr1 1	Fe...	Cu...	Al2...	Ar...	O1...	C1 ...	N1 ...	U1 ...
-0.3	Cr1 2	Fe...	Cu...	Al2...	Ar...	O1...	C1 ...	N1 ...	U1 ...
18	Cr1 3	Fe...	Cu...	Al2...	Ar...	O1...	C1 ...	N1 ...	U1 ...
36	Cr1 4								
54	Cr1 5								
72	Cr1 6	Fe...	Cu...	Al2...	Ar...	O1...	C1 ...	N1 ...	U1 ...

**Selection of data blocks**

and displayed via a scrolled list of display tiles in the left-hand pane.



The keyboard arrow keys can be used to change the selection in the right-hand pane. Each press of an arrow key moves the selection in the right-hand pane with respect to the data block displayed in the active tile in the left-hand pane. Pressing an arrow key causes the newly selected data block to be displayed in the left-hand pane.



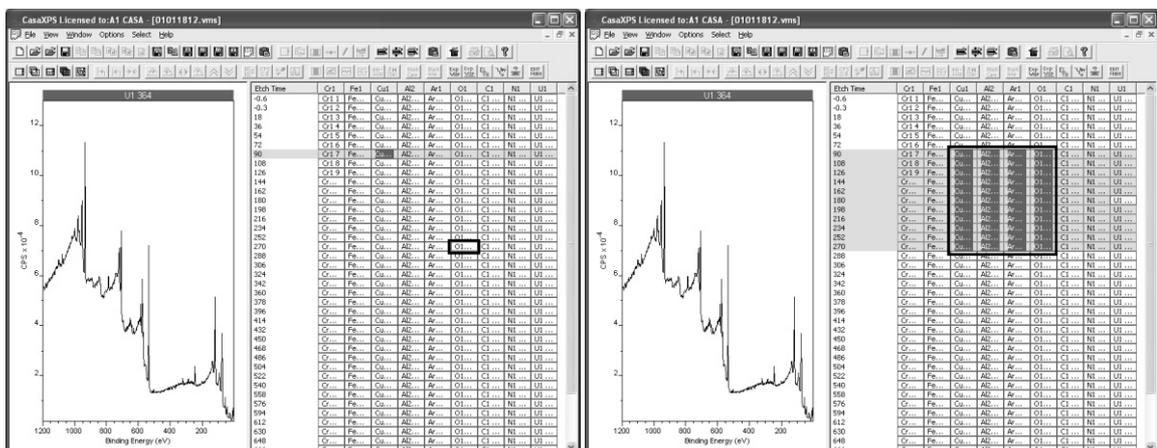
### Selection of Data using the Mouse

Data blocks in the right-hand pane are selected using the mouse and a combination of the Shift key and the Control key.

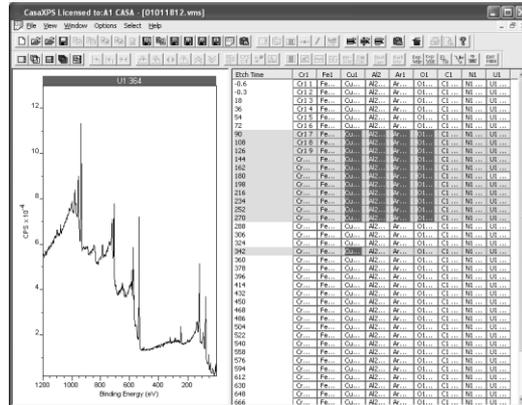


Left click the mouse over a data block in the right-hand pane to make a single selection.

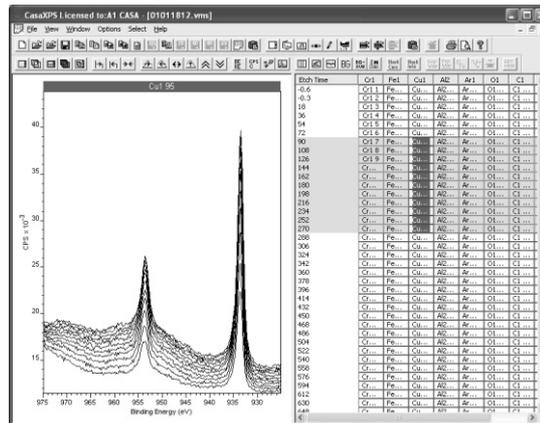
Extend the selection to a contiguous group of data blocks by holding the Shift key down before selecting a second data block using the left mouse button.



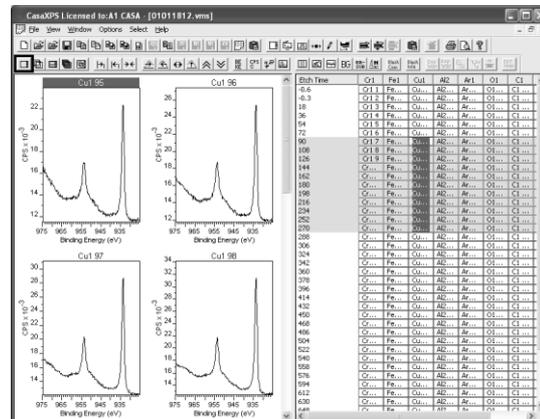
Add to the current selection by holding the Control key down before left-clicking over a data block.



Overlay the current selection of data blocks in the active tile by pressing the overlay toolbar button.

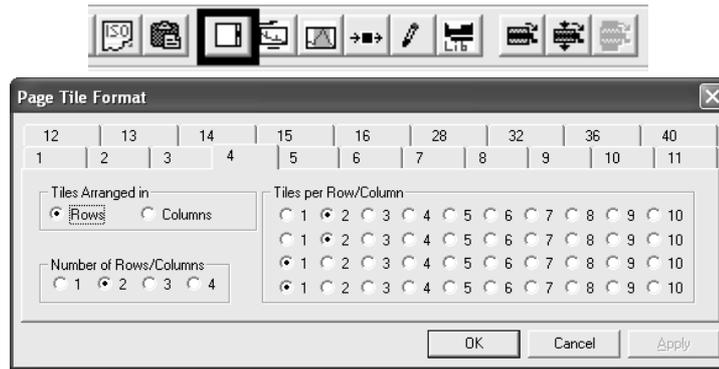


Display the current selection one-per-tile using the display toolbar button.

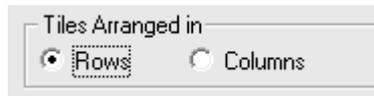


## Tile Format

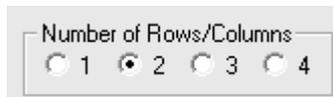
Set the number of tiles-per page using the Page Tile Format dialog window.



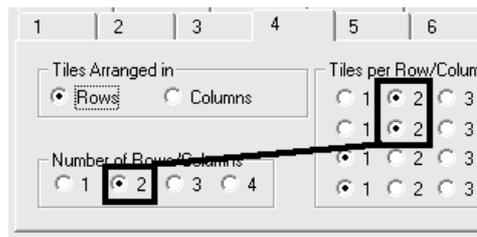
Page tile formats are organized using predefined property pages for a number of tiles per page. Adjustments to the tile format involve choosing the tile alignment type.



Specifying the number of rows (or columns):

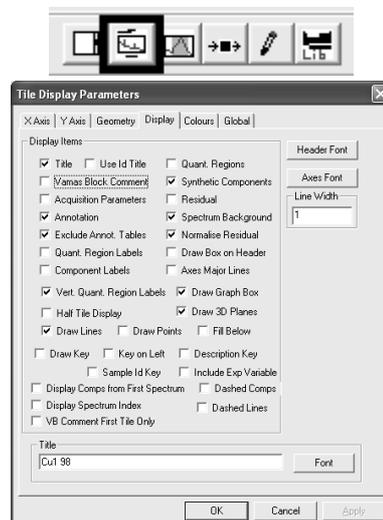


Specifying the number of tiles per row for each row enabled:

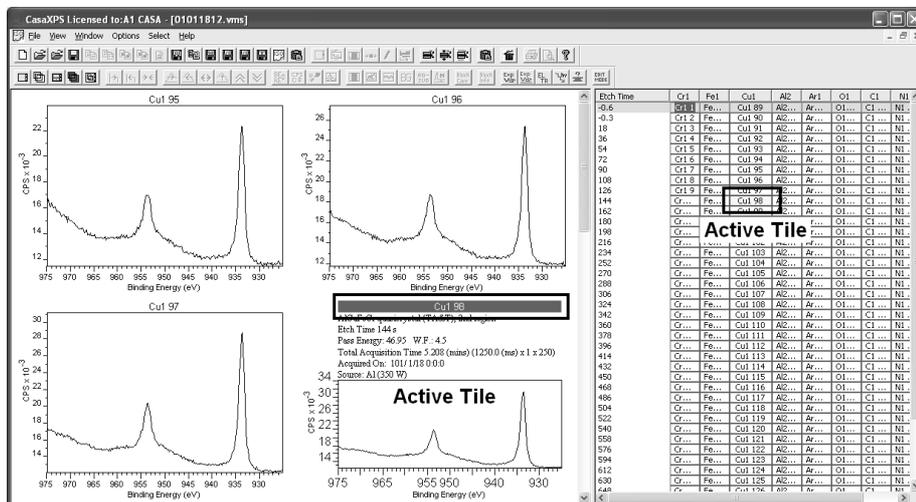


## Tile Display

Each tile used to display data in the left-hand pane maintains a set of display settings. These display settings are adjusted using the Tile Display Parameter dialog window. Various fonts and colours used to draw spectra are adjusted via the property pages on the dialog window.



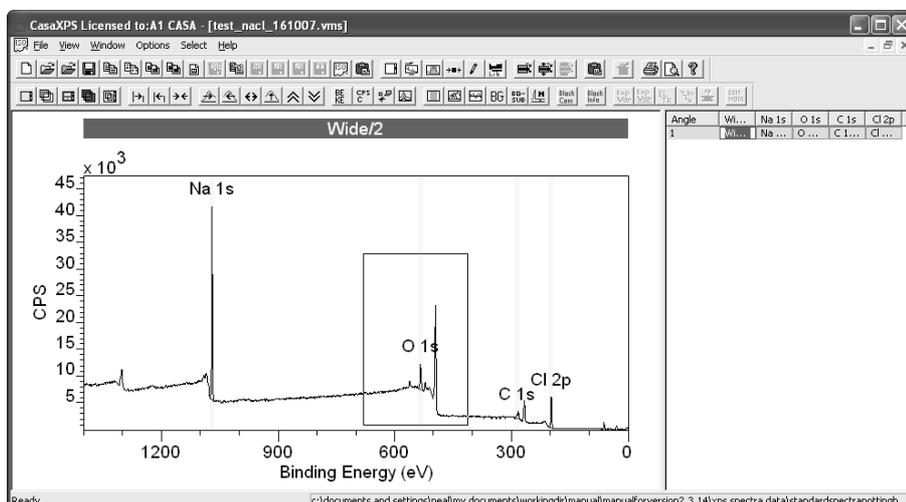
The tile in the left-hand pane with the title highlighted is the active tile. On pressing the toolbar button for the Tile Display Parameters dialog window, the settings entered onto the property pages correspond to the display settings for the active tile. When the OK or Apply button is pressed on the dialog window, the display settings for the active tile are updated.



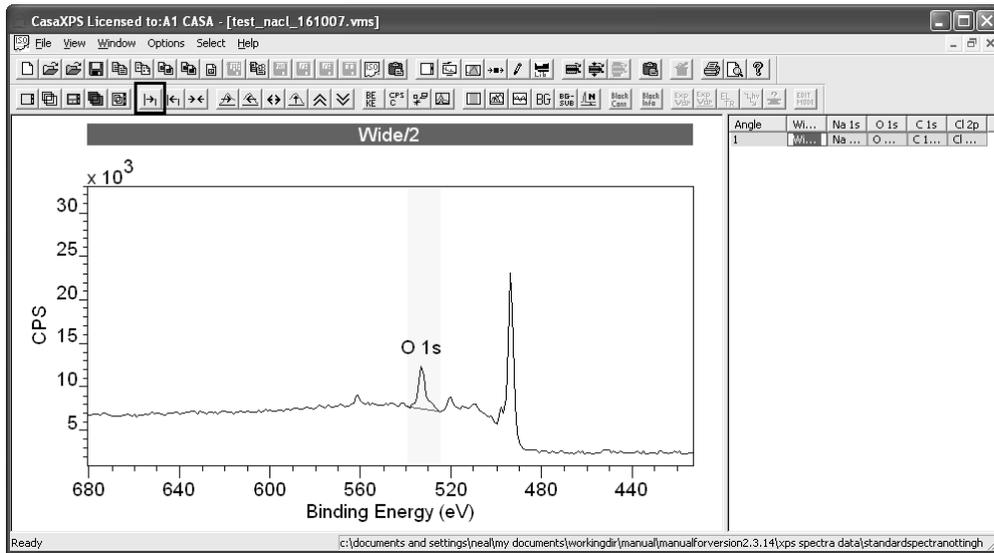
Data displayed in the active tile is indicated in the right-hand pane by a red border around the corresponding data block. The background for the data block in the active tile is also filled with a light yellow colour.

### Zooming into Data

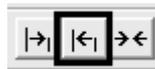
Changing the energy and intensity ranges for a spectrum is achieved using the mouse to draw a zoom box over the data currently displayed in the active tile. A zoom box is drawn over the data by holding down the left-hand mouse button whilst moving the cursor over the spectrum in the active tile. On releasing the mouse button, the drag box becomes a solid box over the data marking the energy limits and also the intensity limits over which it is desired to view the data.



To perform the zoom action, left-click inside the zoom box or press the zoom in toolbar button on the second toolbar.



Each time a zoom action is performed, the parameters from the zoom box is placed on a zoom list. Following a sequence of zoom actions, the set of zoom states on the zoom list can be reviewed by pressing the zoom out toolbar button.



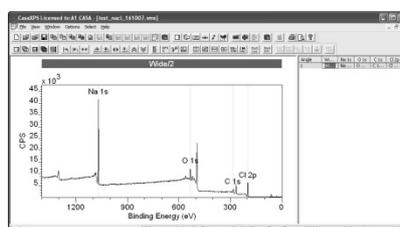
Each time the zoom out button is pressed, the previous energy and intensity ranges defined by zoom boxes are reinstated sequentially until the initial display ranges first used to view the data are recovered. Further pressing of the zoom out button will cause the zoom list to cycle from the initial zoom state.

The zoom list is re-initialised by pressing the reset toolbar button:



If the data are prepared with quantification regions, pressing the reset button loads the zoom list with the quantification region limits. To view a set of peaks on a survey spectrum for which regions are defined, simply press the reset button followed by the zoom out button.

Reset

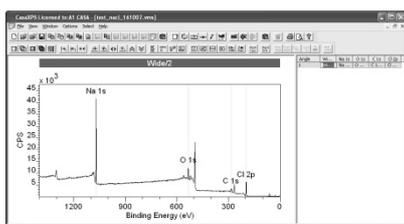
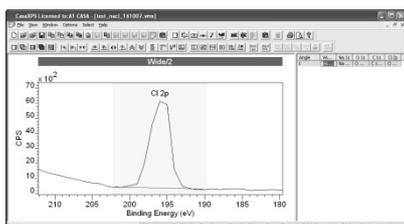
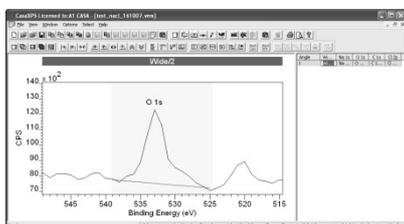
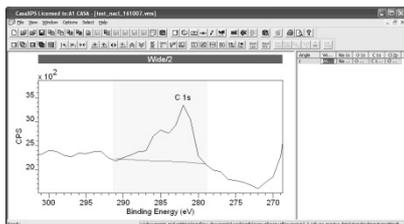
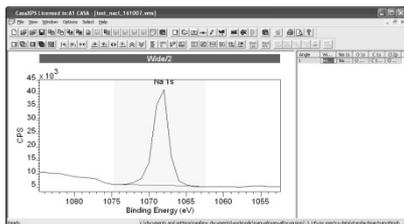


Zoom out



Loads regions

Step to region



Return to the initial display state.

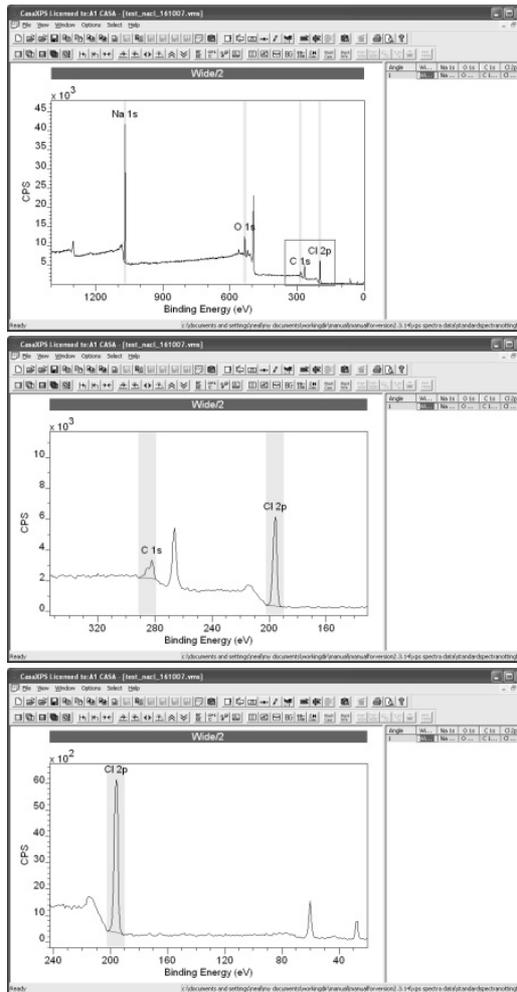
Zooming into a zone based on the mouse may require further adjustments to the display to achieve the desired perspective of the data. Further intensity scaling and positioning of the data with respect to the energy axis are achieved using the toolbar buttons:



Adjustments to the energy interval accompanied by rescaling of the intensity with respect to the data within the energy interval are performed using the toolbar buttons on the second toolbar:



Drag zoom box over data of interest.



Zoom in



Or

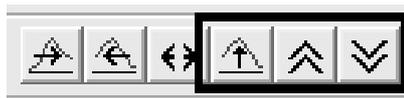
Left-click inside zoom box.

Step right



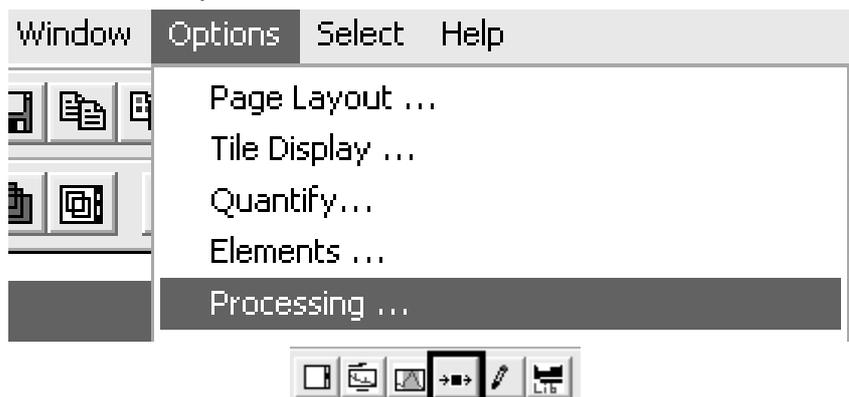
Energy interval shifted by half the display width.

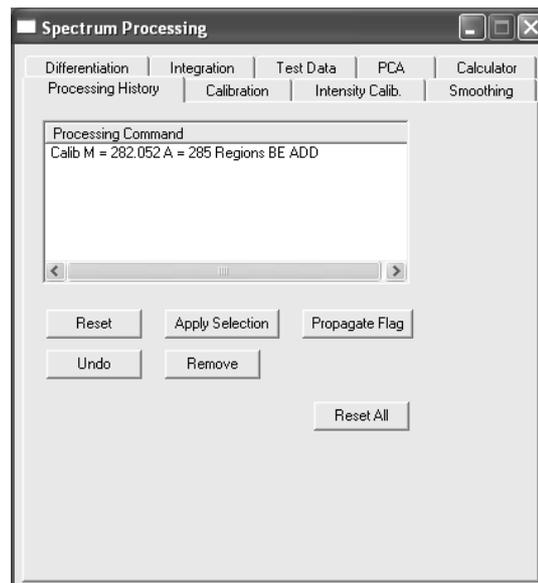
Rescaling using the data within the current energy interval is achieved using the toolbar buttons:



## Processing Spectra

Processing spectra is performed using options on the Spectrum Processing dialog window. The Spectrum processing dialog window is invoked from the Options menu or the top toolbar.

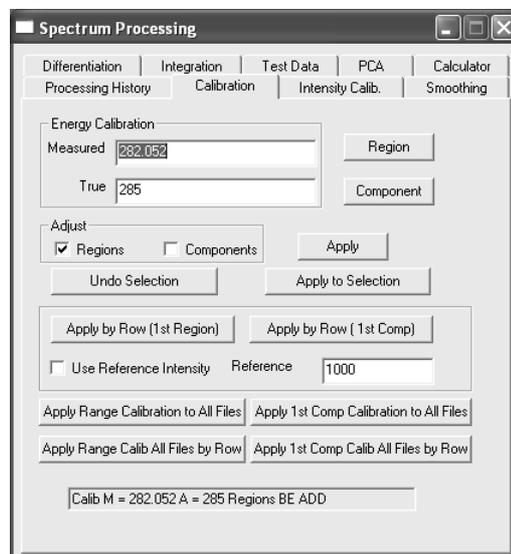




The Processing History property page lists the processing currently contributing to the state of the data displayed in the active tile. Other property pages offer processing options such as charge compensation and data smoothing.

## Basic Energy Calibration

Shifting the energy scale to allow for sample charging is performed on the Calibration property page:



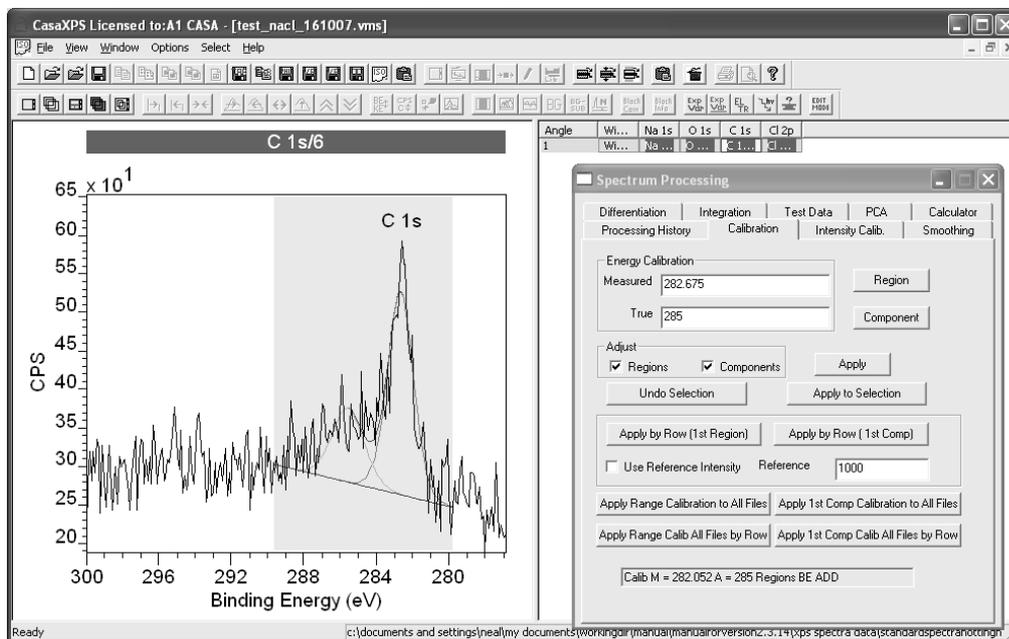
There are many powerful methods for charge compensating data located in many different files or sets of data within the same file, for example a depth profile. Only the basic charge compensation is described here.

Essentially, charge compensation is performed by specifying the location of a peak in the data as recorded. The measured location of the peak is associated with the desired true location of the peak, from which the necessary shift is

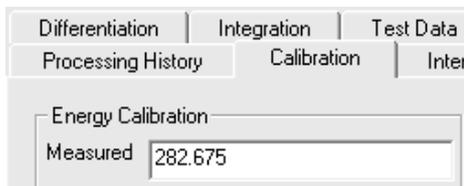
determined. The calculated shift may be applied to one or more spectra as appropriate.

### Charge Compensation for a Set of High Resolution Spectra

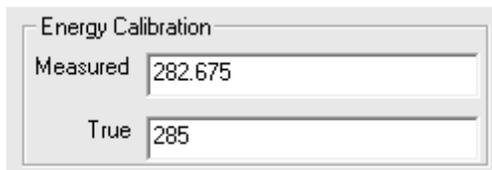
Display the spectrum for which a peak position is known:



Using the mouse, left-click the cursor on the peak as displayed in the active tile. The energy identified by the cursor position is updated in the Measured text-field on the Calibration property page.



Enter the known value for the peak position in the True text-field.



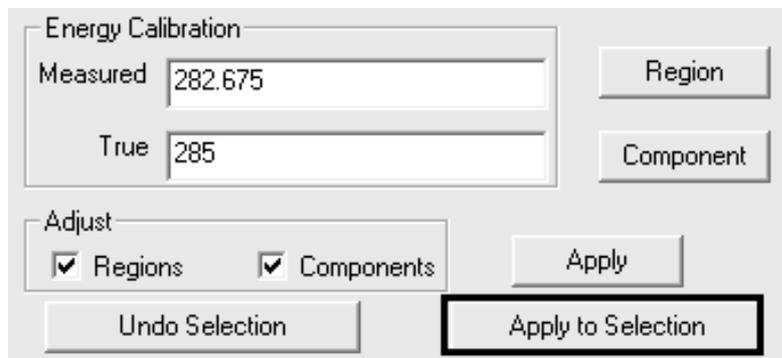
If regions and/or components are defined on any of the VAMAS blocks for which charge compensation will be performed, tick the Region and Component tick boxes.



Select those VAMAS blocks for which the charge compensation shift is appropriately specified by the data in the active tile.



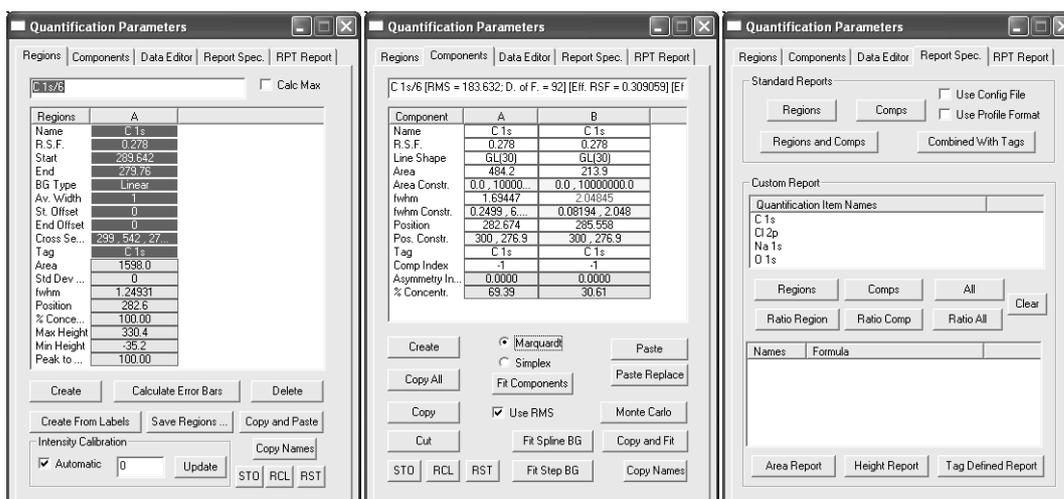
Press the Apply to Selection button.



Each VAMAS block selected in the right-hand pane of the experiment frame will be shifted using the energy difference computed from the Measured and True text-fields on the Calibration property page.

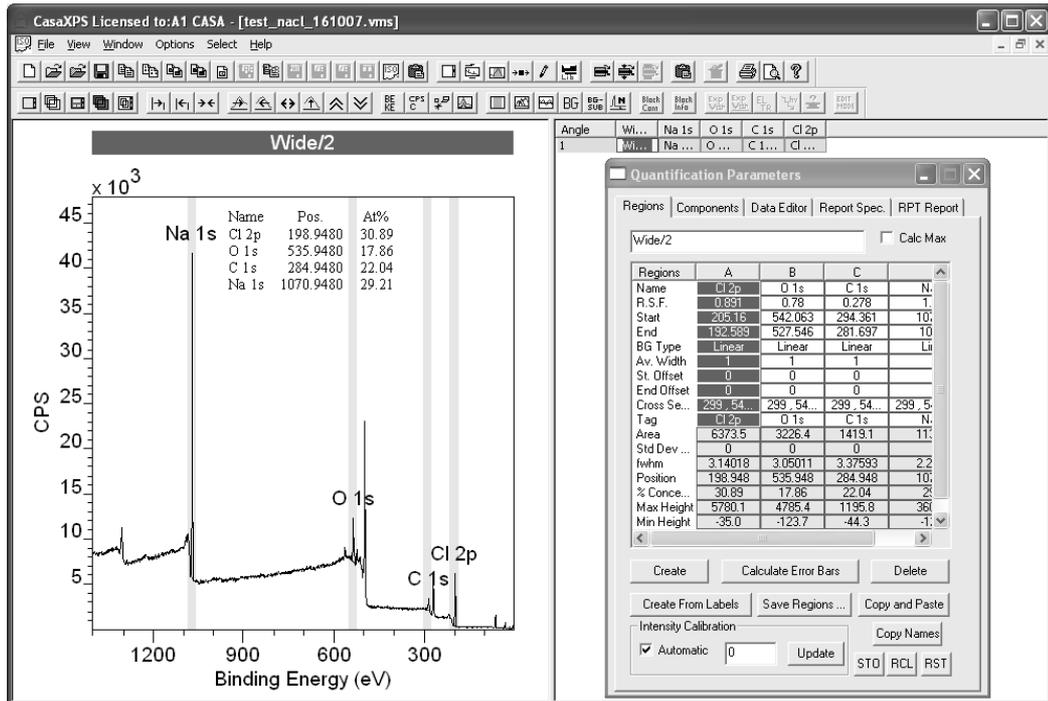
## Quantification of Spectra

XPS quantification in terms of peak intensities is performed by assigning quantification regions and/or peak models containing synthetic components. Quantification in CasaXPS is performed using the Quantification Parameters dialog window where the Regions, Components and Report Spec property pages are central to preparing and extracting quantification information from the data.



## Creating Backgrounds and Regions

Quantification regions are energy intervals over which a background to the peaks is defined.



A region is defined using the Regions property page where each region appears as a column of parameters in a scrolled list.

This is a close-up view of the 'Regions' property page from the CasaXPS software. It shows a table with columns for regions A, B, and C, and rows for various parameters. The parameters include Name, R.S.F., Start, End, BG Type, Av. Width, St. Offset, End Offset, Cross Se..., Tag, Area, Std Dev..., fwhm, Position, % Conce..., Max Height, and Min Height.

Regions	A	B	C	
Name	Cl 2p	O 1s	C 1s	N.
R.S.F.	0.891	0.78	0.278	1.
Start	205.16	542.063	294.361	10.
End	192.589	527.546	281.697	10
BG Type	Linear	Linear	Linear	Li
Av. Width	1	1	1	
St. Offset	0	0	0	
End Offset	0	0	0	
Cross Se...	299.54...	299.54...	299.54...	299.5
Tag	Cl 2p	O 1s	C 1s	N.
Area	6373.5	3226.4	1419.1	11.
Std Dev ...	0	0	0	
fwhm	3.14018	3.05011	3.37593	2.2
Position	198.948	535.948	284.948	10.
% Conce...	30.89	17.86	22.04	2.
Max Height	5780.1	4785.4	1195.8	36.
Min Height	-35.0	-123.7	-44.3	-1.

Each column in the scrolled list is divided into editable parameters and quantities computed for the region defined by the parameters.

This is another close-up view of the 'Regions' property page, similar to the previous one, but with a red rectangular box highlighting the first four rows of the table: Name, R.S.F., Start, and End.

Regions	A	B	C	
Name	Cl 2p	O 1s	C 1s	N.
R.S.F.	0.891	0.78	0.278	1.
Start	205.16	542.063	294.361	10.
End	192.589	527.546	281.697	10
BG Type	Linear	Linear	Linear	Li
Av. Width	1	1	1	
St. Offset	0	0	0	
End Offset	0	0	0	
Cross Se...	299.54...	299.54...	299.54...	299.5
Tag	Cl 2p	O 1s	C 1s	N.
Area	6373.5	3226.4	1419.1	11.
Std Dev ...	0	0	0	
fwhm	3.14018	3.05011	3.37593	2.2
Position	198.948	535.948	284.948	10.
% Conce...	30.89	17.86	22.04	2.
Max Height	5780.1	4785.4	1195.8	36.
Min Height	-35.0	-123.7	-44.3	-1.

To edit a region parameter, left-click the mouse over the value displayed on the table on the Regions property page.

Regions	A	B	C	
Name	Cl 2p	0 1s	C 1s	N.
R.S.F.	0.891	0.78	0.278	1.
Start	205.16	542.063	294.361	10.
End	192.589	527.546	281.697	10
BG Type	Linear	Linear	Linear	Lii

The value modified within the edit text field is only accepted when the enter key is pressed on the keyboard. Before pressing the enter-key, left-clicking the mouse away from the edit field causes the previous value to be reinstated.

Regions are defined in terms of a regions name:

Regions	A	B	C	
Name	Cl 2p	0 1s	C 1s	N.

Region names are user-defined names used to reference the information determined from the region. Quantification tables typically include the region name and more importantly quantities calculated from a region are specified within custom reports using the names assigned to a region.

A Relative Sensitivity Factor or RSF for a peak identified by a region is typically extracted from the element library, but may be adjusted using the RSF row.

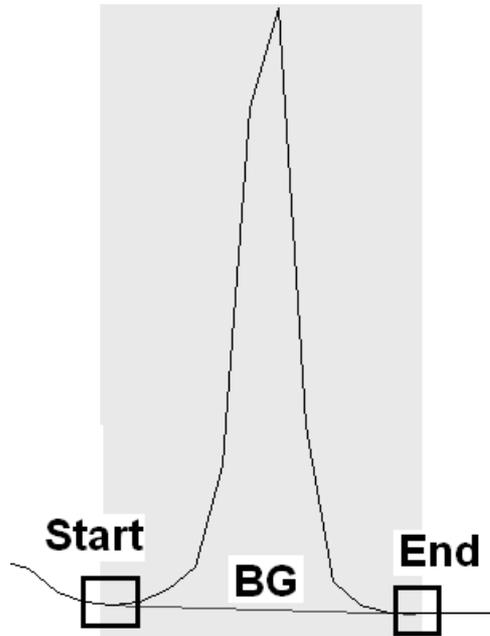
Regions	A	B	C	
Name	Cl 2p	0 1s	C 1s	N.
R.S.F.	0.891	0.78	0.278	1.
Start	205.16	542.063	294.361	10.
End	192.589	527.546	281.697	10

Atomic concentration tables are computed from the raw peak area divided by the RSF parameter. Other corrections to the raw peak area are also applied when determining the atomic concentration; however the instrumental independent correction used to relate the relative intensity of different photoelectric transitions for an element is encapsulated in the RSF.

The start and end parameters define the energy interval over which a peak should be measured.

R.S.F.	0.891	0.78	0.278	1.
Start	205.16	542.063	294.361	10.
End	192.589	527.546	281.697	10
BG Type	Linear	Linear	Linear	Lii

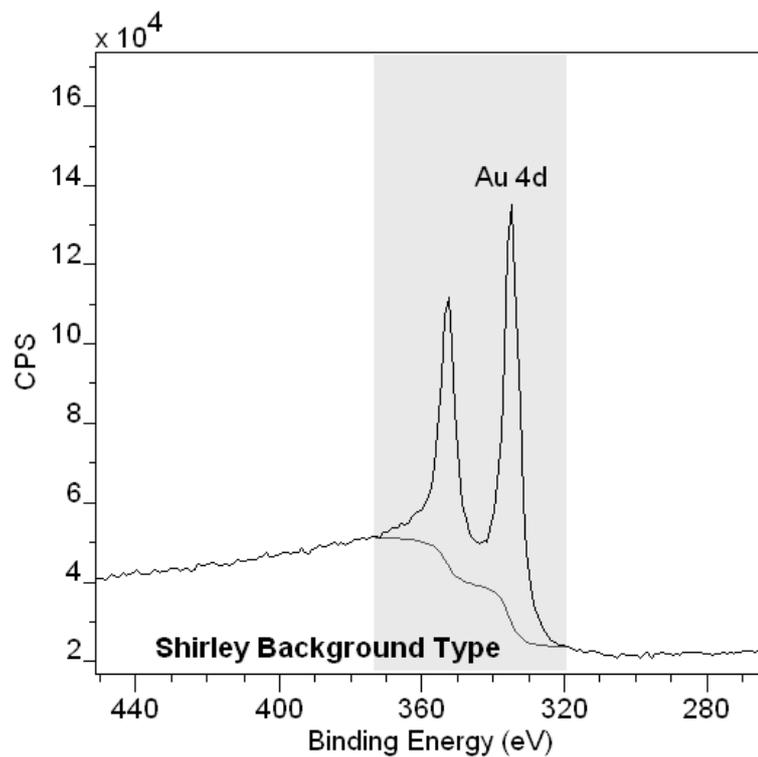
These energy limits define the point at which the background meets the recorded data.



A range of background (BG) types are offered, the most commonly used types are linear, Shirley and Tougaard.

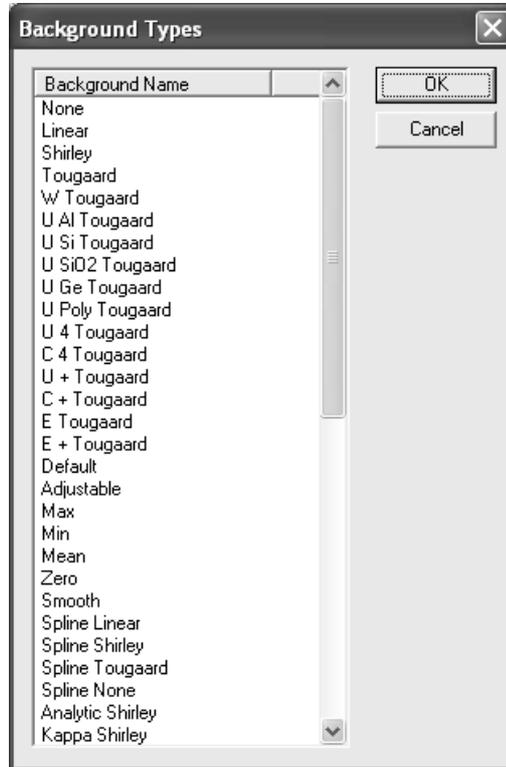
Start	203.10	372.000	237.001	101
End	192.589	527.546	281.697	10
BG Type	Linear	Linear	Linear	Li
Av. Width				
Cl. Off				

Linear backgrounds are typically used for insulating materials, while steps in metallic data are modelled using a Shirley background.





The full set of background types can be selected via a dialog window invoked by holding the Control key down and left-clicking over the current BG-type setting before the parameter is an edit field.

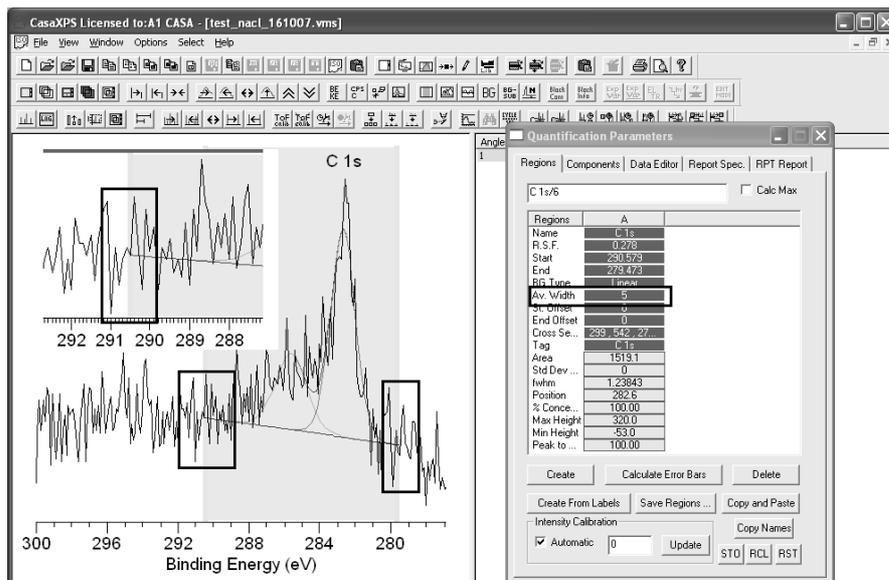


A new background is selected from the list on the dialog window and is loaded into the BG type text field when the OK button is pressed. To accept the selection of the background type, press the enter key on the keyboard.

The BG type field may be typed into the edit-field as an abbreviation. The most commonly used BG types are entered using “l” for linear, “s” for Shirley and “t” for Tougaard.

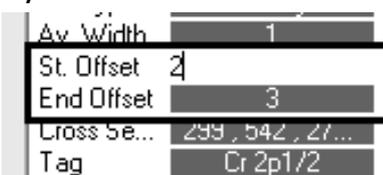


The background and spectrum meet at the two energy limits to the region. Due to noise in the data, the actual data channel corresponding to the region limits may not be most appropriate for defining the background intensity at these limits. The Av Width parameter specifies the number of data channels on either side of the data channel corresponding to the start energy or the end energy over which an average intensity is determined for the background at the limits.



When using the Av Width parameter there must be sufficient data channels to either side of both start and end limits before the background intensity is determined using an averaged intensity. The largest source for precision errors in XPS measurements is due to poorly defined background intensities. The use of an appropriate Av width for the level of noise in the data is important.

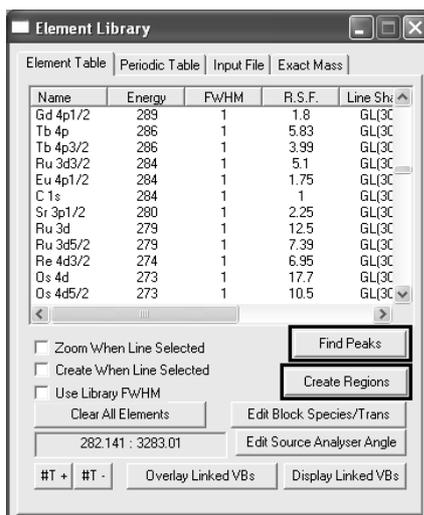
Two additional parameters influence the intensity of the background at the region limits. The start offset and end offset provide a means of scaling the background intensity at the region limits. The value specified for these parameters represents a percentage drop from the initial intensity computed for the background intensity.



The cross section and tag fields are for advanced uses and therefore are not discussed here.

### Quantification of Survey Spectrum using Regions

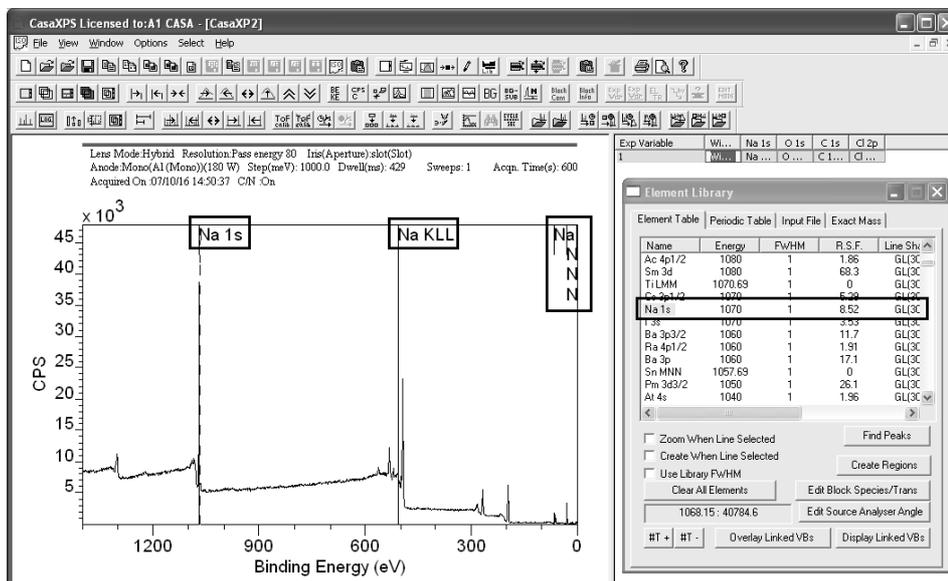
The best route to creating quantification regions is via the Element Library dialog window. The advantage of using the element library lies in the direct link between specifying the peaks and the RSF scaling information from the library. The simplest route to creating quantification regions is via the Find Peak/Create Regions buttons on the element table property page.



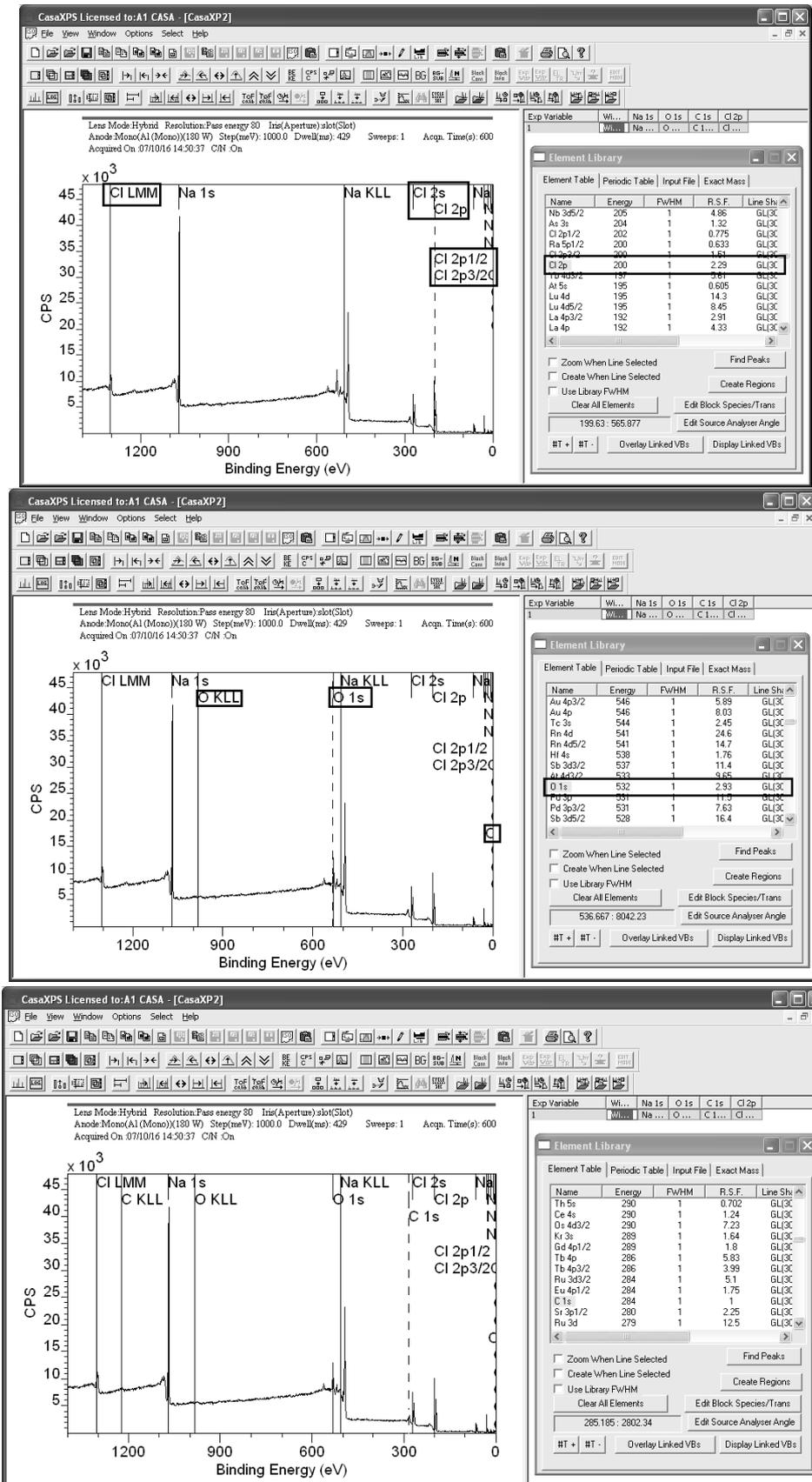
Regions are created via the Create Regions button for all those features on a spectrum for which:

1. An element marker from the element library is active.
2. A feature within the data can be identified.
3. The RSF is the largest or the transition is explicitly selected for use via the CasaXPS\_quant.lib configuration file.

Using the element library dialog window , the first step is therefore to enable element markers for all the appropriate species within the data. The manual route to enabling element markers involves the element table, the left-hand pane and the mouse. With the Element Table property page top-most on the Element Library dialog window, left-click the mouse with the cursor pointing at a peak in the data. The element table scrolls to display those transitions with energies around the energy indicated by the mouse. Select the most likely transition from the table on the Element Table using the name field.



Element markers are placed on the data for all transitions in the element table from the indicated element. The process is repeated for each peak in the data until all peaks are assigned to element markers.



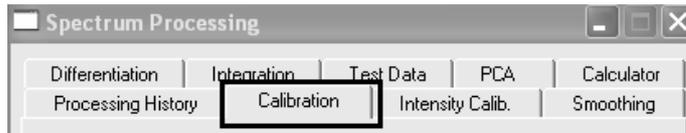
Regions are created based on the proximity of element markers to the peaks in the data. In the event the energy scale needs calibrating, the calibration step should be performed before attempting to create regions.

To calibrate the energy scale for an individual spectrum:

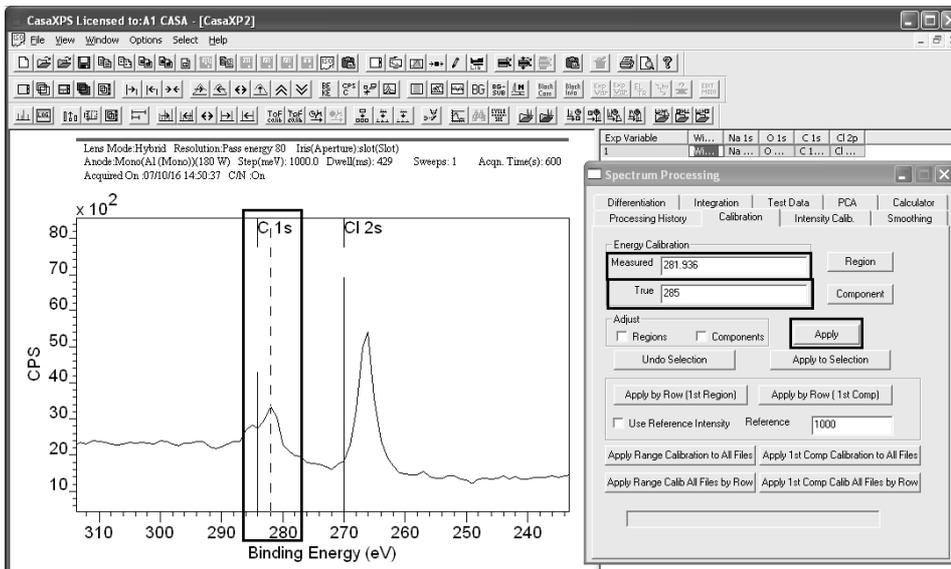
Select the Spectrum processing dialog window



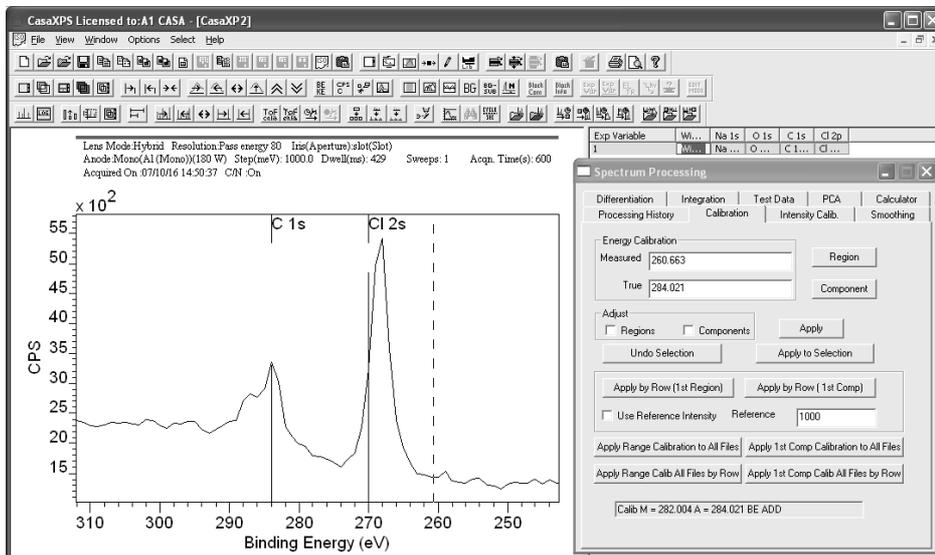
Select the Calibration property page



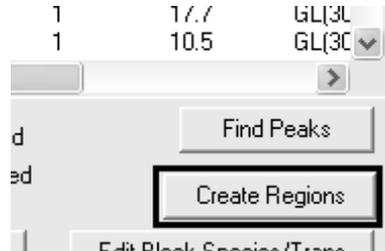
Left click the cursor pointing at the peak maximum of an appropriate peak in the left-hand pane and enter the True energy for the indicated peak.



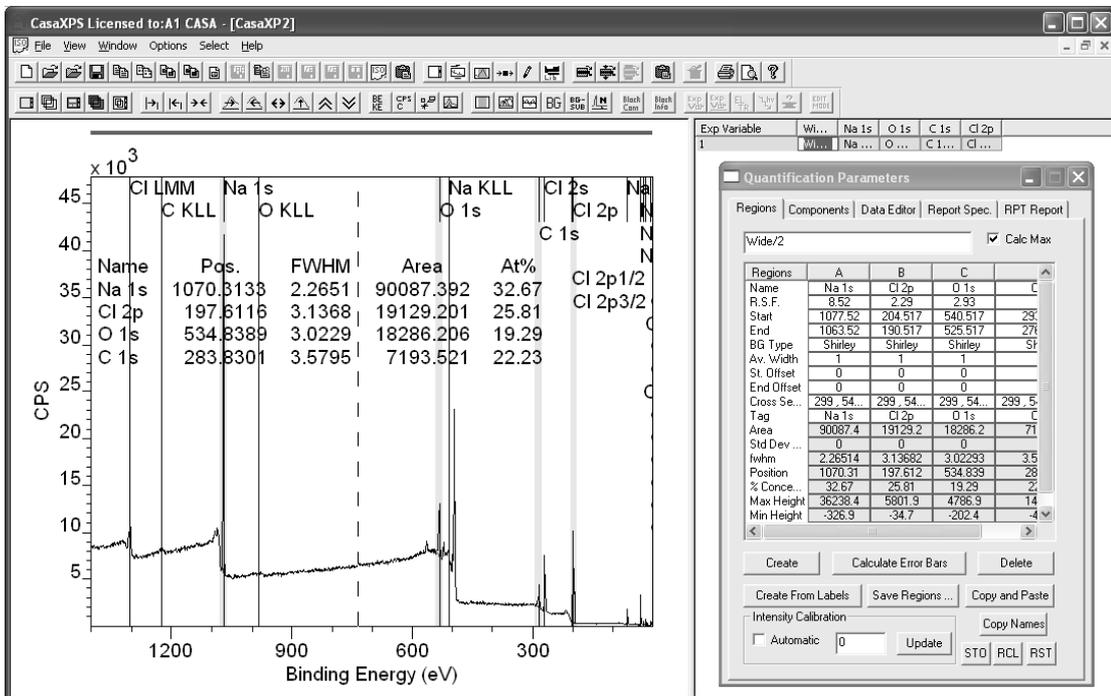
Press the Apply button to calibrate the spectrum in the active tile.



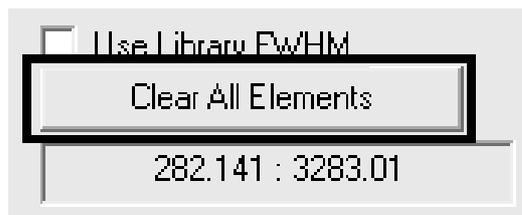
Provided the peaks are within a tolerance of the element markers and the peaks of interest are accounted for by the element markers, pressing the Create Regions button on the Element Table property page will create a set of regions on the spectrum.



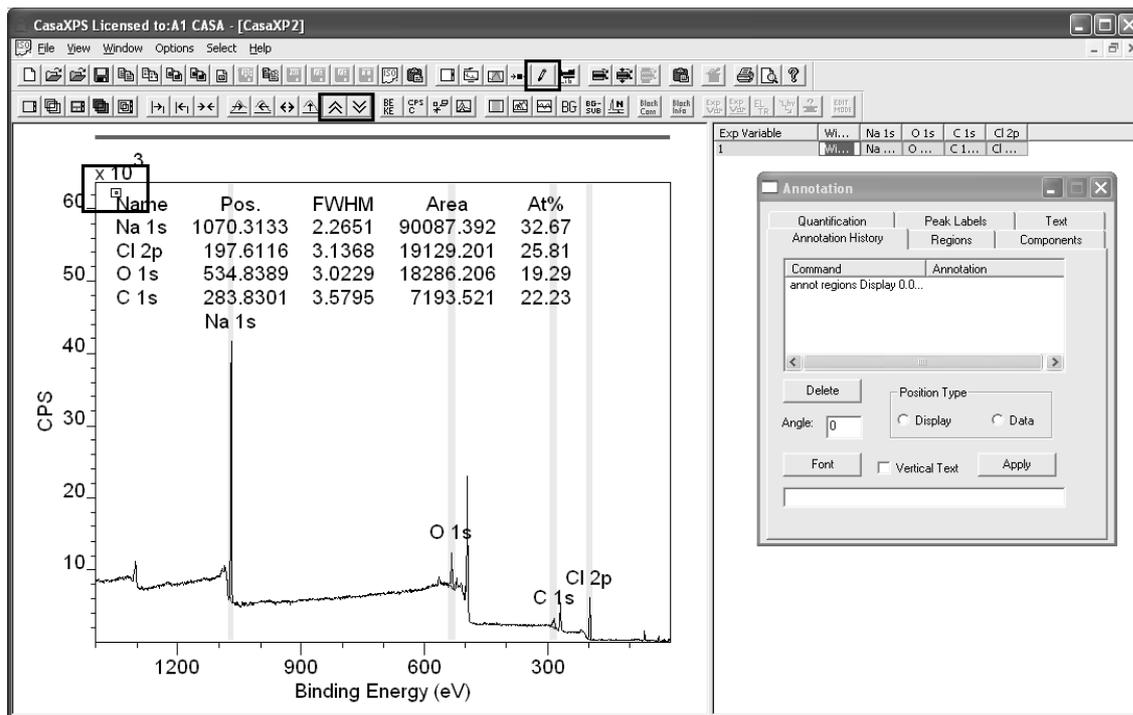
An annotation table offering a quantification table is added to the spectrum.



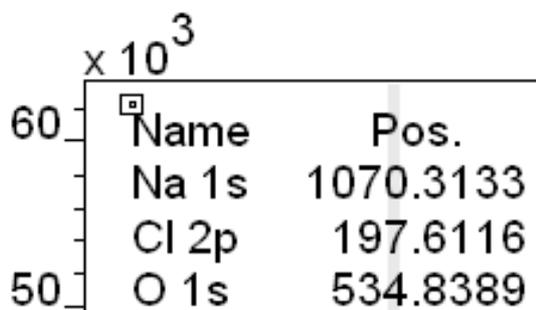
The element markers used to identify and link the peaks in the element library may be removed from the display by pressing the Clear All Elements button on the Element Table property page.



The quantification table may be repositioned on the data using the Annotation History property page.



With the Annotation History property page top-most on the Annotation dialog window, a small box appears above the top left-hand corner of the annotation table.



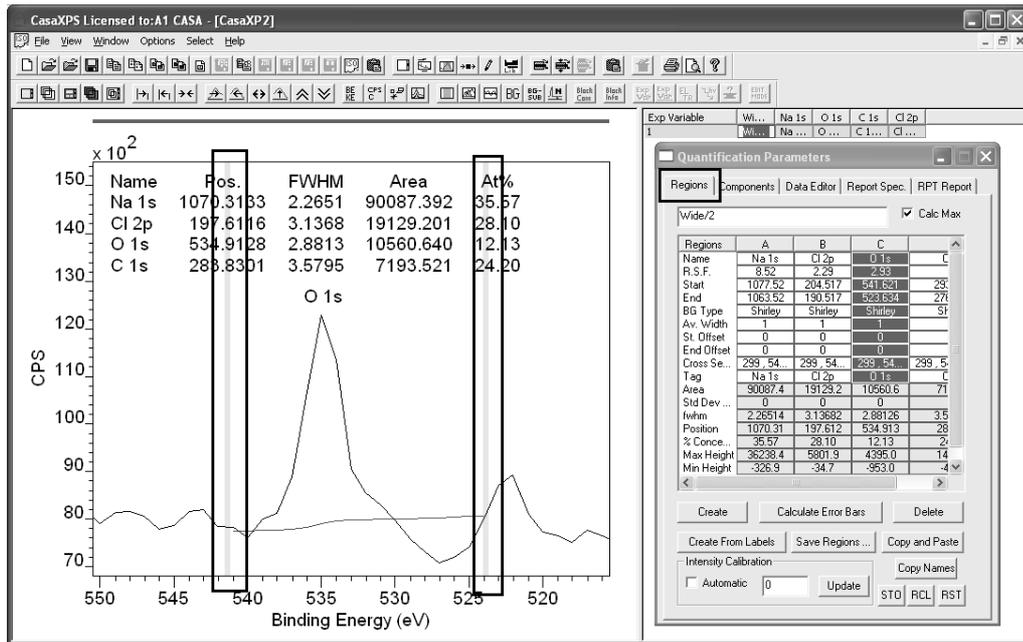
Pointing at the centre of the small box then dragging the mouse causes the annotation to move to a new position the moment the mouse button is released. Other adjustments to the intensity scale for display purposes can be made using toolbar buttons.



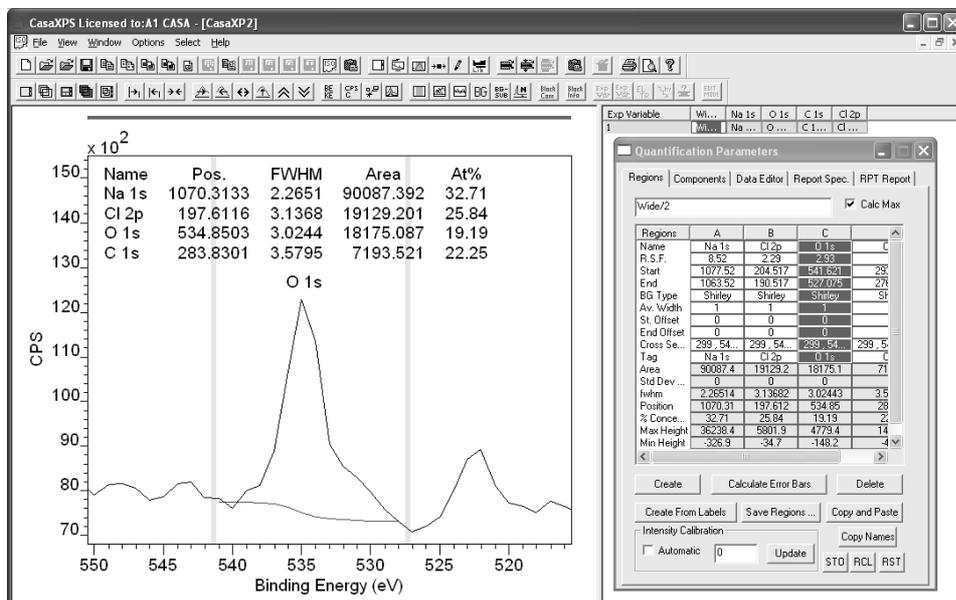
It is also advisable to check the quantification regions created automatically on the data. The zoom options described above provide a means of systematically stepping through the current list of quantification regions. If the Regions property page on the Quantification Parameters dialog window is top-most, stepping through the set of regions using the zoom options allows

the limits for the regions to be visually inspected and adjusted under mouse control.

Adjusting the limits for a region under mouse control involves using the mouse to drag a limit to a new position. Region limits can be adjusted under mouse control only when the Region property page is top-most on the Quantification Parameters dialog window. A grey vertical zone indicates that the mouse is active with respect to adjusting the region end points.



Following an adjustment to the limits, the annotation table and Regions property page are updated with the start and/or end energies defined by the cursor.

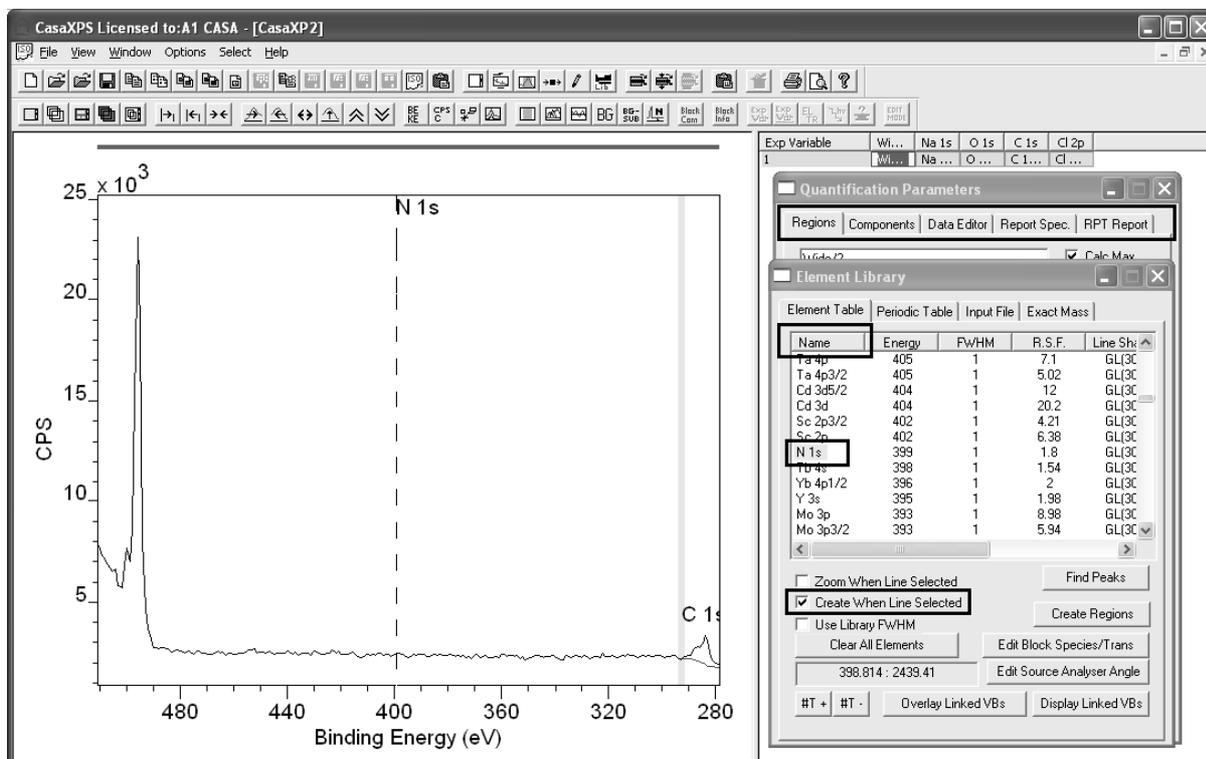


## Manual Creation of Regions

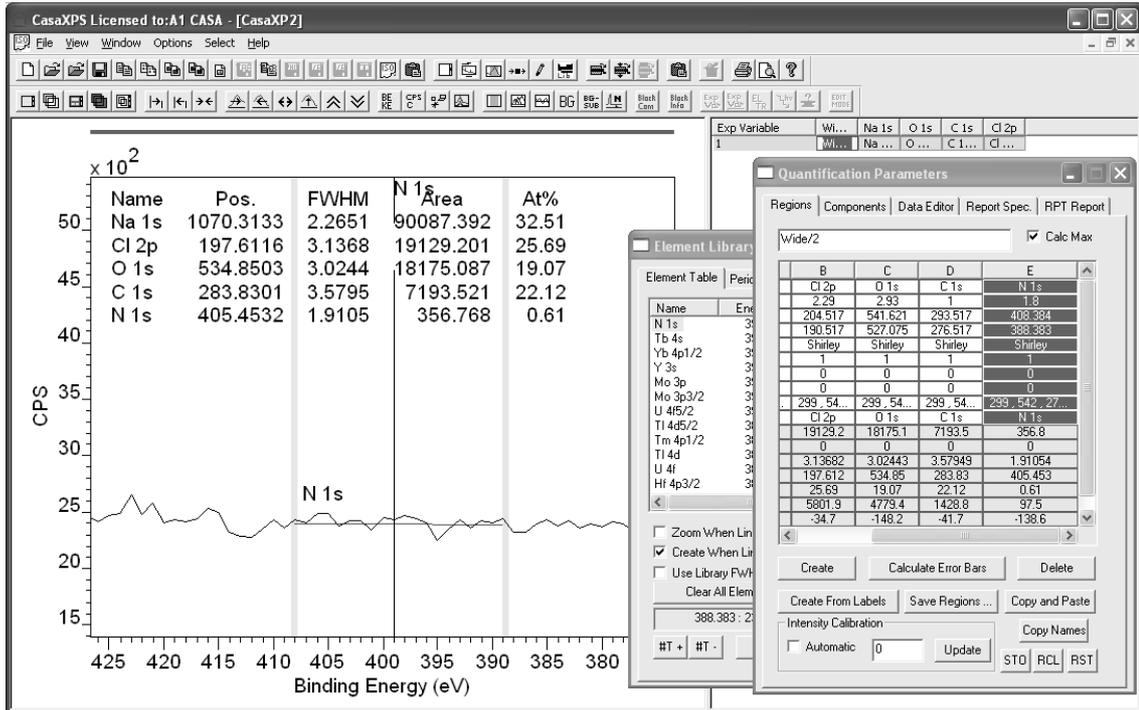
Regions created based on element markers require an identifiable peak to exist. If no such feature is located near the element markers no region is created for the element in question. Under these circumstances manual creation of regions is appropriate. While a Create button is available on the Regions property page of the Quantification Parameters dialog window, peaks from a survey spectrum have no means of assignment to transitions; therefore the Element Table property page includes a feature for manually creating regions specified via the name field in the element table.

To create regions one at a time:

1. Invoke the Quantification Parameters dialog window and ensure the Regions property page is top most
2. Tick the box on the Element Library dialog window on the Element Table property page labelled Create When Line Selected.
3. In the active tile, zoom the display to the energy interval about the transition for which a region is required.
4. Left click the name field on the Element Table appropriate for the transition.



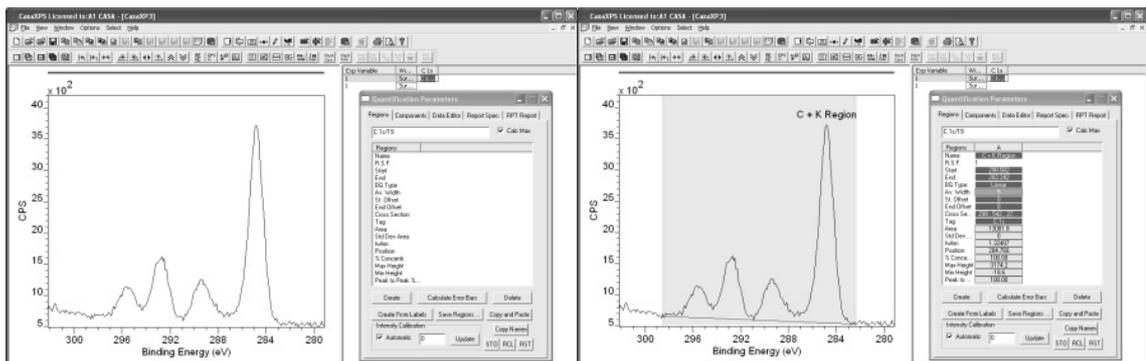
Adjust the start and end limits using the mouse or otherwise position the region appropriately for the transition selected.



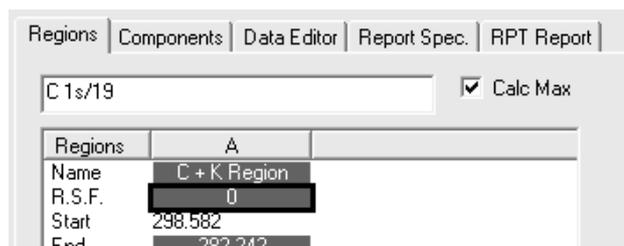
### Creating Peak Models

Constructing a peak model requires the definition of a background using the Regions property page and the introduction of synthetic component peaks via the Components property page.

The Regions property page is used to define a background to the data envelope.

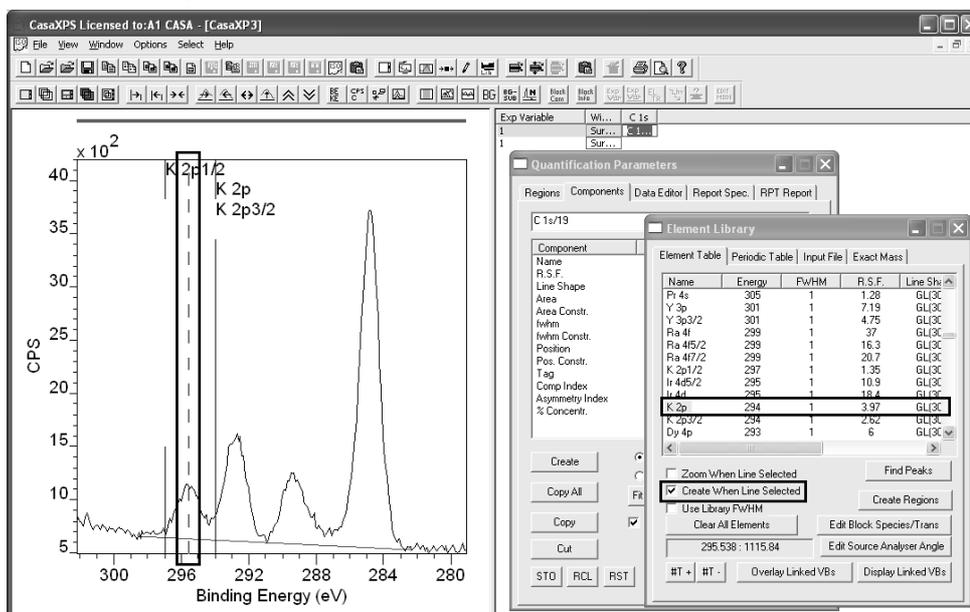


The intensity from a quantification region can be explicitly excluded from a quantification report by entering an RSF of zero.

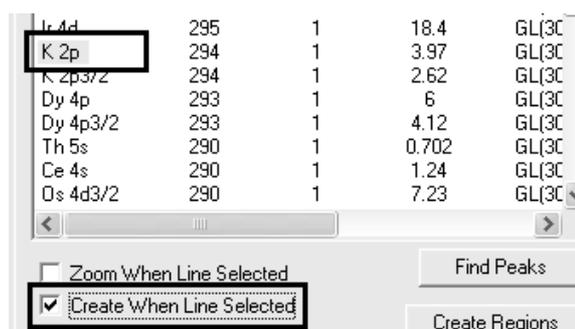


The function of the region is to define the background only allowing the intensities from the synthetic components to estimate the sample composition.

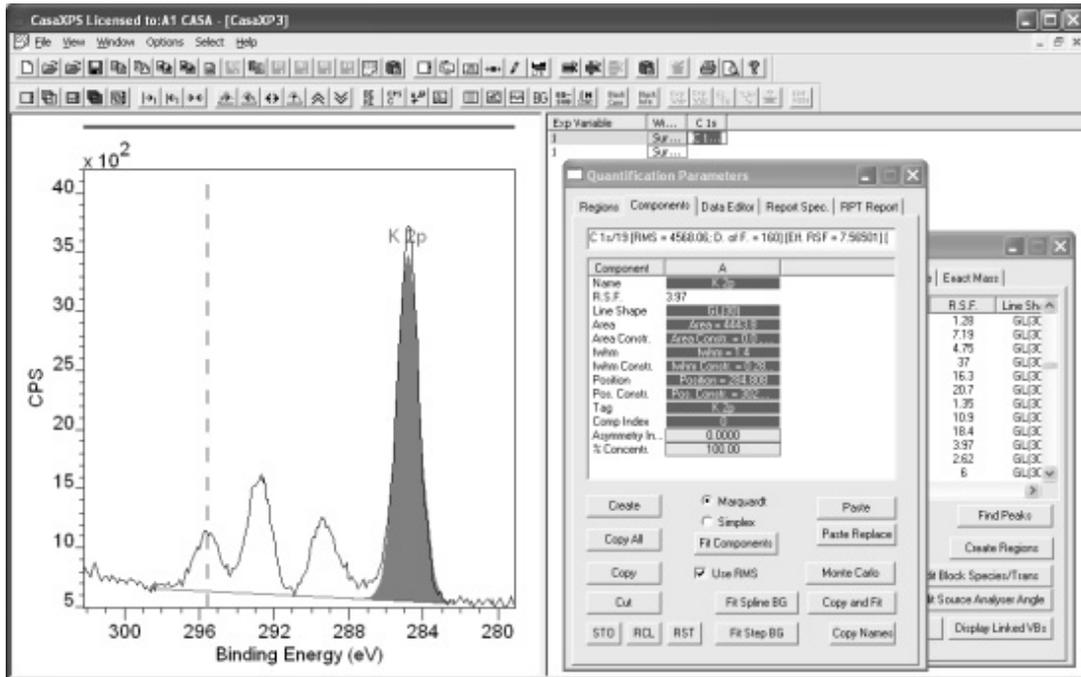
Components are created using the Element Table property page in an analogous way to the method for creating individual regions. Left-click the mouse with the cursor over a peak as displayed in the left-hand pane. The Element Table scrolled list changes to display those transitions around the energy indicated by the cursor.



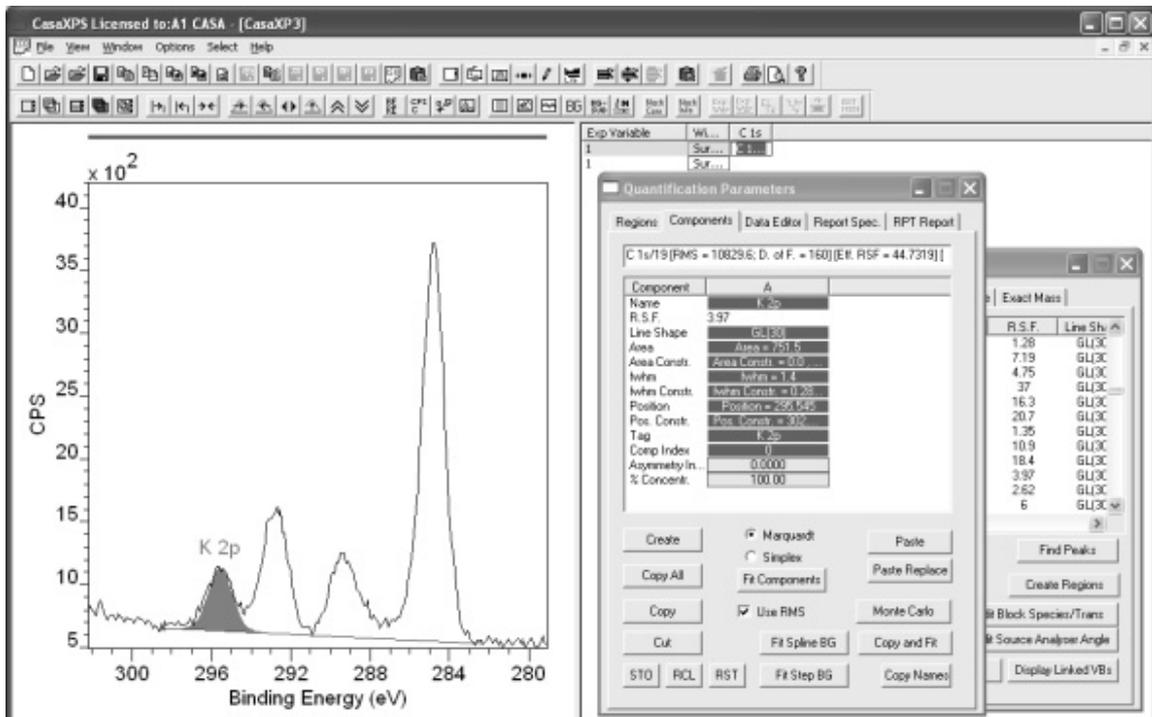
Tick the box on the Element Table property page labelled Create When Line Selected. With the Components property page top-most on the Quantification Parameters dialog window, left-click the appropriate name field within the element table for the transition identified in the left-hand pane.



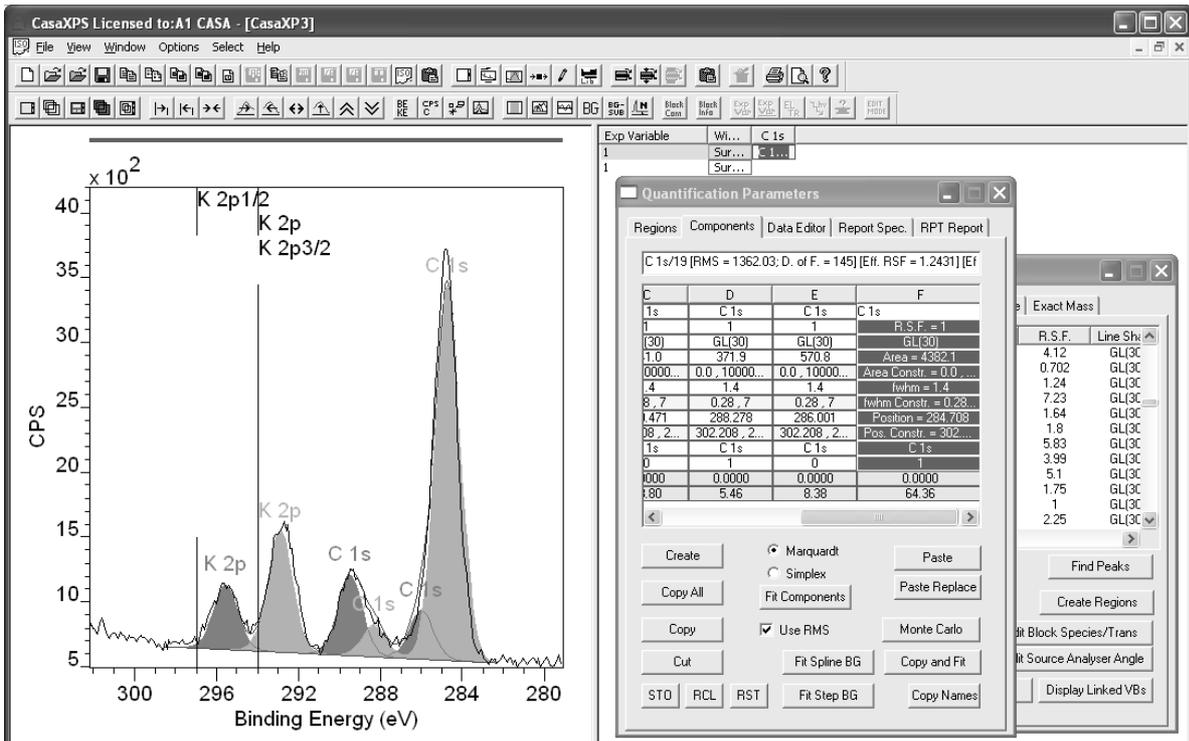
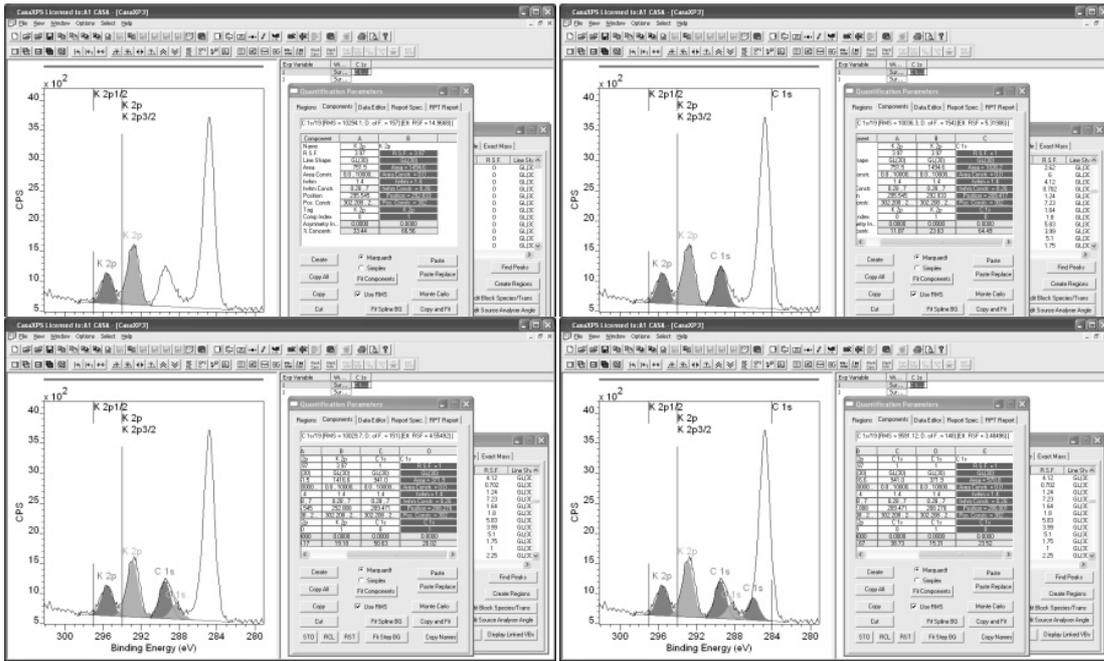
A peak is added to the display and the Component property page is updated.



New peaks are added to the data where the residual is the greatest. The new peak is therefore unlikely to appear in the correct position with respect to the peak envelope. Using the mouse, point at the peak maximum for the newly created peak and drag the cursor to the appropriate position for the synthetic component.



Repeat the process for each peak believed to be part of the model.

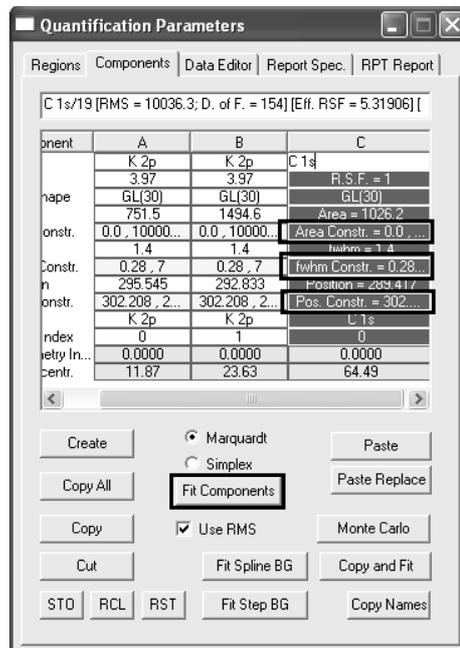


The example involves two elements and potentially five chemical states: one chemical state for the potassium and four for the carbon data. The two potassium peaks are part of a double pair; therefore the RSF for the combined pair of peaks is used when quantification is performed.

While it would be possible at this stage in the peak modelling process to press the Fit Component button on the Component property page, the number of peaks and level of noise in the data suggests that constraints will

be required to achieve a valid physical description based on non-linear least squares peak fitting.

A peak model is defined in terms of a name field and RSF serving exactly the same function as the name and RSF fields for regions. Fields specific to components are the line-shape parameter and the three parameters for area, position and full width at half maximum (FWHM) of the synthetic component. The parameters determined in a least squares sense are the area, position and FWHM. Constraints are available for restricting the possible values for these parameters during optimisation.



Constraints take two forms:

1. Parameter intervals offering a range of acceptable values for each parameter adjusted during a least squares optimisation.
2. Relational constraints between parameters from different components.

An interval is specified as a pair of numerical values separated by a comma:

	E	F
	C 1s	C 1s
	R.S.F. = 1	1
	GL(30)	GL(30)
	Area = 302.2	4432.4
0	Area Constr. = 0.0 , 10000000.0	0.0 , 10000000.0
	fwhm = 1.4	1.4
	fwhm Constr. = 0.28 , 7	0.28 , 7
	Position = 288.307	284.708
08	Pos. Constr. = 302.208 , 279.108	302.208 , 279.1
	C 1s	C 1s
d		1

Relational constraints involve specifying a parameter as related to a parameter from a second component in terms of an offset or a factor. For

example, the area ratio of two peaks from a p-orbital doublet pair is in theory 2:1. To impose this theoretical relationship for a potassium doublet, for example, the following constraint forces the 2p<sub>3/2</sub> peak to be twice the size of the 2p<sub>1/2</sub> peak:

Component	A	B	C
Name	K 2p 1/2	K 2p 3/2	C 1s
R.S.F.	R.S.F. = 3.97	3.97	1
Line Shape	GL(30)	GL(30)	GL(30)
Area	Area = 747.3	1494.6	1026.2
Area Constr.	B * 0.5	0.0, 10000...	0.0, 1000000
fwhm	fwhm = 1.4	1.4	1.4

Relational constraints are defined in terms of the column header letters, thus to force the area of the peak in column A to be half the area of the peak in column B, the constraint entered in column A is “B\*0.5”. Similarly, the FWHM can be defined as a factor constraint, while a position constraint is defined in terms of an offset to a second parameter.

Component	A	B	C
Name	K 2p 1/2	K 2p 3/2	C 1s
R.S.F.	3.97	R.S.F. = 3.97	1
Line Shape	GL(30)	GL(30)	GL(30)
Area	822.6	Area = 164...	845.1
Area Constr.	B * 0.5	Area Constr...	0.0, 1000000
fwhm	1.54865	fwhm = 1.5...	1.36625
fwhm Constr.	0.28, 7	fwhm Constr...	0.28, 7
Position	295.578	Position = 2...	289.476
Pos. Constr.	302.208, 2...	A - 2.777	302.208, 275
Tag	K 2p	K 2p	C 1s

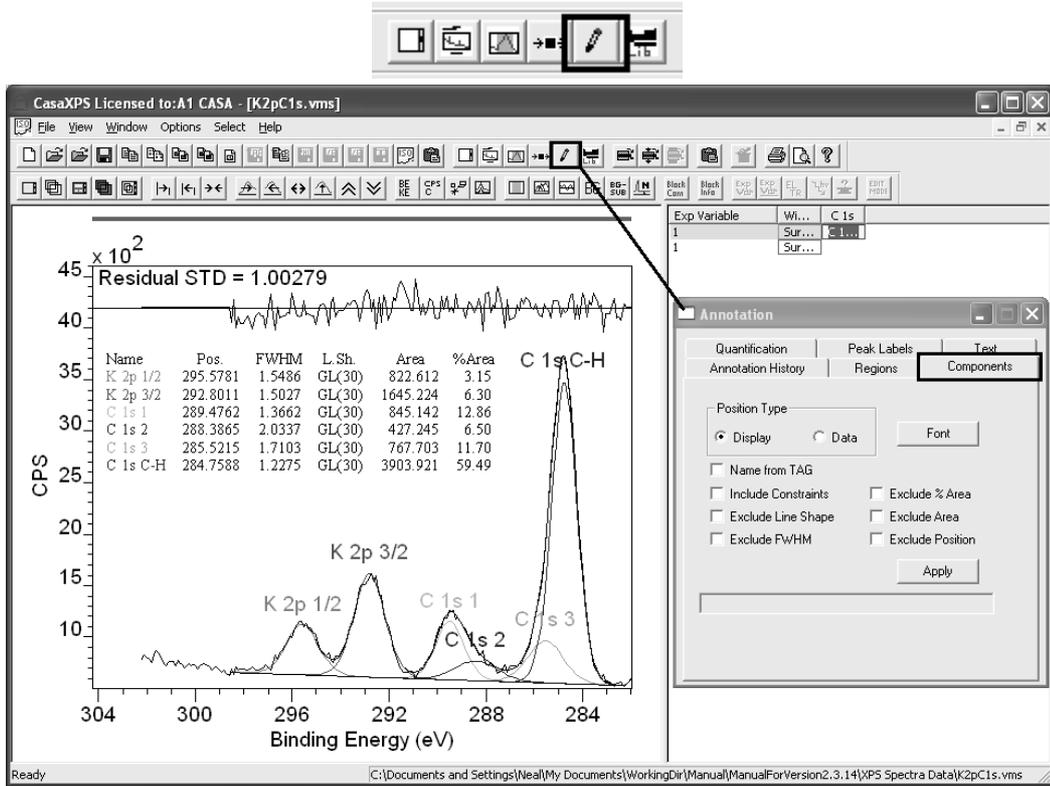
### Line Shapes

CasaXPS offers many different functional forms for synthetic components. The line-shapes are specified using strings entered into the line-shape field on the Components property page. Line-shapes are described in detail elsewhere in the CasaXPS manual; however the most commonly used synthetic line shapes are product Gaussian-Lorentzian GL(m) and sum Gaussian-Lorentzian SGL(m), where m=0 is a pure Gaussian and m=100 is a pure Lorentzian shape.

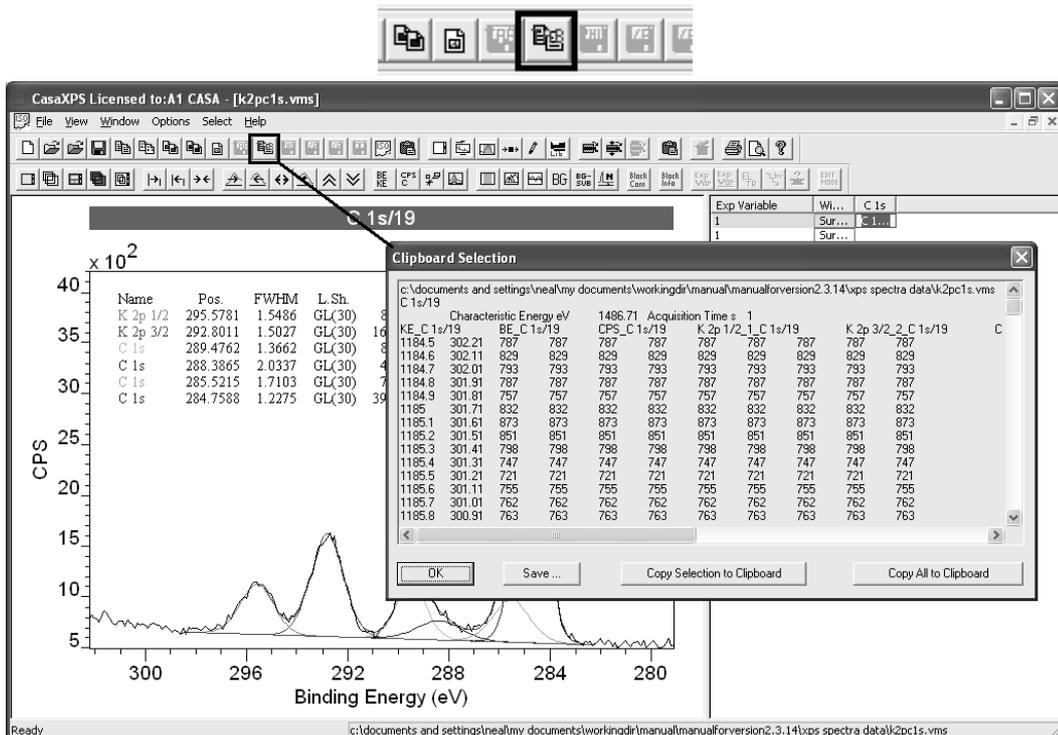
Component	A	B	C
Name	Si 2p 3/2	Si 2p 1/2	SiOx 1
R.S.F.	0.328	0.328	R.S.F. = 0
Line Shape	LA(1.4,2,10)	LA(1.4,2,10)	GL(30)
Area	3941.1	1970.6	Area = 2b2...
Area Constr.	0.0, 10000...	A * 0.5	Area Constr...
fwhm	0.423031	0.446088	fwhm = 1.5...
fwhm Constr.	0.2, 5	0.06207, ...	fwhm Constr...
Position	99.9097	100.521	Position = 1...

The line-shape LA(a,b,n) offers asymmetric line-shapes based on the Lorentzian functional form convoluted with a Gaussian.

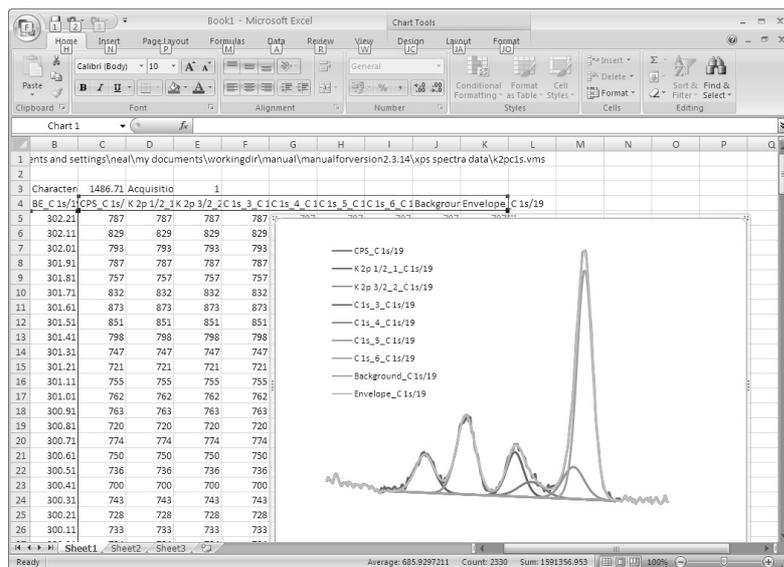
A useful means of monitoring complex peak models is via a components annotation table displayed over the data.



### Exporting Peak Models as Data

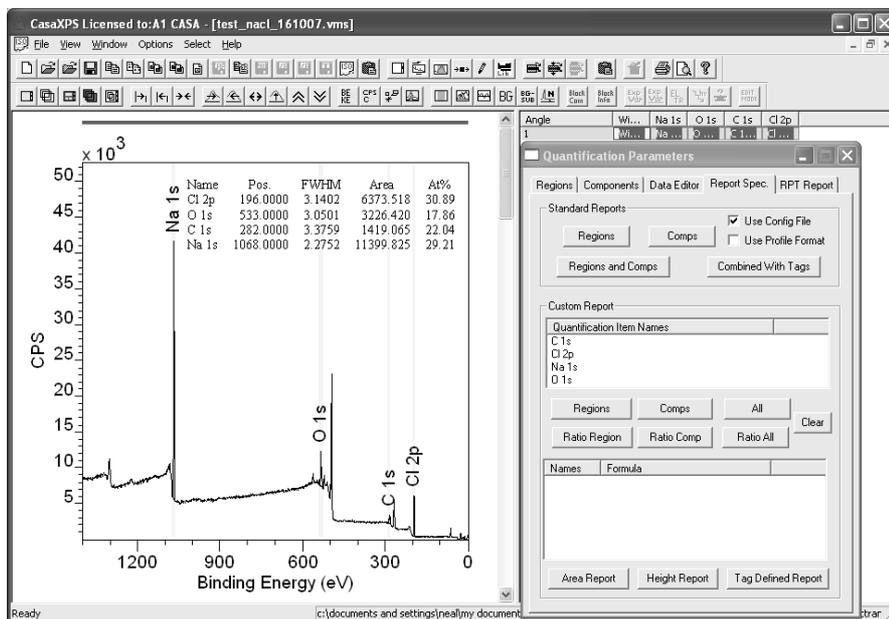


Peak model data are exported via the clipboard. Display the VAMAS block for which a peak model is prepared in the active tile and press the toolbar button. A clip board selection dialog offering a table of data, where the table includes columns for binding energy, kinetic energy, spectral data in CPS, component data, the background intensities and the total synthetic envelope. These data can be saved as a TAB spaced ASCII file or copied onto the clipboard and pasted into software capable of accepting text data through the clipboard.



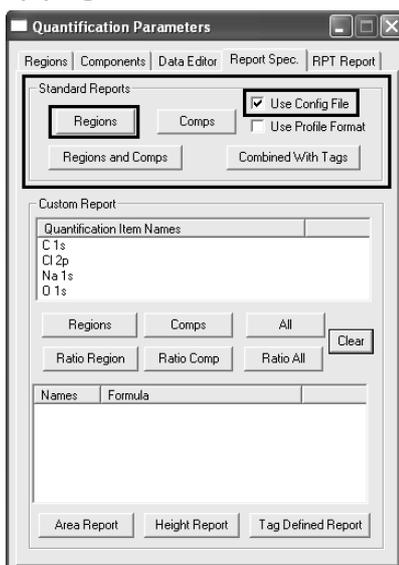
### Quantification using Standard Reports

Quantification reports are text-based information generated from quantification regions and/or components defined on VAMAS blocks. The most common form for a quantification report is a tabulation of atomic concentrations calculated from regions on survey spectra.

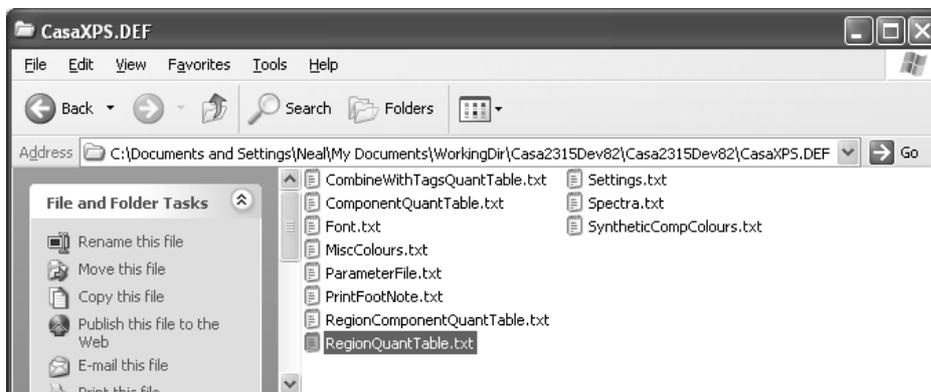


The Report Spec property page on the Quantification Parameters dialog window provides the means of creating quantification reports from VAMAS blocks selected in the right-hand pane of the experiment frame. Creating a quantification table from regions on a survey spectrum involves:

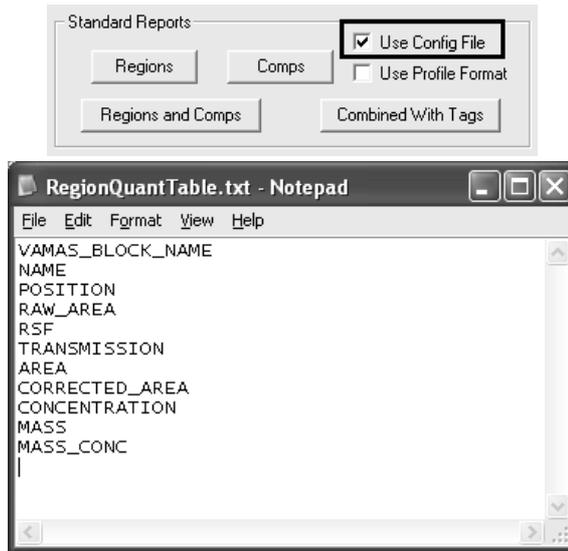
1. Defining a configuration file.
2. Selecting the VAMAS block in the right-hand pane of the experiment frame.
3. Pressing the Region button in the Standard Report section of the Report Spec property page.



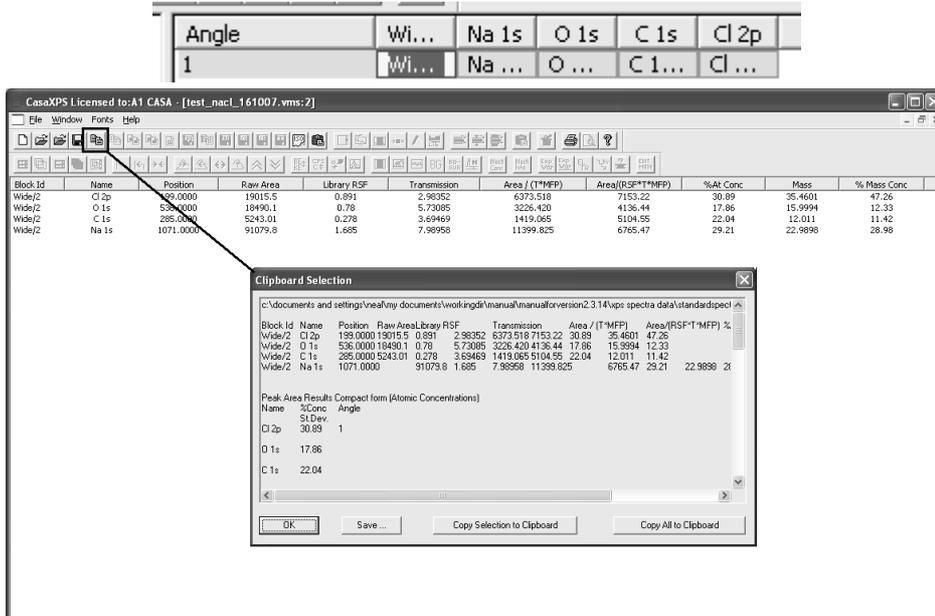
The configuration files for the Standard Report section are a set of ASCII files located in the CasaXPS.DEF directory. These configuration files contain keywords, one per line, specifying the type of information included in the columns of the text base report. The configuration file for the Standard Report Regions Move button is called RegionQuantTable.txt.



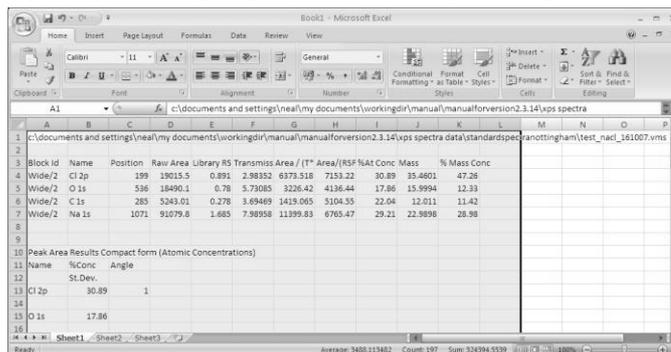
The keywords listed in the file RegionQuantTable.txt are used to arrange the columns of the quantification report provided the Use Config File tick-box is ticked.



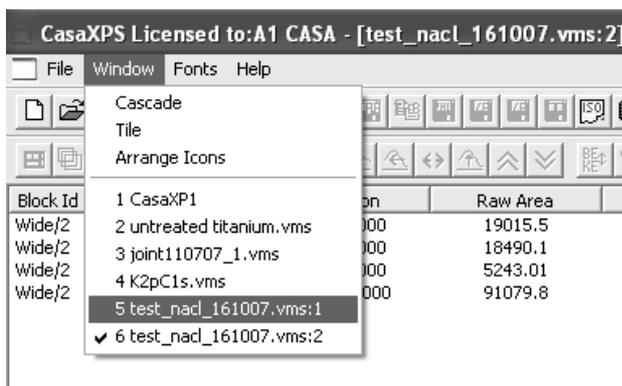
Selecting the VAMAS block in the right-hand pane before pressing the Region button causes a new view into the experiment frame to appear within the CasaXPS window.



The quantification table displayed in the new window can be copied through the clipboard or saved to disk by pressing the Copy toolbar button. Once on the clipboard, any program capable of accepting text from the clipboard may receive the data by requesting a paste action (usually Control-V).



To return to the experiment frame displaying the spectra either switch windows via the Window menu of CasaXPS or close the text report window.

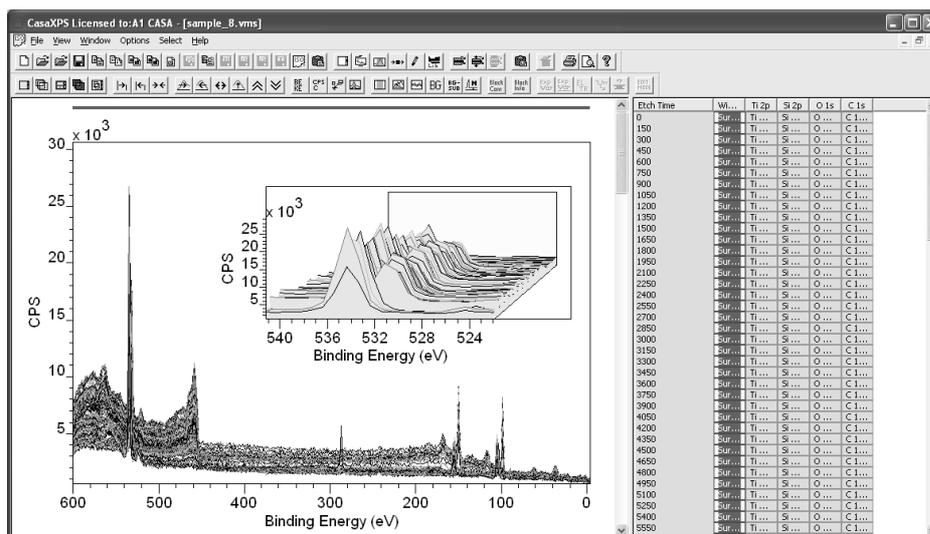


Similar configuration files are available for configuring reports for each of the buttons in the Standard Report Section.

### ***Transferring Regions and Components to other Data***

Depth profiles are just one example of data sets where quantification information needs to be propagated throughout a set of similar spectra. The techniques described below are equally applicable to data from a range of experiments and apply to data spread over many VAMAS files as it does for data collected into a single experiment frame.

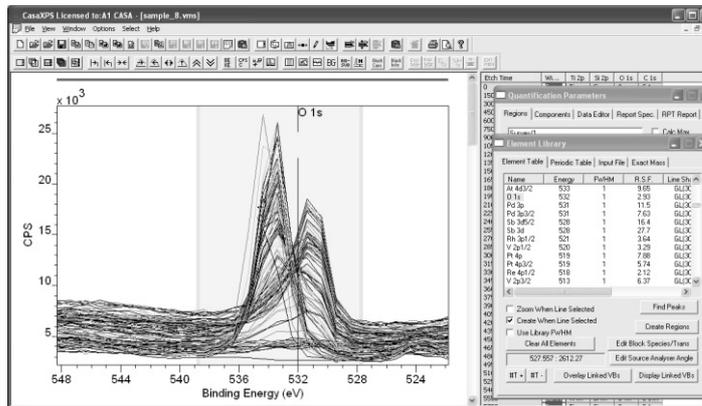
The propagation of quantification information to other spectra will be discussed using an example of a depth profile performed on a multi-layer material.



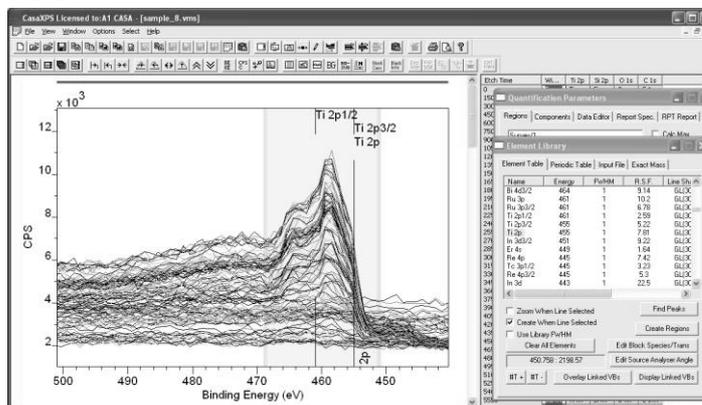
The data set consists of a set of survey spectra measured following a sequence of etch cycles. To examine the change in composition with etch time, the survey spectra require quantification regions appropriate for the entire set of spectra. Ultimately, each spectrum in the profile will have

regions defined on it and therefore minor adjustments on a spectrum-by-spectrum basis are possible; however to obtain a reasonably good initial set of regions, the spectra are overlaid in the active tile so that all variations of the peaks can be assessed whilst defining the regions.

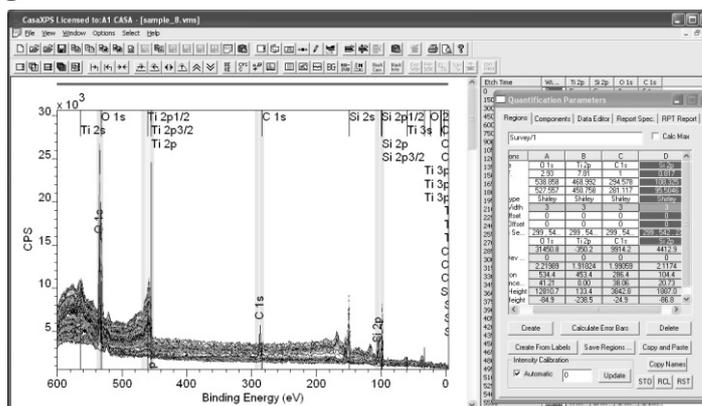
Create a region for each line in the survey spectrum representative of the elements present. First create a region for the O 1s peak using the element table method described above. Two chemical states of oxygen are clearly present in the data; however a single region will monitor the amount of oxygen in the profiled material.



Zoom into the Ti 2p peak envelope and add a region to measure titanium based on the Ti 2p peaks.

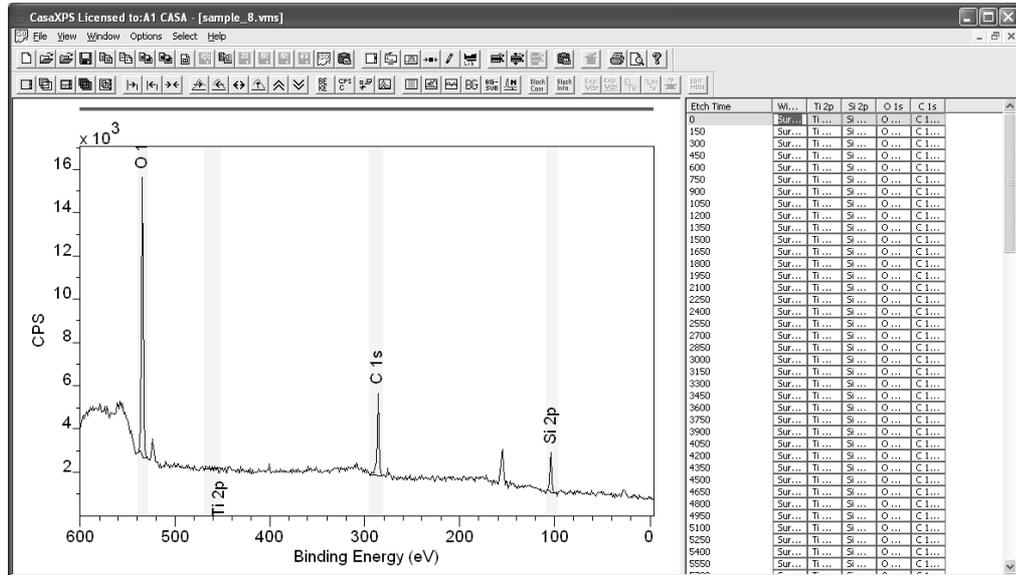


Similarly add regions for carbon and silicon.

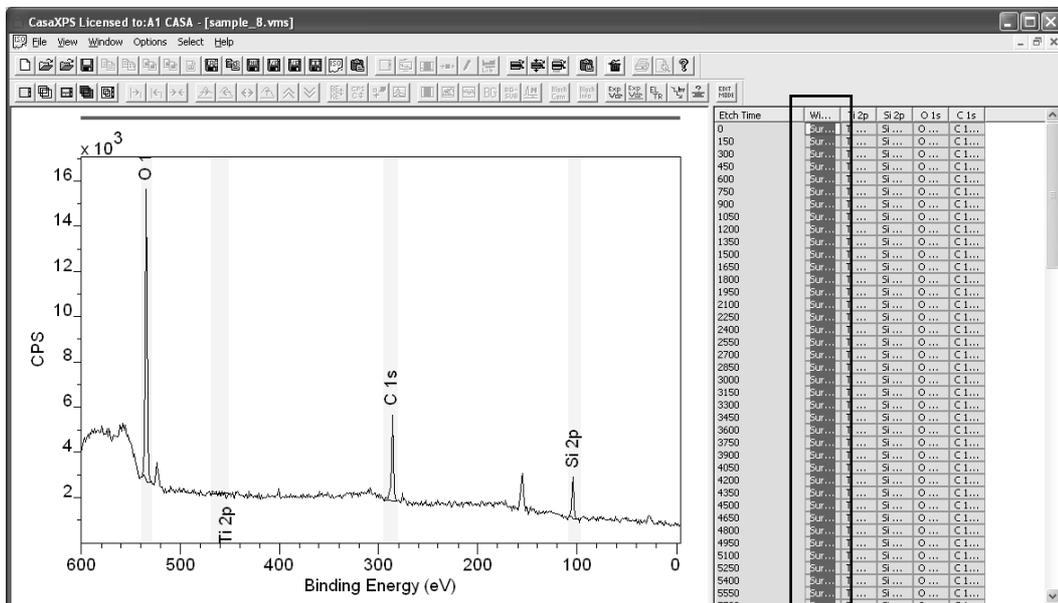


The regions as the data stands are all defined on the first spectrum displayed in the active tile. The next task is therefore to propagate the regions from the first spectrum to the remaining set of spectra.

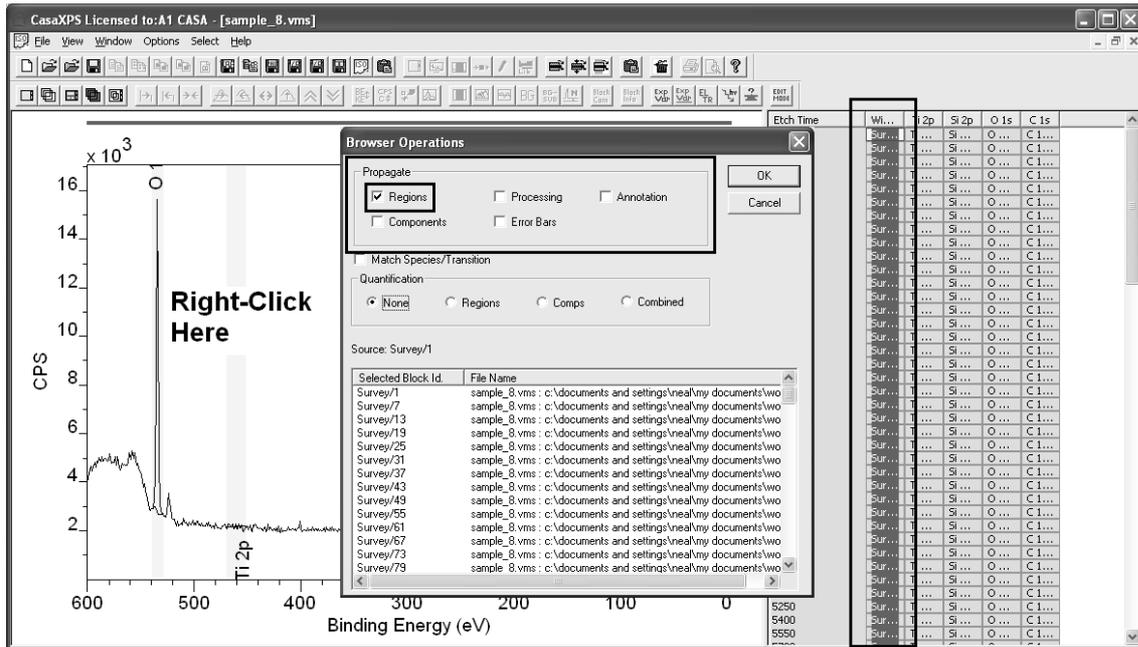
Ensure the spectrum for which the regions are defined is displayed in the active tile in the left-hand pane.



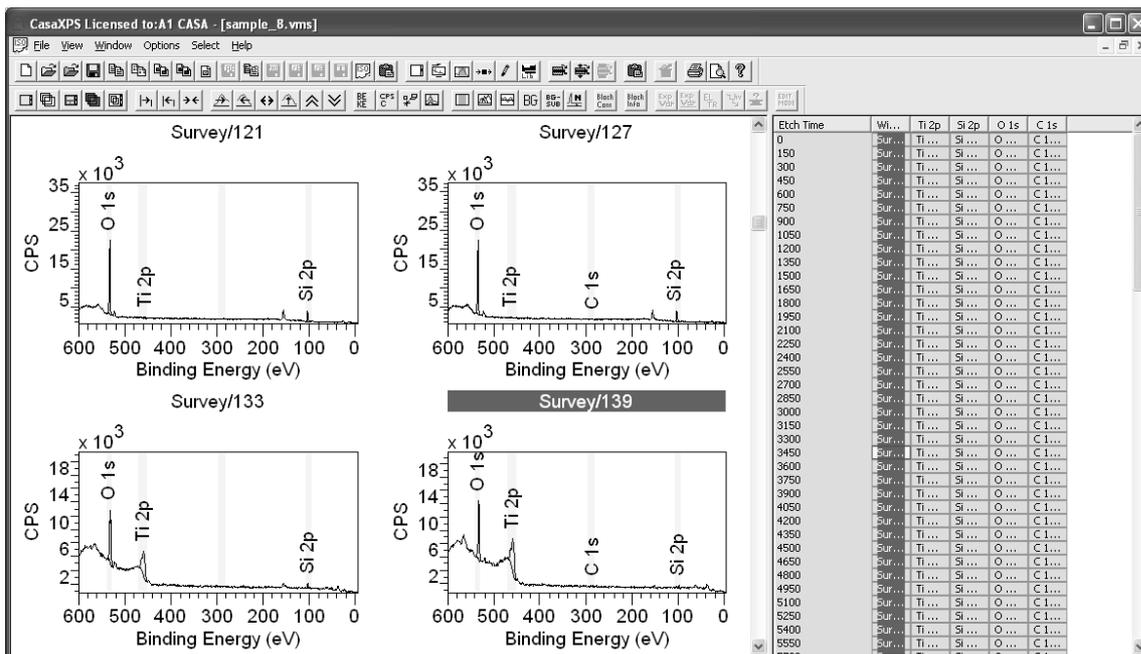
Select the set of survey spectra in the right-hand pane.



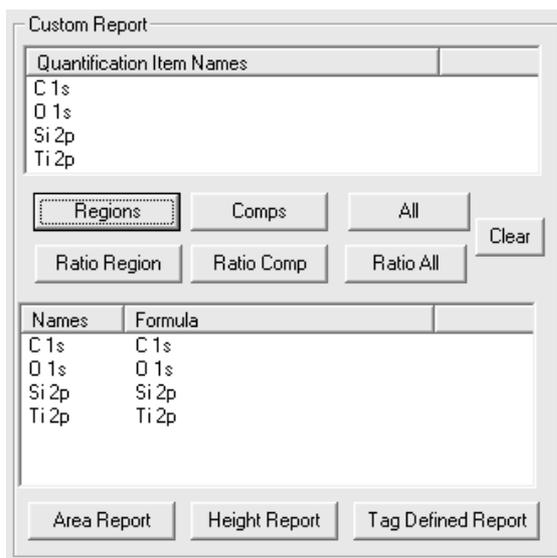
Move the cursor over the active tile displaying the spectrum for which the regions are defined and right-click the mouse. A Browser Operations dialog window lists the set of selected VAMAS blocks. Tick the Regions tick-box in the Propagate sections and press the OK button.



A progress dialog may appear briefly and on completion, the regions are transferred to the selected VAMAS blocks.



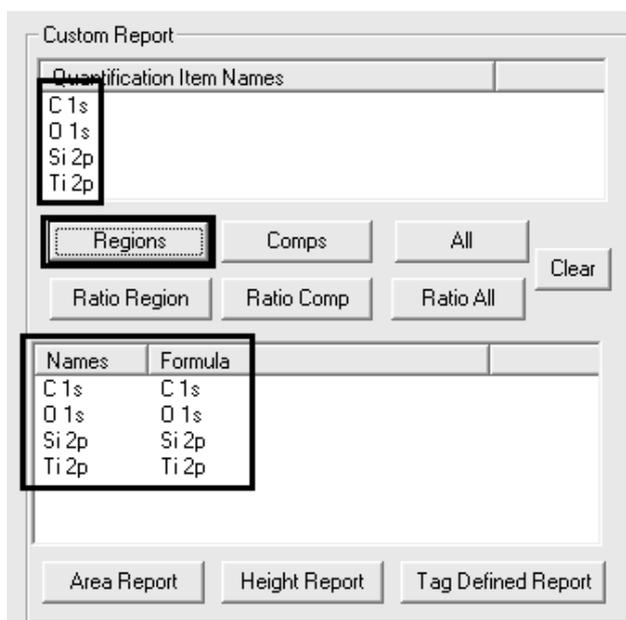
The objective for a depth profile is to display the variation of the signal as a function of depth. For this example, the depth will be measured in terms of etch-time; nevertheless, the type of report required to produce the profile differs from the format obtained from the Standard Report. To generate a profile as a function of time, the Custom Report section on the Report Spec property page is employed.



The custom report is designed for profiling experiments. The set of quantification items (regions and components) defined on the selected VAMAS blocks are listed in the Quantification Item Names table. From these quantification item names a set of named formulae are prepared.

**NB: The name fields are used to define the relationships between the intensities in a profile. A special relationship is automatically applied to any quantification items assigned the same name. Specifically, if two quantification items have the same name then the intensity for the items with the same name are added together. It is therefore very important to name regions and components with different names whenever a custom report is used.**

Since the current example includes only regions, pressing the Region button transfers the region names into the table of names and formulae.

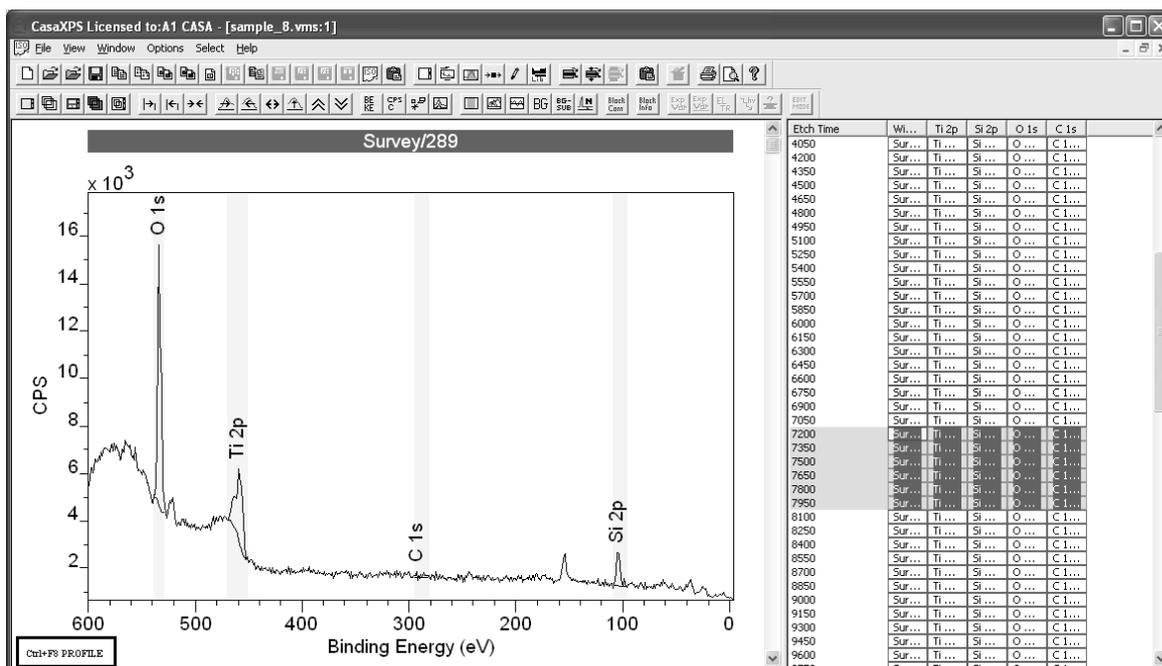


On pressing the Apply button in the Custom Report section, a column orientated quantification report is generated.

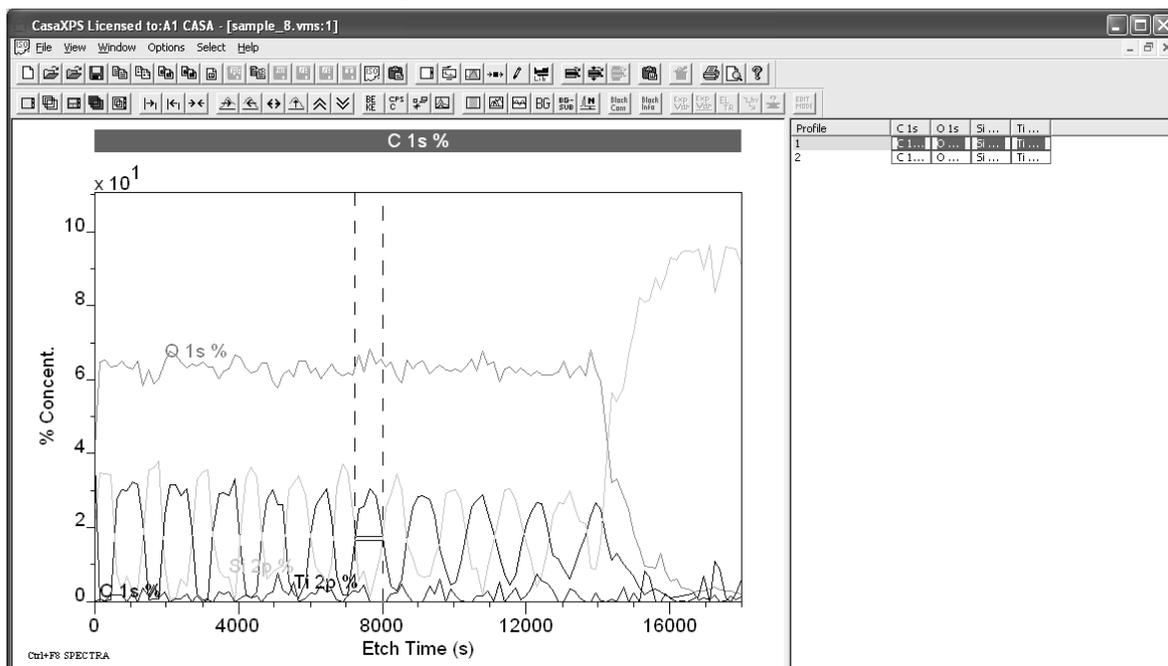
Ech	C 1s CPSeV	O 1s CPSeV	Si 2p CPSeV	Ti 2p CPSeV	C 1s %	O 1s %
0	9914.16	10734	5401.35	44.0370	38.0536	41.2363
150	-151.538	19552.9	10480.7	171.435	0	64.734
300	47.0543	19475.7	10236.6	12.9159	0.158047	65.4155
450	553.102	18912.9	10258.4	145.864	1.85168	63.3168
600	279.3	10745.8	1230.6	4643.88	1.6527	63.5862
750	251.056	9909.68	494.338	459.61	1.64901	65.0896
900	-435.297	9301.82	967.983	4370.92	0	63.5339
1050	350.085	9306.77	369.754	4772.91	2.36552	62.8856
1200	-214.632	9797.9	553.228	4732.16	0	64.9687
1350	639.647	10015.1	2796.7	3707.2	3.72783	58.2677
1500	368.83	15748	8956.99	72.4418	1.46674	62.6257
1650	1194.23	15997.5	9828.47	177.528	4.39093	58.8193
1800	262.364	16530	10480.7	174.323	0.955879	60.2243
1950	473.187	11333.3	1662.95	4011.14	2.70699	64.8381
2100	-19.9089	10987.5	117.491	5093.92	0	67.8287
2250	129.021	12181.7	187.895	5746.85	0.707139	66.7657
2400	159.056	13015.5	1224.2	5726.73	0.790322	64.6717
2550	370.461	11793.1	809.761	5701.72	1.98372	63.1491
2700	-28.9953	13755.4	3474.59	4175.29	0	64.2618
2850	398.662	18051.2	9299.94	572.941	1.40757	63.7339
3000	-503.386	16944	9162.38	77.104	0	64.7125
3150	76.8781	16828.3	9453.79	161.41	0.289883	63.4542
3300	-175.459	11524.1	3125.23	3492.25	0	63.5231
3450	450.057	10281.5	1406.38	4929.16	2.6494	60.0545
3600	325.656	9821.72	989.025	4619.43	2.06689	62.3371
3750	410.115	10311.1	1032.73	4679.08	2.49568	62.7461
3900	-13.0751	10004	-11.4083	4965.11	0	66.8311
4050	210.322	14700.8	4402.23	2964.75	0.944076	65.9877
4200	541.63	19412.6	10216.2	595.905	1.76023	63.0807
4350	303.294	20189.1	11902	339.45	0.926699	61.648
4500	444.763	19454.6	10507	773.303	1.42645	62.3951
4650	-253.464	14325.2	3908.95	3958.1	0	64.5506
4800	277.594	10534.7	1005.95	4480.1	1.70296	64.6369
4950	-410.691	9209.91	1200.93	4674.92	2.65023	59.4324
5100	1329.33	10174.6	1546.37	4622.16	7.52208	57.5731
5250	548.599	10442.8	1611.3	4413.02	3.22407	61.3715
5400	420.058	15118.2	7275.17	1368.35	1.73708	62.519

The text based report may be transferred through the clipboard to other programs or plotted within CasaXPS either as a separate file or appended to the current VAMAS file. Appending the profile data to the current file allows cross referencing the profile to the spectra. Both options are available on the File menu offered when the profile is tabulated.

Choosing the Add Profile menu option on the File menu adds the profile data to the original spectra as a temporary additional VAMAS file. The presence of a profile file is indicated in the bottom left-hand corner of the active tile.



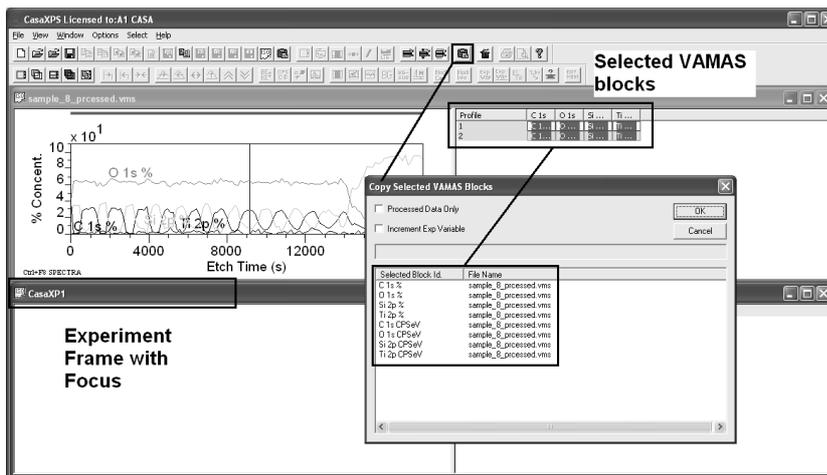
To switch between viewing the spectra and the profile derived from the spectra, press Control-F8 on the keyboard. The profile view of the data set can be used to mark a set of etch times using a cursor drag-action coupled with holding the Shift Key down; on switching the display to the spectra using Control-F8, the set of etch times marked by the cursor become selected. Similarly, a contiguous selection in the spectrum view will determine the location of a cursor on the profile view of the data.



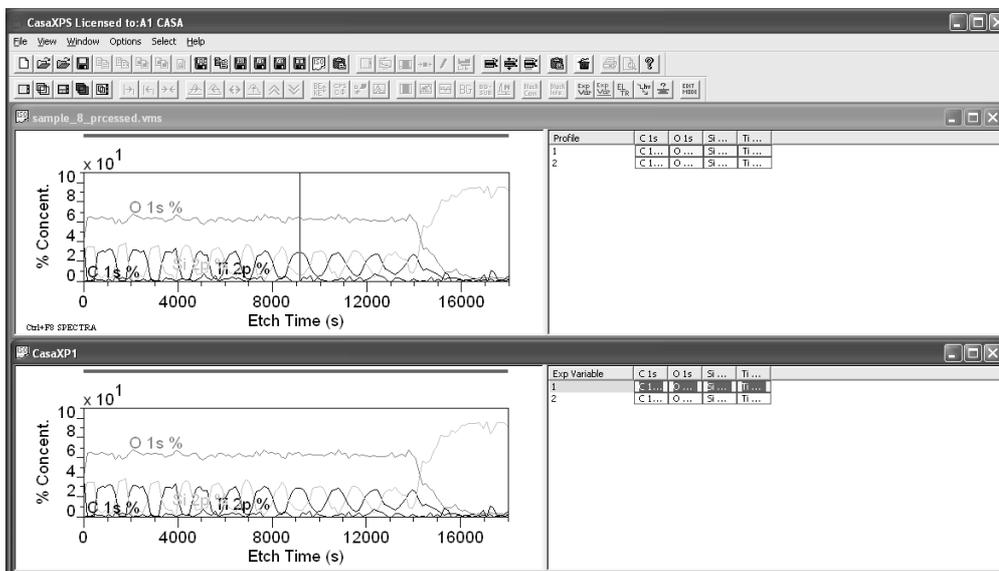
## Copying Data to a New Experiment Frame

The depth profile VAMAS file continues to only contain the spectral data even after the Add Profile menu option is applied. To preserve a profile the VAMAS blocks containing the profile traces must be copied to a new experiment frame. The new experiment frame can be saved once populated with the profile VAMAS blocks. To copy VAMAS blocks between experiment frames:

1. Select the VAMAS blocks in the right-hand pane.
2. Either, create a new experiment frame using the File menu or toolbar button, or switch focus to an existing experiment frame.
3. Press the Copy and Paste VAMAS blocks toolbar button.
4. Press the OK button on the Copy Selected VAMAS blocks dialog window.

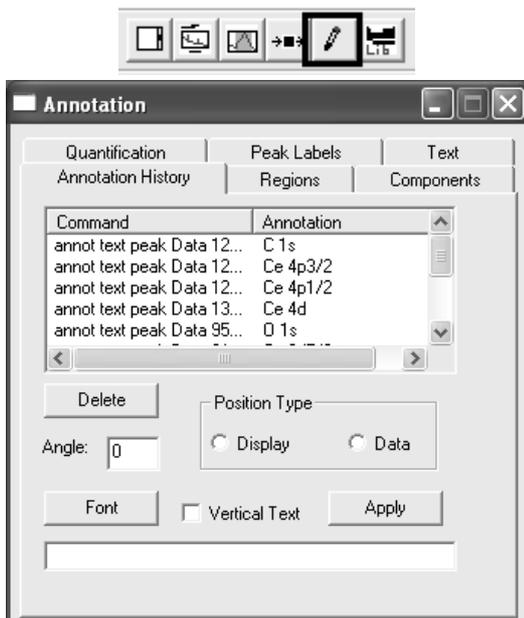


The new experiment frame contains a copy of the VAMAS blocks.



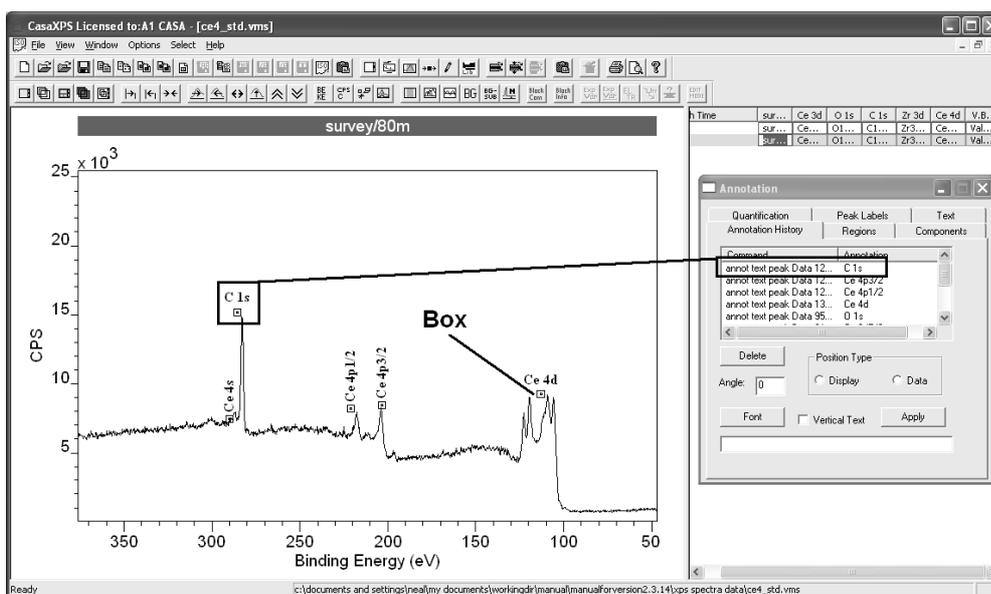
## Annotating Spectra

Text and tables are added to spectra via the Annotation dialog window.

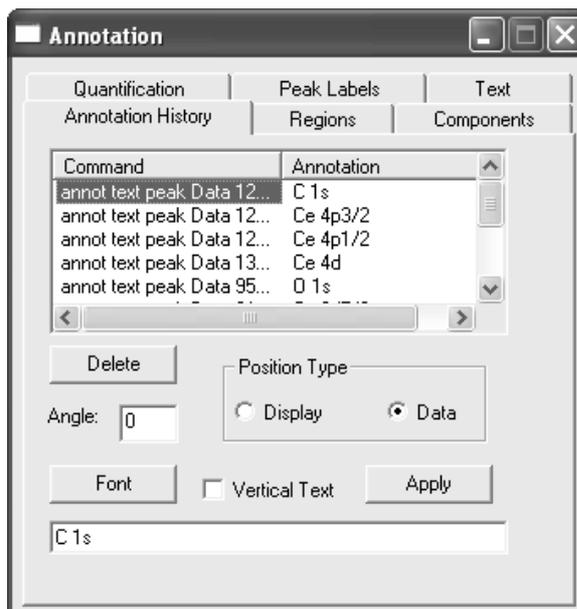


Text may be added to the display as individual items of annotation. Each piece of annotation appears in a list on the Annotation History dialog window. The list allows the annotation items to be selected, amended and deleted using the options on the Annotation History property page.

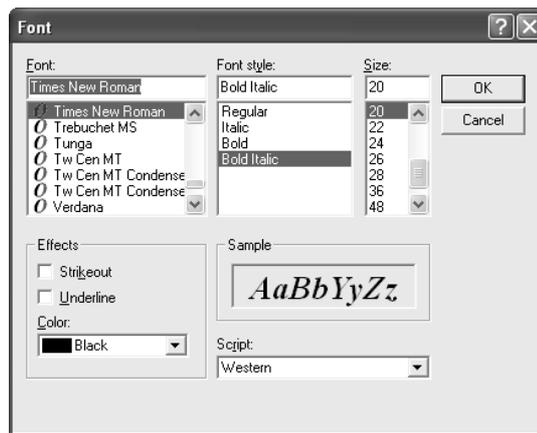
The position of the annotation on the display is indicated by a small box next to the annotation text. Pointing the cursor at the box and dragging the cursor to a new position causes the annotation to move the moment the mouse button is released.



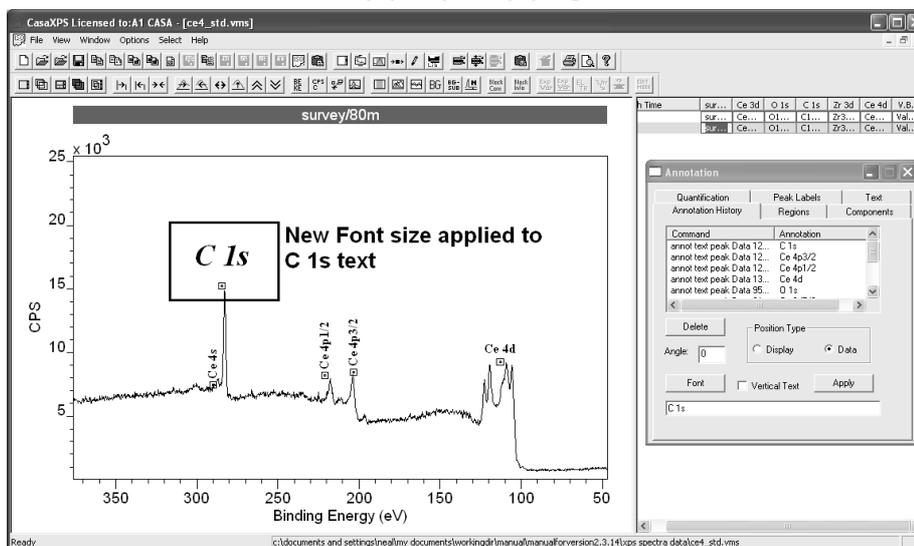
Modifying a piece of annotation involves selecting the annotation in the Annotation History list.



To alter the font, press the Font button and choose a new font for the selected annotation item.

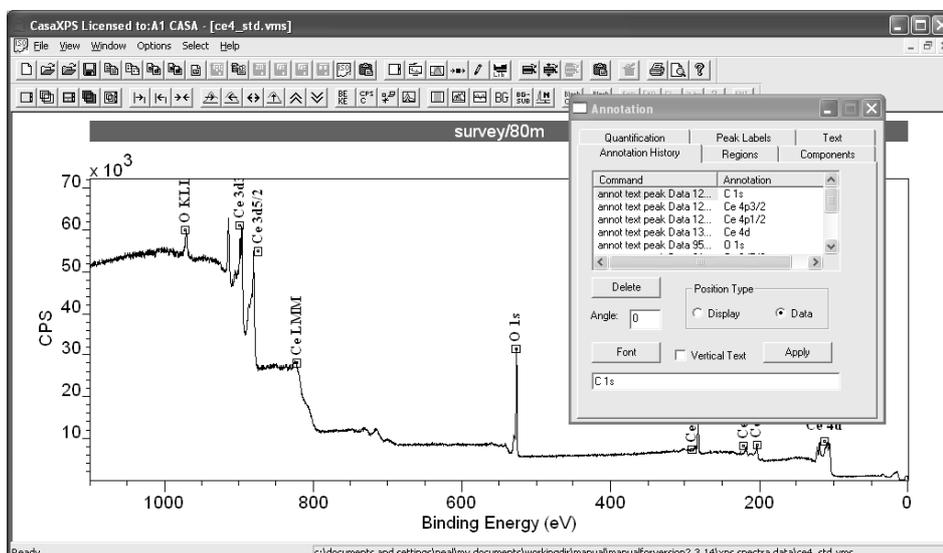


Press the OK button on the Font dialog window and then press the Apply button on the Annotation History text property page.

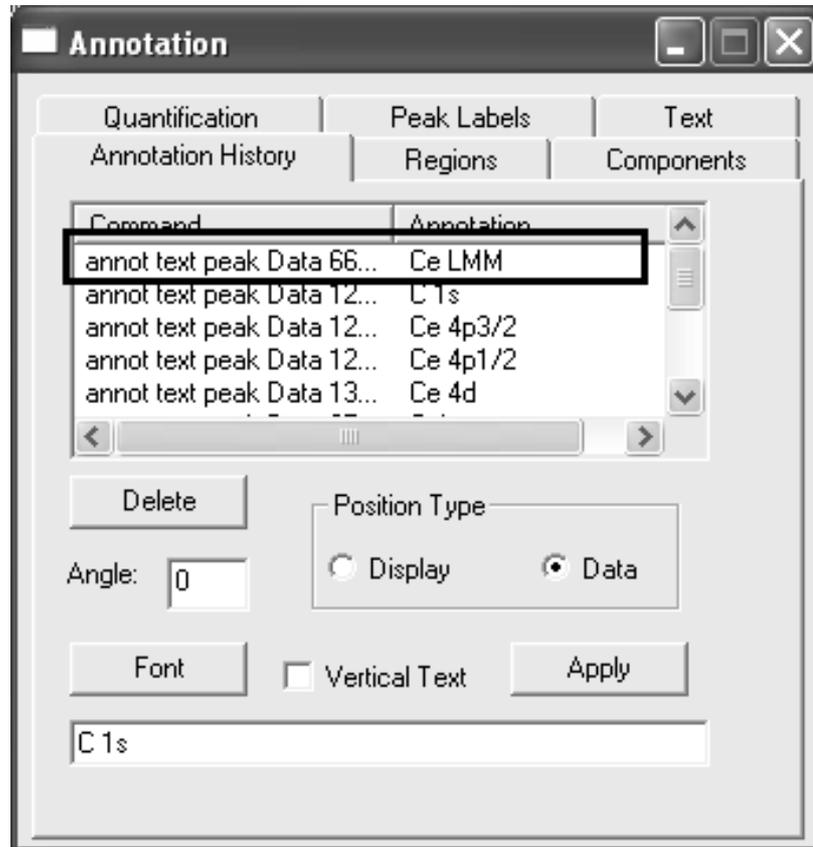


To adjust a specific annotation item, left-click the box located next to the annotation on the display. As a result, the annotation item is to move to the top of the list on the Annotation History property page.

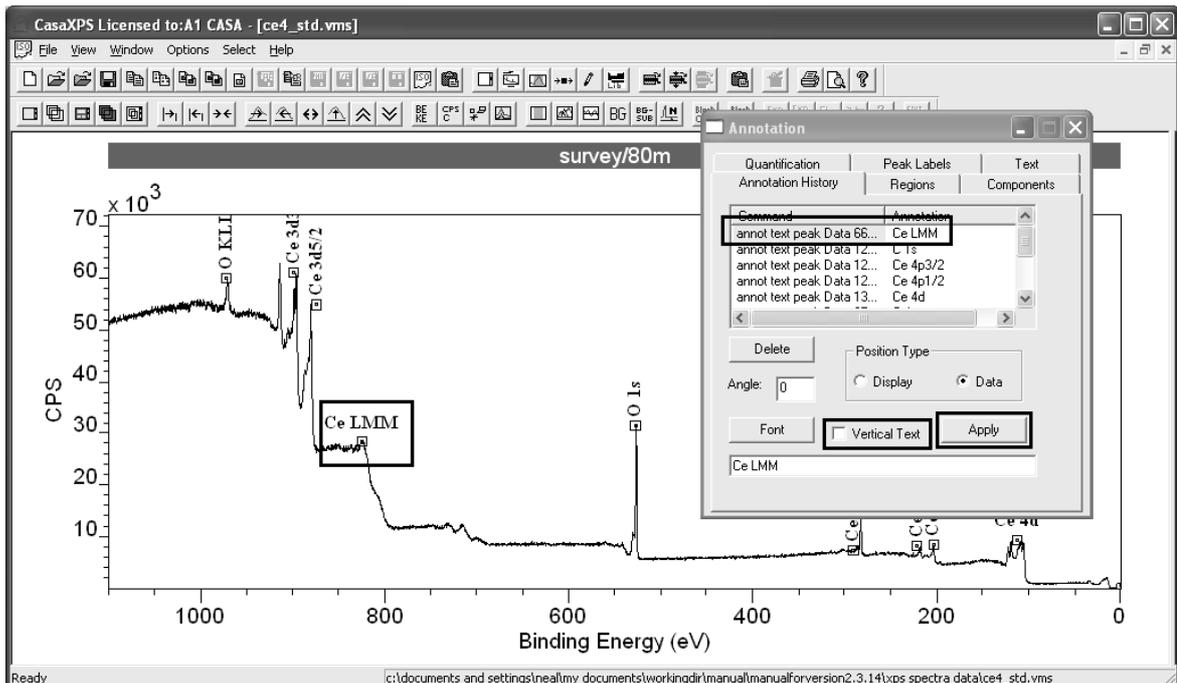
Initially Ce LMM text is not visible in the scrolled list without scrolling through the list.



Left click the box beneath the Ce LMM annotation text on the display in the left-hand pane. Clicking the box causes the annotation item to move to the top of the list.

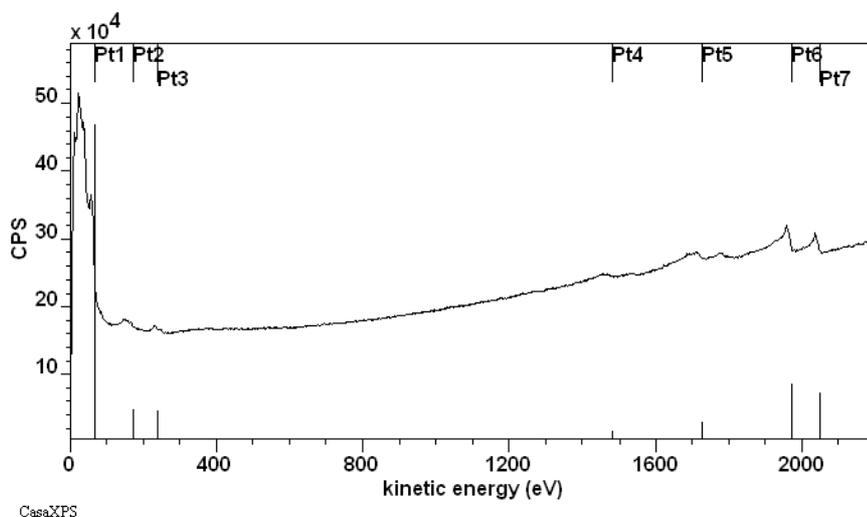


Select the Ce LMM item on the Annotation History property page. To make the annotation horizontal rather than appearing in the initial vertical orientation, un-tick the Vertical Text tick-box and press the Apply button.



# Auger Spectroscopy

Auger peaks in an energy spectrum are an indirect consequence of the excitation of core level electrons. Subsequent relaxation of the excited state induced by the interactions of a primary electron with an atom may result in the emission of an electron with a characteristic energy. These Auger electrons appear superimposed on a background of secondary and backscattered electrons.



The energy from the excitation source, typically an electron gun, alters the electronic state of an atom within the surface by ejecting a core level electron. The relaxation of the excited state occurs as a separate event from the core level excitation, so the characteristics of the excitation source have no influence on the energy with which Auger electrons are ejected from the surface. Auger electrons for an atom in a given chemical state always have the same energy regardless of the energy imparted by the primary electron beam or even when excited by other means such as x-rays. An oxygen Auger line, O KLL for example, appears at the same kinetic energy in a spectrum for both electron bombardment induced Auger or XPS induced Auger, regardless of the anode material in the x-ray gun.

Thanks to Tyne R. Johns of Sandia National Laboratories for her assistance in editing this manuscript.

Data used in the preparation of this text are kindly provided by:

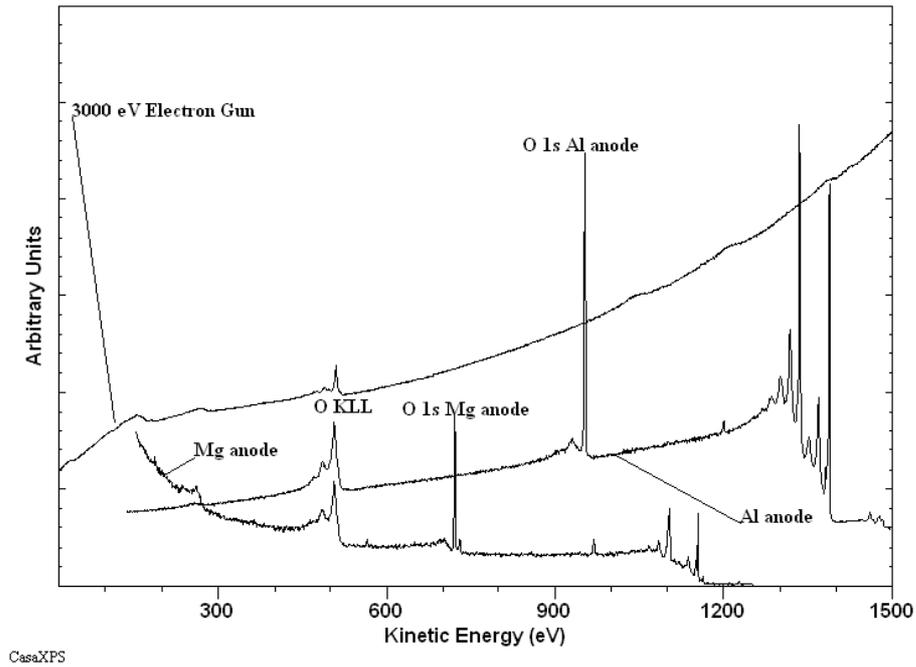
Prof Bridget Rodgers (Vanderbilt University)

Tyne R. Johns (Sandia National Laboratories)

Data provided courtesy of Sandia National Laboratories. All rights in the data are reserved by the US Government. Neither the US Government nor Sandia Corporation makes any warranty, express or implied, or assumes any liability with respect to the use of these data, and publication of these data does not constitute express or implied endorsement of any kind.

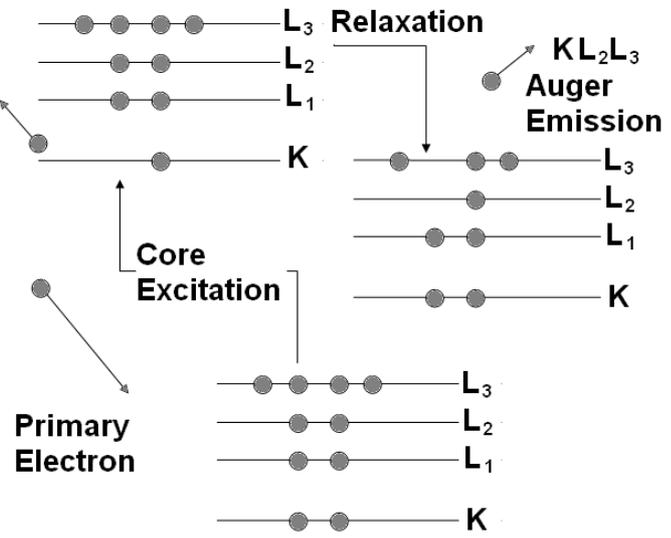
RBD Instruments Inc.

IFOS, Kaiserslautern, Germany



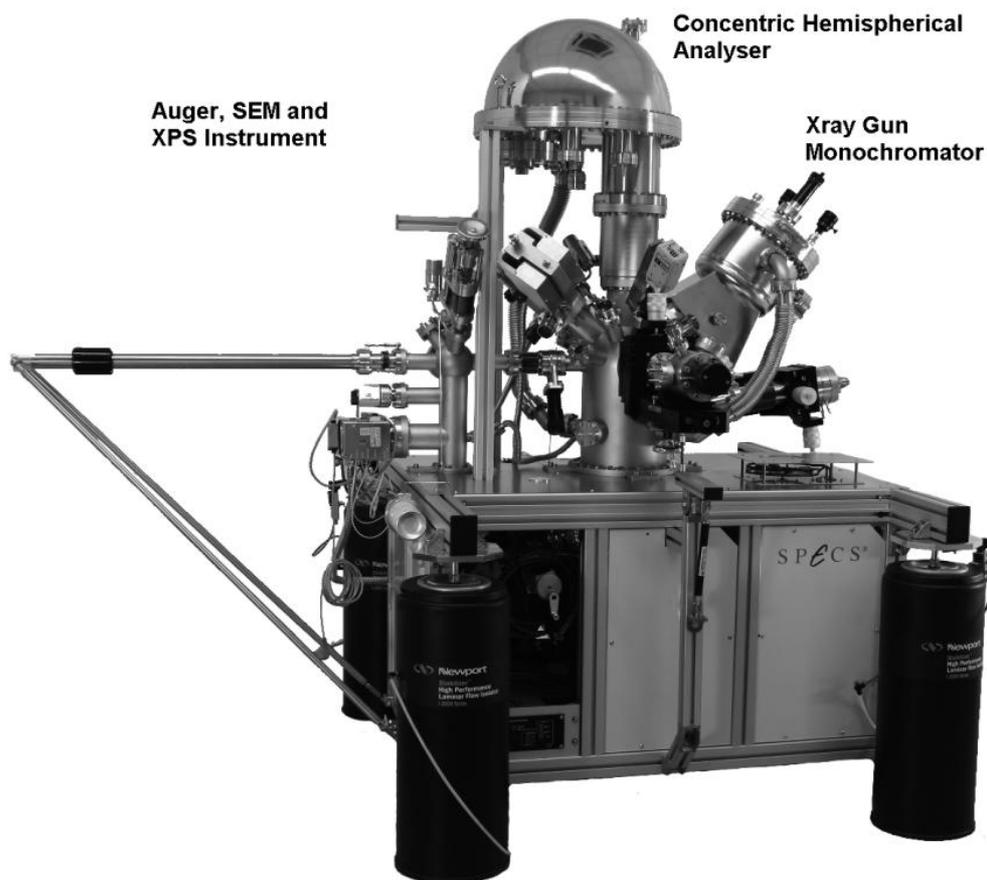
Auger peak intensities do depend on the excitation source and therefore Auger element libraries must include relative sensitivity factors for the specific electron gun energy used to excite the surface material.

The Auger mechanism involves exciting a core electron followed by the decay of an outer electron to fill the core level. The new electron configuration is energetically unstable and results in the emission of energy by ejecting an electron with an energy characteristic of the intermediate states. These Auger transitions are often labelled using the letters assigned to the principal quantum numbers for the electronic shells: K, L, M, N, ... with subscripts differentiating the sub-shell structure.



For a more complete description of the Auger mechanism see Briggs and Grant ISBN 1 901019 04 7.

Auger Electron Spectroscopy (AES) is performed using a Concentric Hemispherical Analyser (CHA or HSA) or a Cylindrical Mirror Analyser (CMA). The AES technique is offered in a stand-alone form and also as a multi-technique instrument, often including XPS to complement the advantages of AES. Sub-micron spatial resolution requires a means of isolating vibrations and Mu-metal shielding from stray electric and magnetic fields.



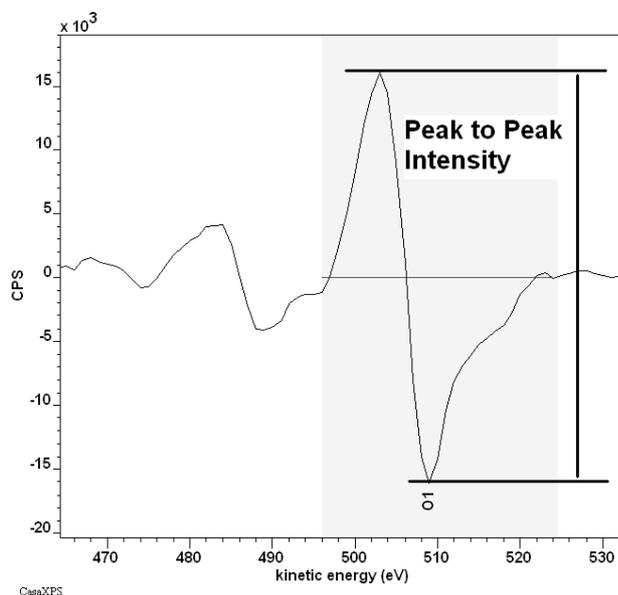
The following is concerned with spectra acquired using a CHA operating in fixed retard ratio mode or a CMA.

## Quantification of AES Data

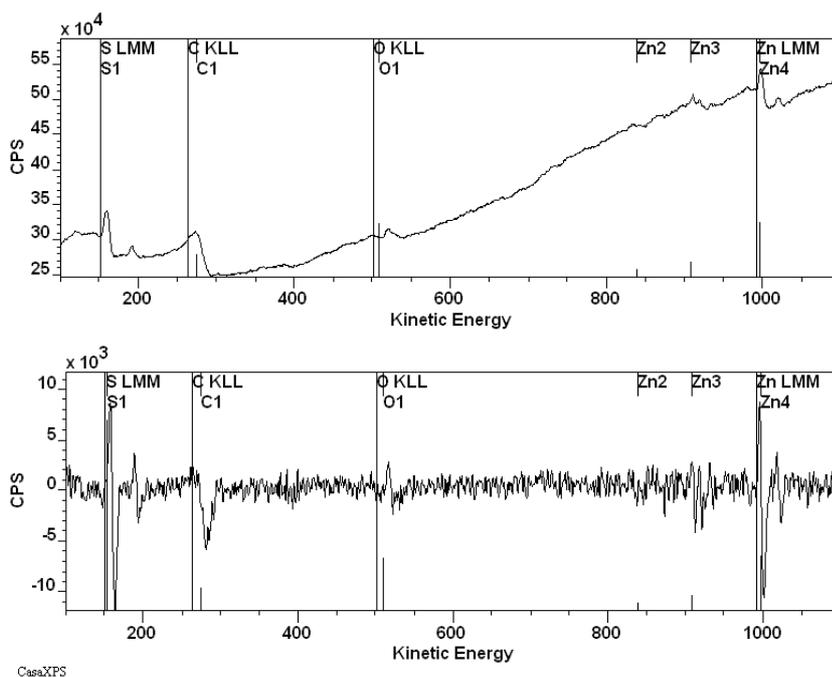
The acquisition mode for AES data determines the characteristics of the spectra and hence the quantification of peak intensities. CHA instruments typically have a response as a function of kinetic energy which behaves as an inverse power of the kinetic energy

$$R(E) \propto \frac{1}{E^n}$$

where the exponent  $n$  is typically in the range 0.5 to 1. Historically AES spectra are measured using a fixed retard ratio FRR mode for the CHA. The FRR mode records the number of electrons reaching the detector as the kinetic energy of the ejected electrons is stepped such that the ratio of the initial kinetic energy of the electron to the pass energy of the analyser is maintained as a constant during the acquisition. A consequence of using FRR mode is that the energy resolution of the data changes with kinetic energy so that at high kinetic energy where the response of the CHA is reduced, the energy width accepted by CHA increases; the signal accepted by the CHA for electrons emitted with higher kinetic energy is greater than for lower energy electrons. The resulting spectra are therefore more uniform in intensity over a wide energy range. In particular, the high yield of secondary electrons at low kinetic energies is attenuated by the FRR mode, thus protecting the detector system from excessive count rates. As a result of these practical considerations, AES data are more difficult to quantify in terms of peak areas, therefore the method used to quantify Auger spectra is to measure the intensity of a transition using a differentiated spectrum, determining the peak intensity by the difference in the positive and negative going derivative peak heights.



The so called direct spectra, as recorded, must be numerically differentiated to provide the data in a form suitable for quantification in terms of peak to peak intensities.



Some instruments, in keeping with the past, acquire the data using hardware signal differentiation, which partially accounts for the quantification based on peak-to-peak intensities. Most AES spectra acquired from modern instruments are in direct mode and so must be numerically differentiated before quantification is performed.

The energy window for a CMA instrument is proportional to the kinetic energy of the analysed electrons. The CMA acquisition characteristics are therefore equivalent to data acquired using a CHA in FRR mode.

### ***Differentiation of Spectra***

Differentiating data in which noise is a component requires the use of a more subtle approach than Newton-Cotes differentiation. A least squares approach attempts to mitigate the influence of noise on the resulting derivative.

### **Savitzky-Golay Method**

Two options on the Spectrum Processing dialog window commonly used for smoothing of experimental data and the determination of derivatives are performed using the algorithm proposed by Savitzky and Golay (A. Savitzky and M. J. E. Golay, *Anal. Chem.*, 36, 1627 (1964)). The same algorithm is employed to differentiate spectra as is used to smooth data and therefore it should be clearly understood that the act of differentiating a spectrum using the Savitzky Golay method necessarily includes a smoothing operation.

## ***Theory***

Given a set of data containing both signal and noise, the initial objective of the Savitzky-Golay method is to replace the raw data by a smoother set of data representing the true signal responsible for the record intensities. For a constant underlying signal, the most natural means of estimating the true signal from a set of measurements would be to average the values. The act of averaging a set of values is in fact one example and possibly the simplest applications of the linear-least-squares principle. Spectral data, on the other hand, typically contain peaks superimposed on a background signal and therefore a more subtle use of averaging is required if the essential structure in the data set is to be retained. One way to use the averaging process, but to maintain information relating to the variation in the intensities, is to perform a local averaging for each bin within a spectrum; for example, each data bin could be replaced by the average of three bins, the bin itself and the two bins on either side of the bin. The averaging operation could be applied to a data set via a digital convolution of the data bins with a convolution kernel consisting of the values  $\{1/3, 1/3, 1/3\}$ . These simple, yet often used concepts are at the basis of the Savitzky-Golay method, which in essence applies the least-squares principle to determine an improved set of kernel coefficients for use in a digital convolution, where these improved coefficients are determined, in the least-squares sense, using polynomials rather than, for the case of averaging, simply assuming a constant value determined from a sub-range of data bins. Indeed, the Savitzky-Golay method could be seen as a generalisation of averaging data, since averaging a sub-range of data corresponds to using a Savitzky-Golay polynomial of degree zero.

To illustrate the Savitzky-Golay method, consider the specific example in which five data bins are used to approximate a quadratic polynomial. The polynomial can be expressed in the form:

$$p(x) = a_0 + a_1x + a_2x^2$$

where the coefficients  $a_0$ ,  $a_1$  and  $a_2$  are determined from the simultaneous equations in which the abscissa  $x$  is the index for the data bin; the origin is always placed at the central data bin, thus the abscissa values corresponding to each of the data bins are  $\{-2, -1, 0, 1, 2\}$ :

$$\begin{bmatrix} 1 & -2 & 4 \\ 1 & -1 & 1 \\ 1 & 0 & 0 \\ 1 & 1 & 1 \\ 1 & 2 & 4 \end{bmatrix} \begin{bmatrix} a_0 \\ a_1 \\ a_2 \end{bmatrix} = \begin{bmatrix} d_{-2} \\ d_{-1} \\ d_0 \\ d_1 \\ d_2 \end{bmatrix}$$

or

$$\underline{A}\underline{a} = \underline{d}$$

where the evenly spaced data bins  $\{d_{-2}, d_{-1}, d_0, d_1, d_2\}$  are selected with the target of replacing the value for  $d_0$  with the value for the polynomial at  $x = 0$  or  $p(0) = a_0$ . Since there are five equations and only three unknowns, the coefficients to the polynomial must be determined in the least-squares sense, where the linearly independent basis functions are  $1, x$  and  $x^2$ . The normal equations yield:

$$\underline{A}^T \underline{A} \underline{a} = \underline{A}^T \underline{d}$$

Since  $\underline{A}^T \underline{A}$  is a square symmetric matrix of rank three, the coefficient vector  $\underline{a}$  is determined from  $[\underline{A}^T \underline{A}]^{-1} \underline{A}^T$ , the top row of which yields the prescription for computing the value of  $a_0$ , namely:

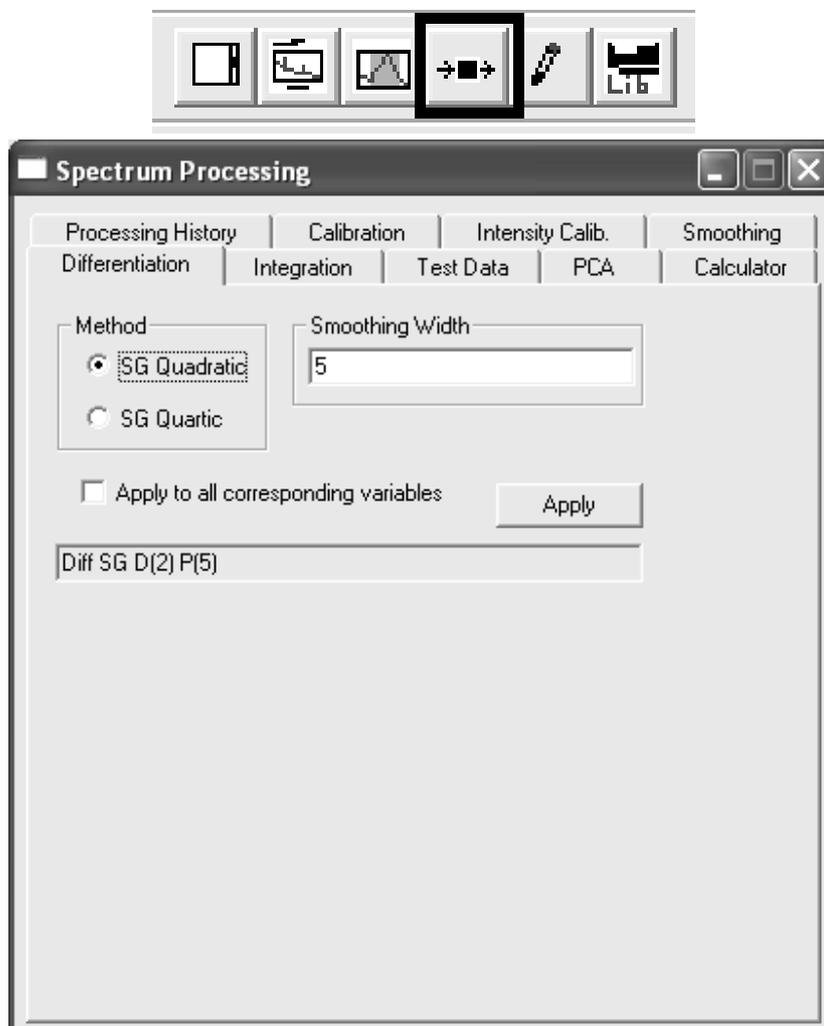
$$\underline{a}_0 = [s_0, s_1, s_2, s_3, s_4] \begin{bmatrix} d_{-2} \\ d_{-1} \\ d_0 \\ d_1 \\ d_2 \end{bmatrix}$$

Thus, for each set of five such data bins, the central bin can be replaced by the value determined for  $a_0$ . In other words, a digital convolution using the five point kernel  $\{s_i\}$  and the raw data bins results in a smoothed set of data bins, where a linear least squares quadratic polynomial is used to model the data, five channels at a time.

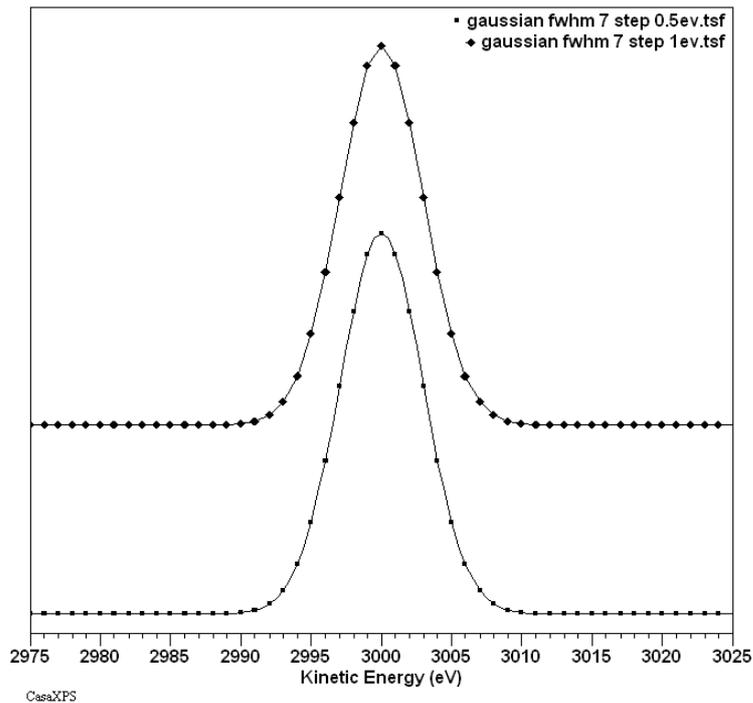
Similarly, the derivative of a spectrum can be computed using the Savitzky-Golay polynomial. Again the intention is to approximate the derivative at a given point in the spectrum using the derivative of the polynomial at  $x = 0$ . Since  $dp(0)/dx = a_1$ , the second row of the matrix  $[\underline{A}^T \underline{A}]^{-1} \underline{A}^T$  yields a second convolution kernel for computing the derivative of the spectrum and, apart from the difference in the kernel values, the computation of the derivative proceeds in an analogous fashion to that of the smoothing calculation.

## Creating Derivative Spectra for Peak-to-Peak Quantification

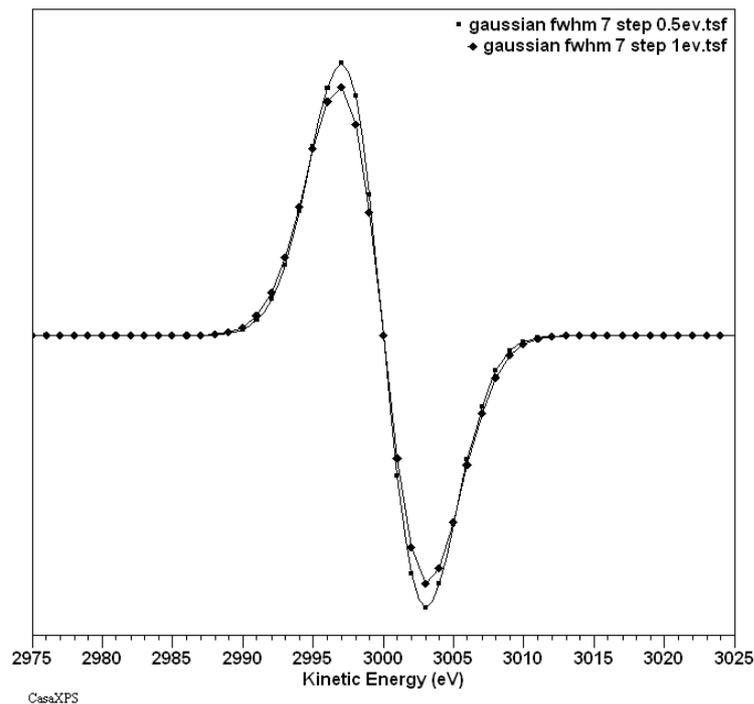
Direct spectra are converted to differentiated spectra using the Spectrum Processing dialog window.



The Differentiation property page on the Spectrum processing dialog provides a choice of two Savitzky Golay methods and a smoothing width value. The parameters used in the Savitzky Golay differentiation option depend on the source of the relative sensitivity factors used to quantify the data. For example, the set of RSFs in Appendix C of Briggs and Grant are designed for data acquired using an energy step size of 1 eV and differentiated using a 5 point quadratic Savitzky Golay differentiation method. Matching the acquisition step size and Savitzky Golay parameters is important because these influence the peak-to-peak height determined for an Auger peak. Consider a Gaussian peak with a FWHM of 7 eV tabulated at 1 eV and 0.5 eV step-sizes:



If differentiated using a 5-point quadratic Savitzky Golay method the peak-to-peak measurement for the same functional form differs by 10%.



The FWHM used for the Gaussian is typical of an oxygen KLL peak. The scale of the difference between peak-to-peak intensities for peaks of different FWHM when measured using different step-sizes also varies. A peak-to-peak intensity for a peak with FWHM 10 eV when measured using 1 eV and 0.5 eV and differentiated using a 5-point Savitzky Golay method differs by 5%.

The RSFs in Briggs and Grant are specified for a 4 eV energy interval numerical differentiation. In principle data acquired at 0.5 eV should

therefore be differentiated using a 9-point Savitzky Golay method, while data acquired at 1 eV would require a 5-point Savitzky Golay differentiation. While matching the number of points used in the Savitzky Golay method to the step-size can improve the acquisition step-size dependency, the test peak of FWHM 7 eV still results in a 1.8% difference in peak-to-peak height when tabulated at 0.5 eV steps and differentiated with a 9-point quadratic Savitzky Golay than when tabulated at 1 eV and differentiated with a 5-point quadratic method.

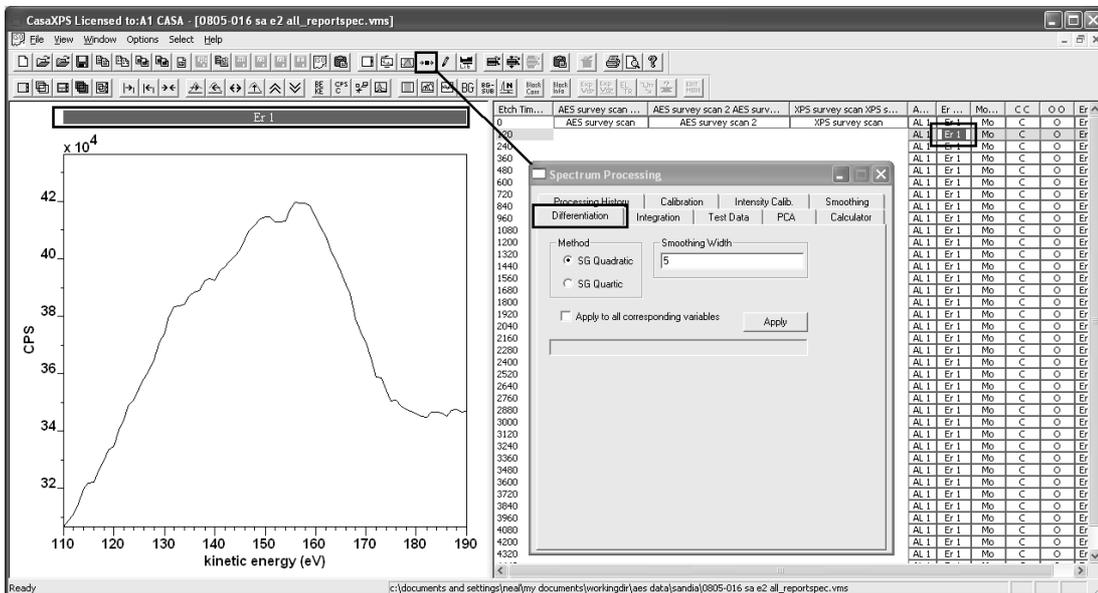
### Converting Direct Spectra to Differentiated Spectra

To convert a spectrum from direct form to differentiated form:

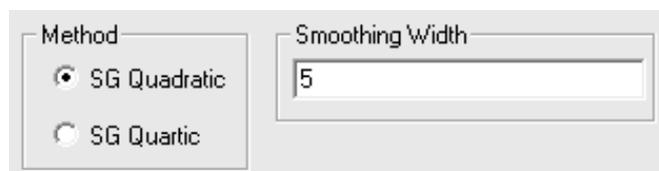
1. Display the spectrum in the active tile.



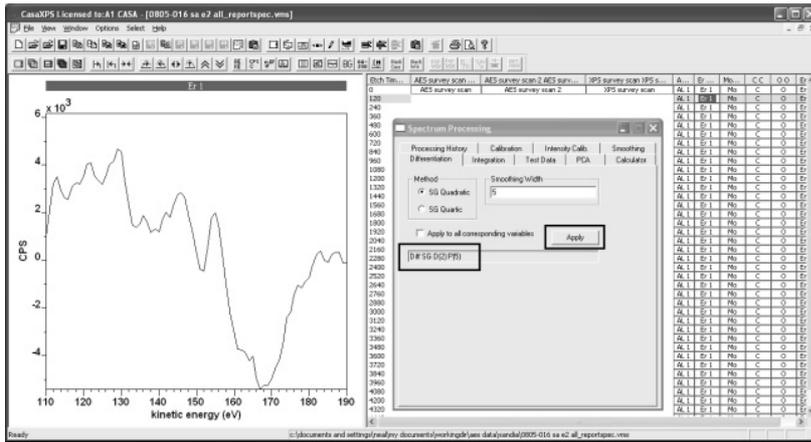
2. Invoke the Spectrum Processing dialog window and select the Differentiation property page.



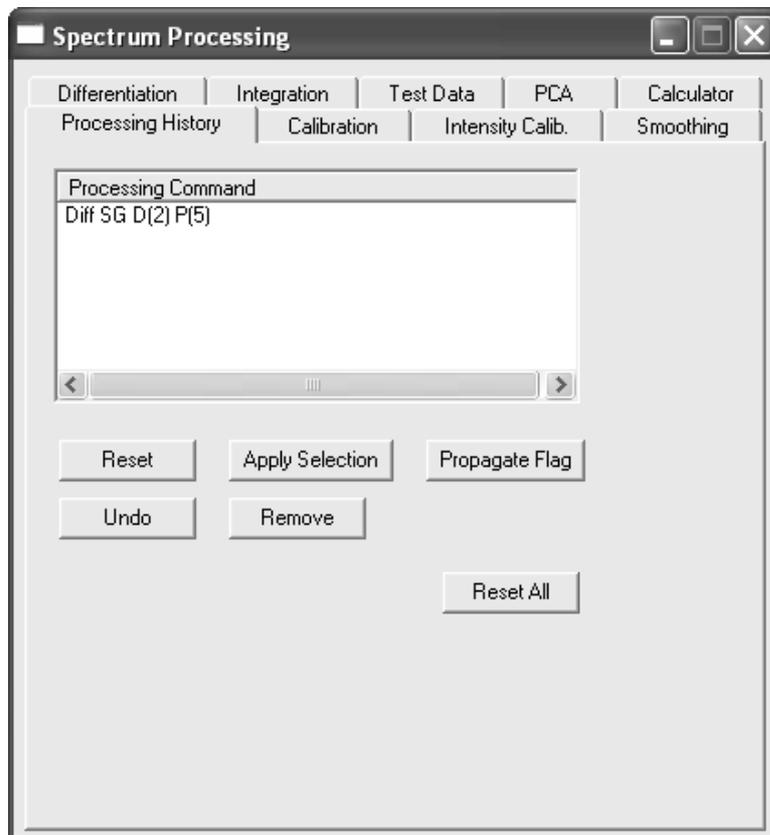
3. For data acquired using 1 eV step-size, select the SG Quadratic radio button and enter 5 into the smoothing width text box.



4. Press the Apply button on the Differentiation property page.

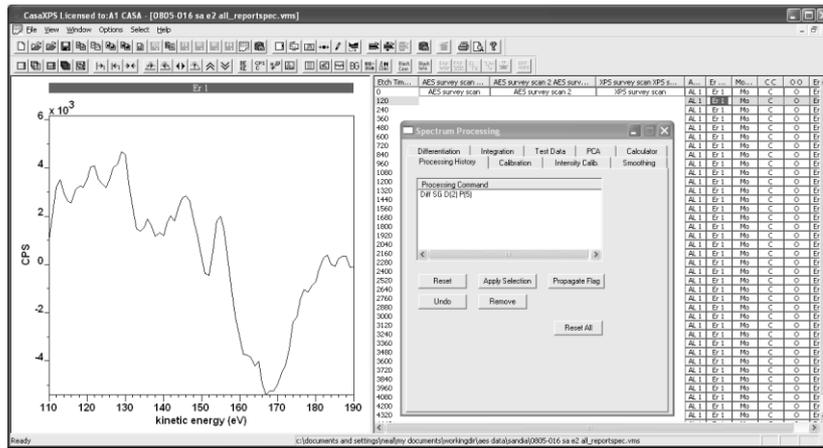


An entry appears in the scrolled list on the Processing History property page.

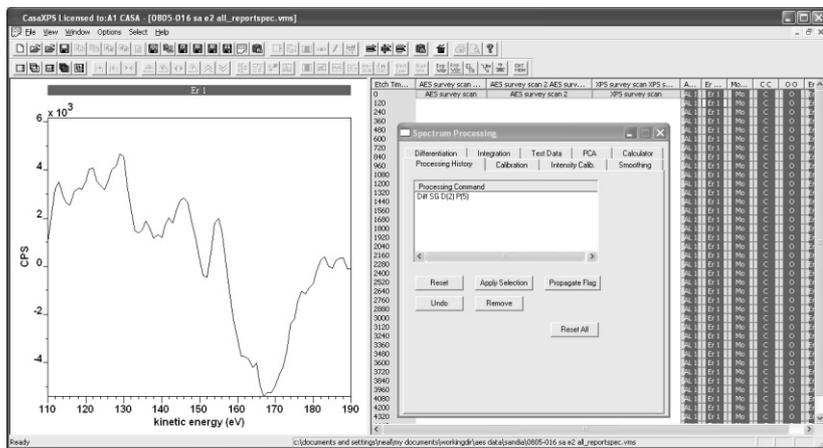


Only the spectrum in the active tile is affected by the Differentiation property page. When other spectra are included in the experiment and also require differentiation, the processing performed on the spectrum in the active tile can be propagated to data selected in the right-hand panes of the experiment frame as follows:

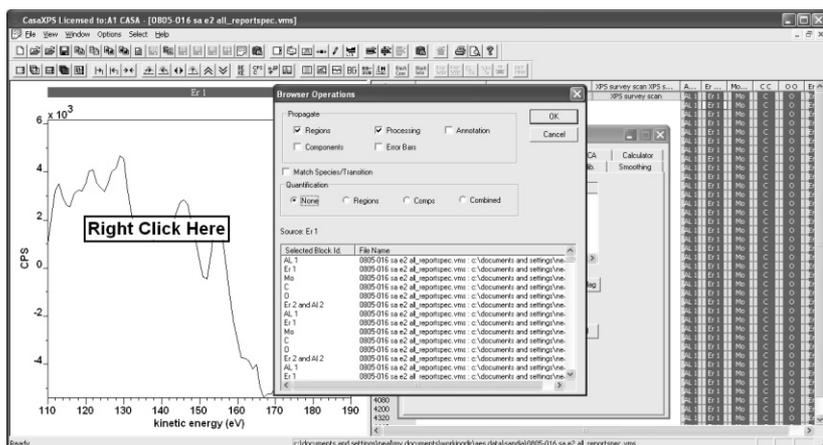
1. Display a spectrum in the active tile for which the differentiation operation is already performed and the Processing History property page displays the text string for the differentiation instruction (e.g. Diff SG D(2) P(5)).



2. Select the data blocks in the right-hand pane for which the differentiation operation is also required.



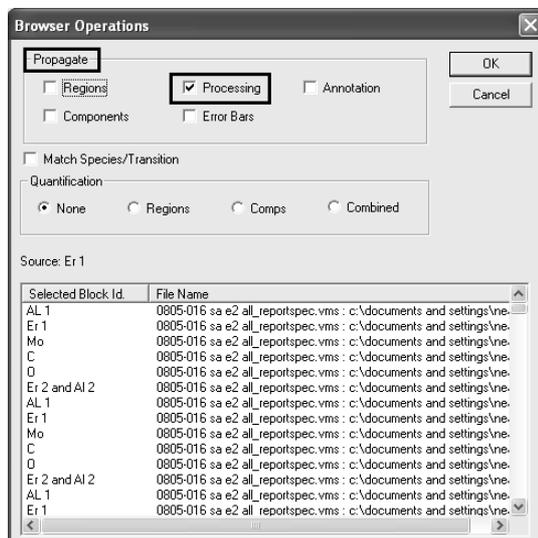
3. Place the cursor over the active tile in the left-hand pane and invoke the Browser Operations dialog window by right-click the mouse button.



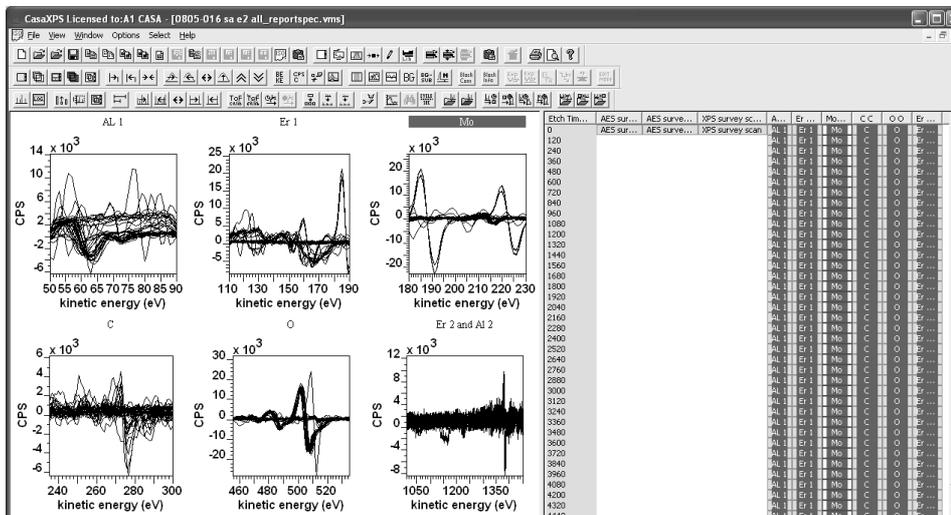
The Browser Operations dialog window lists those VAMAS blocks selected in the right-hand pane of the experiment frame and offers a set of tick-boxes which specify the type of information to be propagated from the VAMAS

block displayed in the active tile to the set of VAMAS blocks in the scrolled list.

4. Check the list of selected VAMAS blocks on the dialog window and tick the propagate Processing tick-box.



5. Press the OK button on the dialog window and confirm that the data are now displayed as differentiated spectra.



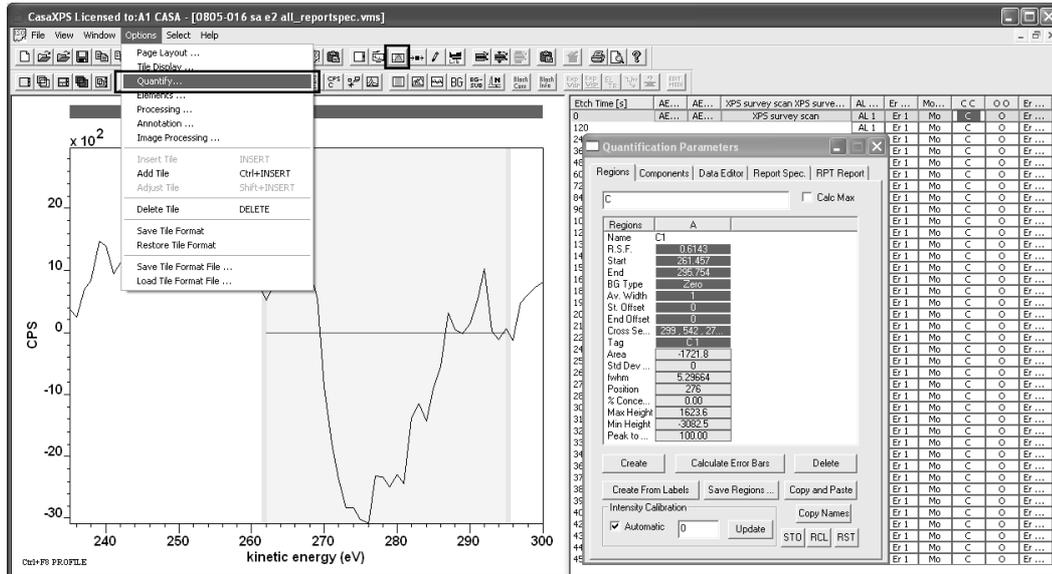
## Quantification Regions for AES data

Peak-to-peak intensities are measured using quantification regions. Quantification regions specify:

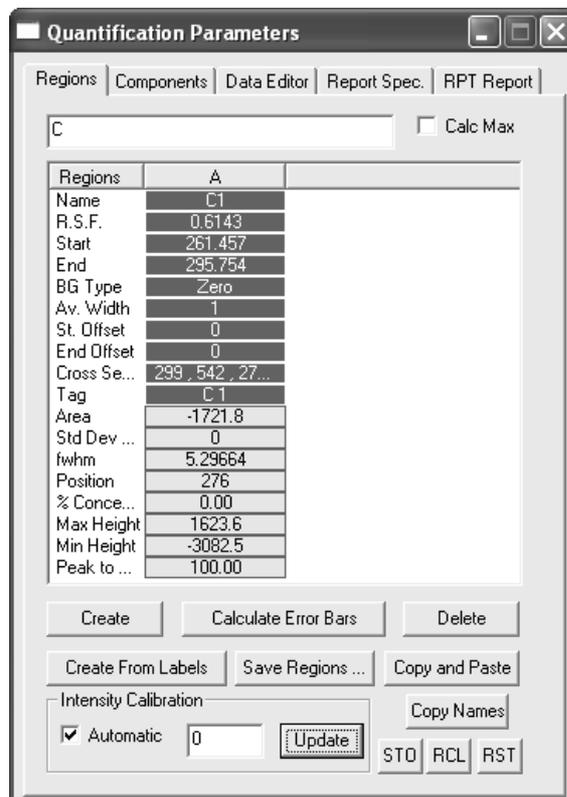
1. The name for the region; also referred to as the quantification item name.
2. The relative sensitivity factor, labelled RSF, for the peak intensity.
3. The energy interval over which the peak-to-peak intensity should be determined.

Quantification regions are used for XPS data and therefore other fields such as background type are also present on the Regions property page, but for peak-to-peak measurements these other fields are of no importance.

The Quantification Parameters dialog window is available from the Options menu or via the top toolbar.



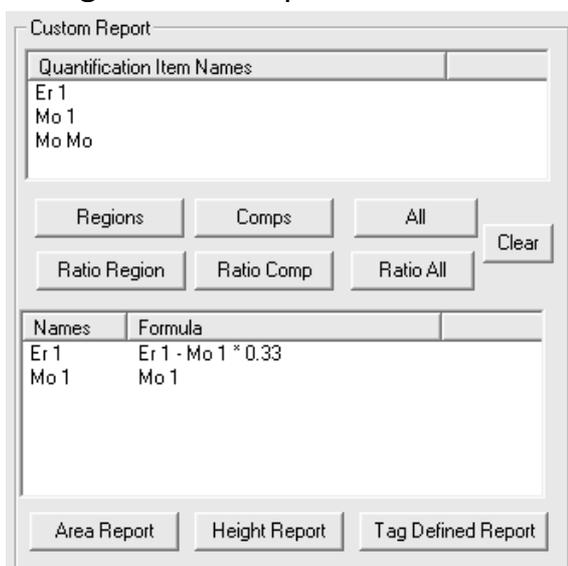
A region is manually specified using the Regions property page on the Quantification Parameters dialog window:



The name field in the quantification region is used to label the values computed for the region in quantification reports.



Meaningful names improve the readability of quantification reports. Further, the name field is used for manipulating intensities in the Custom Report used for depth profiling experiments and therefore region names used in the Custom Report should begin with an alphabetic character.



The peak-to-peak intensity is scaled using the RSF field on the Regions property page.



The RSF is typically stored in the element library and retrieved using the Element Library dialog window as described below.

The energy interval over which the peak-to-peak intensity is computed is defined using two limits labelled start and end.

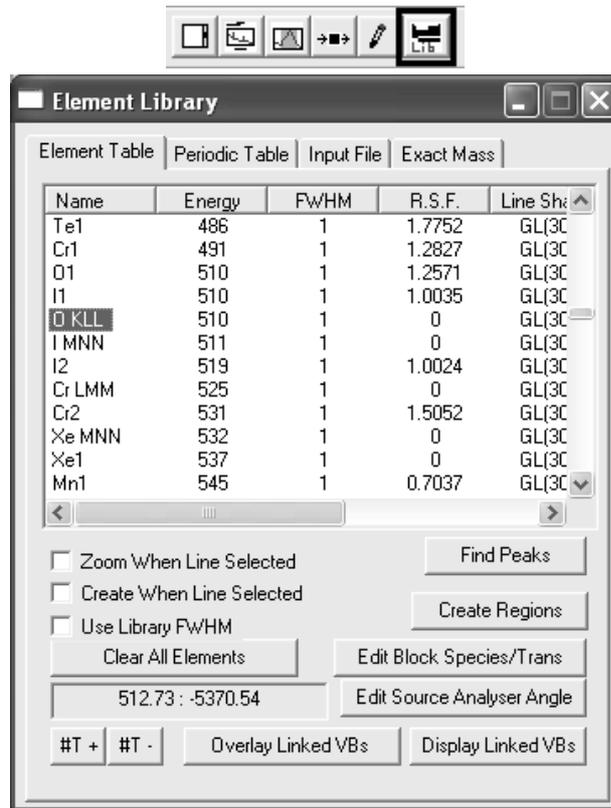


While the background type for peak-to-peak intensities is irrelevant from the computational point of view, from a display perspective a background type of zero provides a more meaningful reference than the typical XPS background types.

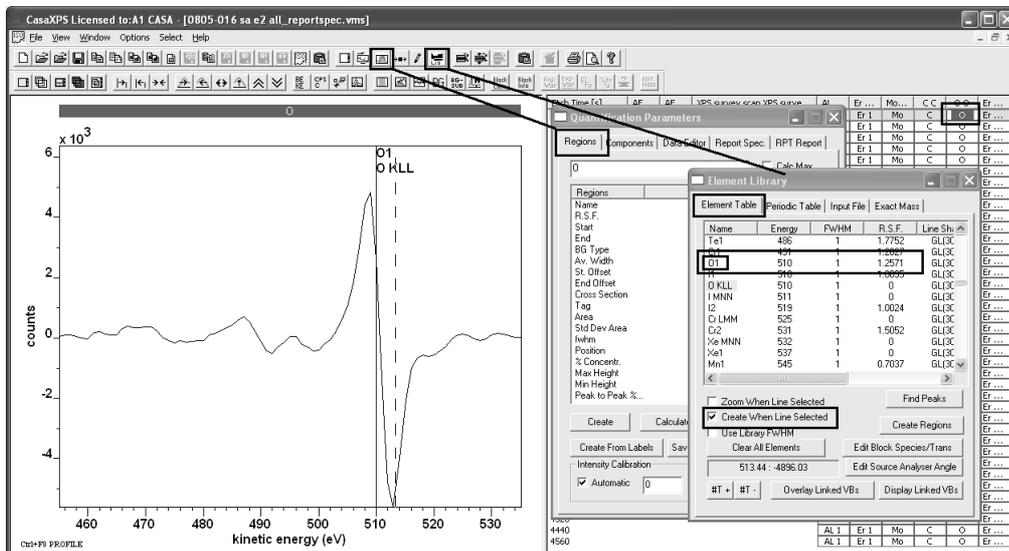
END	430.754
BG Type	Zero
...	1

## Creating Quantification Regions using the Element Library

The advantage of creating quantification regions using the element library lies in an explicit selection of the transition and therefore RSF appropriate for the Auger peak. Regions are created using the Element Table property page.



The scrolled list on the Element Table property page combines with the Regions property page on the Quantification Parameters dialog window to create regions for the spectrum displayed in the active tile.

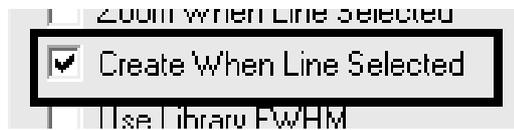


To create a region using the Element Table property page:

1. Display a spectrum in the active tile.
2. Invoke both the Quantification Parameters and Element Library dialog windows.



3. Left-click the mouse with the cursor over the Auger peak in the left-hand pane of the experiment frame. The table on the Element Table property page scrolls to display those energies around the energy indicated with the cursor and mouse.
4. Tick the box on the Element Table property page labelled Create When Line Selected.



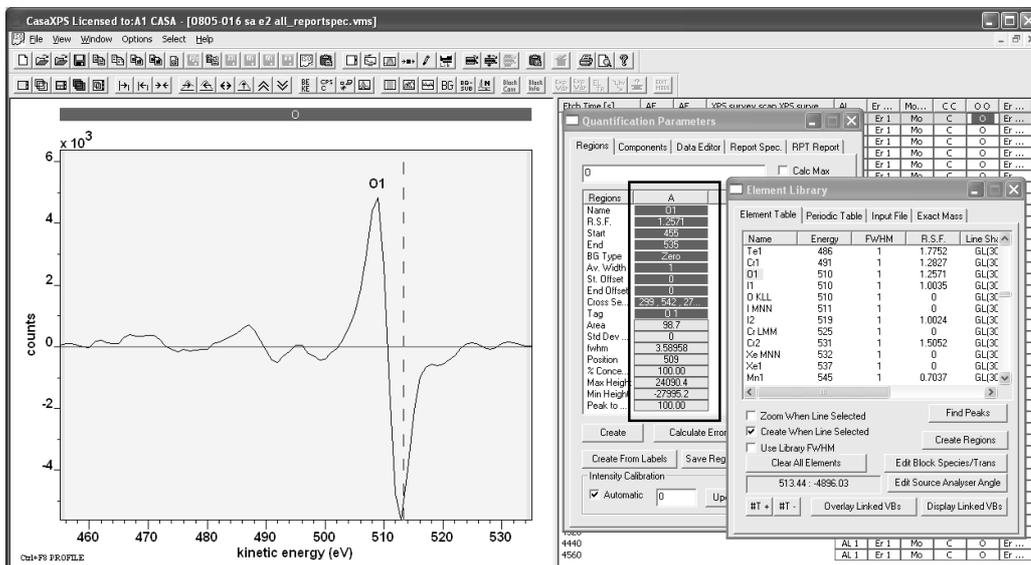
5. Ensure the Regions property page is top-most on the Quantification Parameters dialog window.



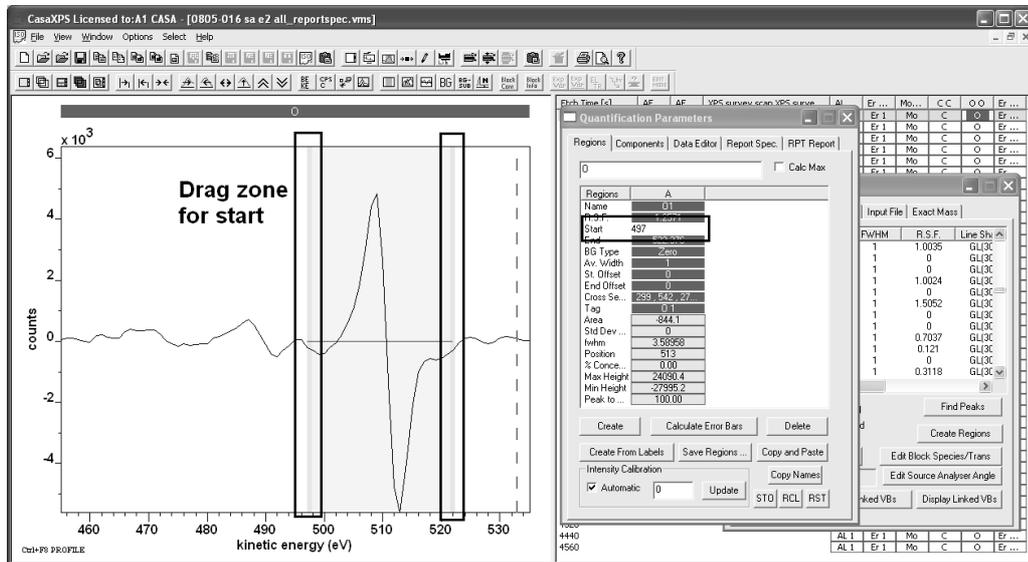
6. Using the name field on the Element Table list, select the transition corresponding to the data in the active tile.

O1	491	1	1.2827
O1	510	1	1.2571
O1	510	1	1.0035

A region is created with name and RSF assigned from the element library entry selected.



- Adjust the start and end for the quantification region by either entering new values on the Regions property page or under mouse control.

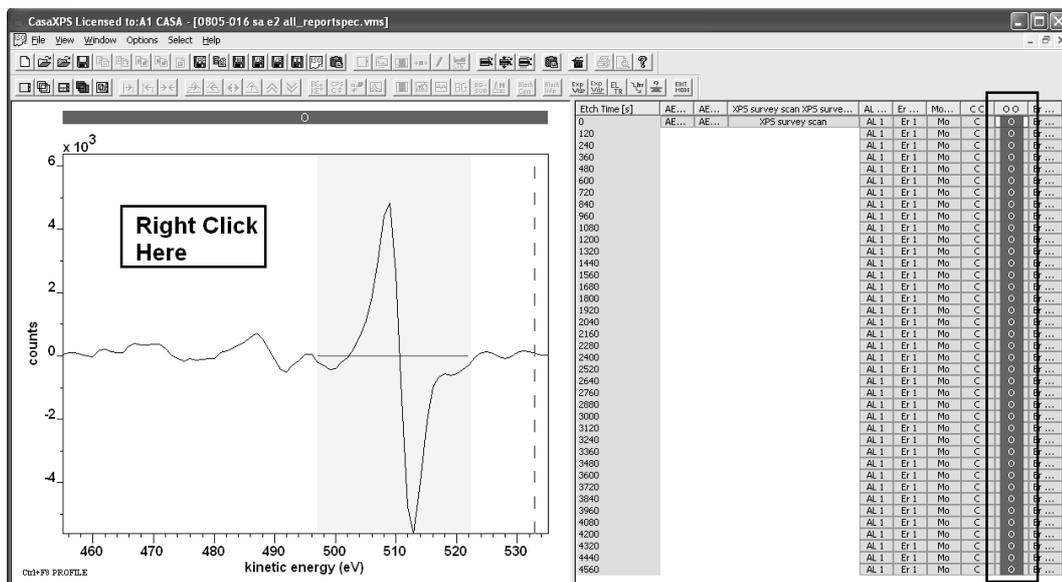


## Propagation of Quantification Regions

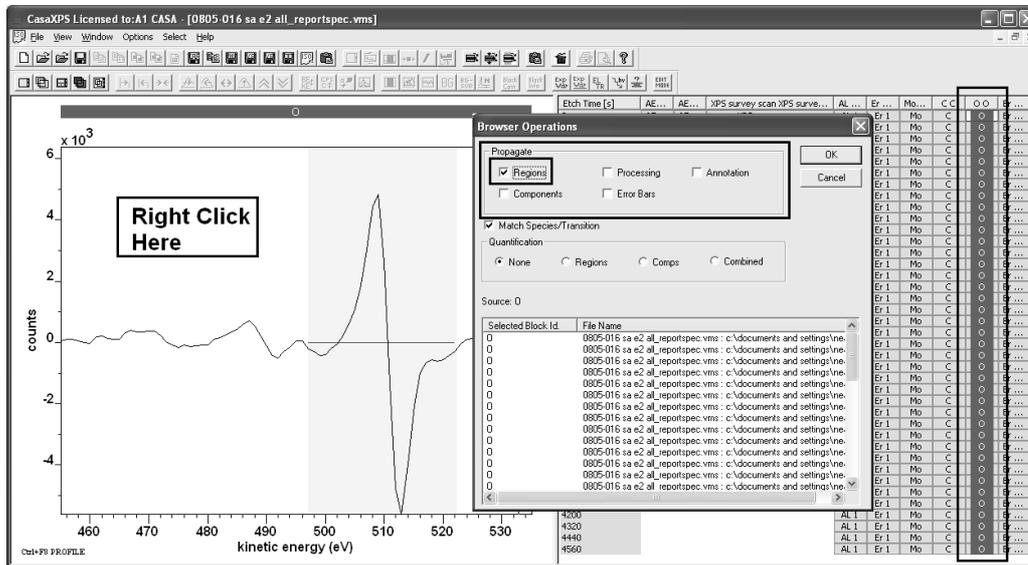
A region defined on a spectrum can be propagated to other spectra for the same transition. The propagation of regions is analogous with the propagation of processing operations described above in the context of differentiating a data set of many direct spectra.

To propagate a region:

- Display the spectrum for which a region is defined in the active tile.
- Select the set of VAMAS blocks in the right-hand pane to which the region in the active tile is to be copied.

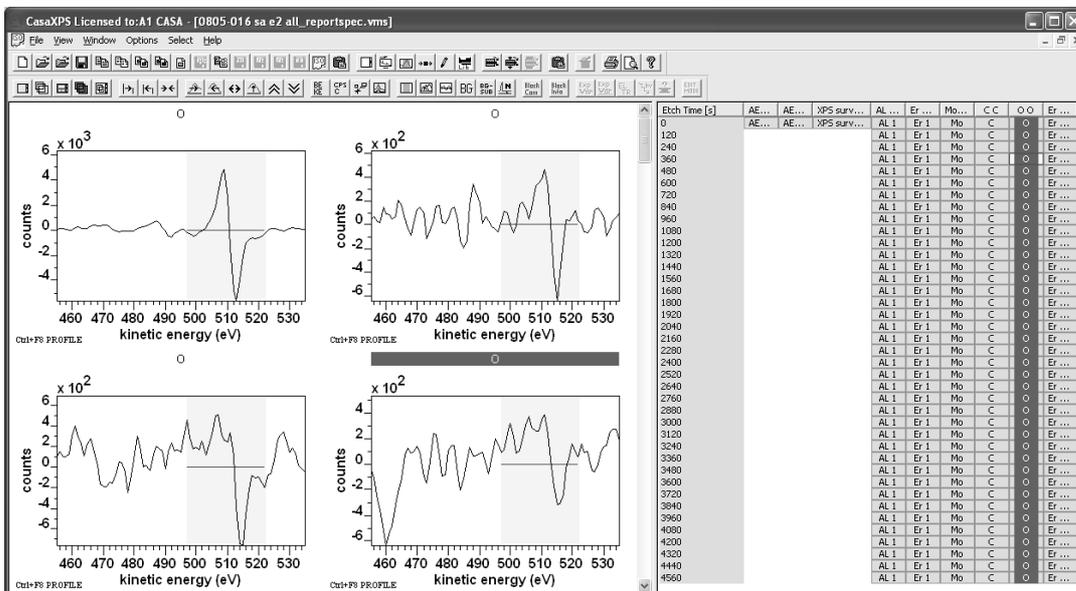


- Right click the mouse with the cursor over the left-hand pane and select the tick box labelled Regions in the Propagate section of the Browser Operations dialog window.



- Check that the scrolled list on the dialog window contains the intended set of VAMAS blocks and press the OK button.

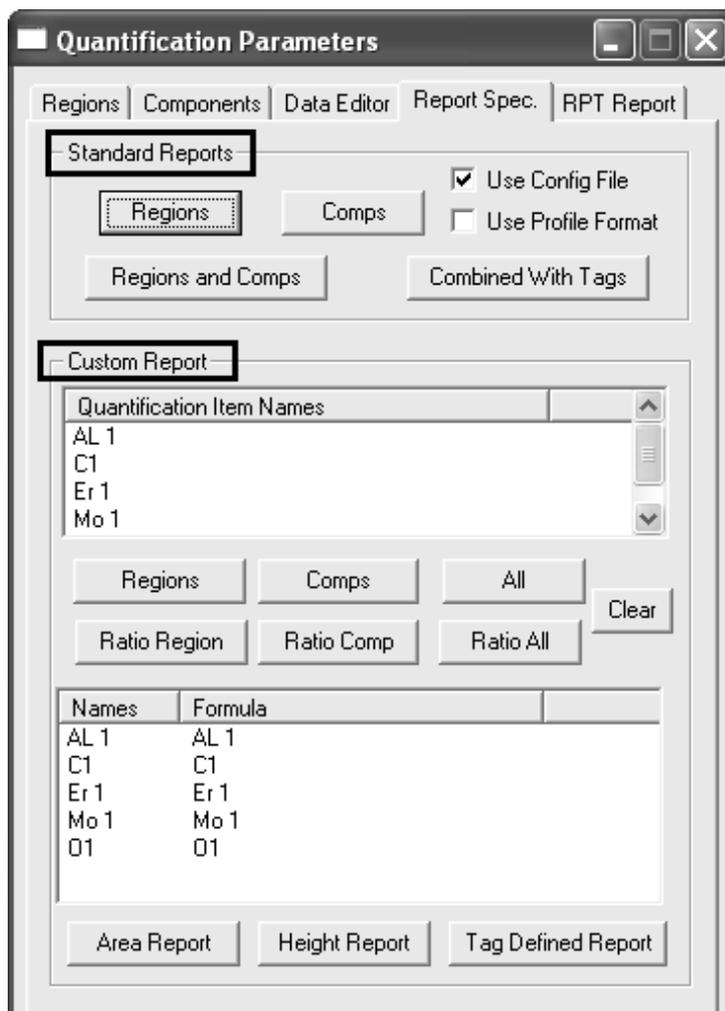
On completion, the set of spectra selected in the right-hand pane are populated with copies of the region or regions defined on the spectrum in the active tile.



## Quantification Reports

Quantification reports are generated from those VAMAS blocks selected in the right-hand pane of the experiment frame for which regions are defined. The Report Spec property page on the Quantification Parameters dialog

window offers the two principal mechanisms by which quantification reports are generated, namely, Standard Reports and Custom Reports.

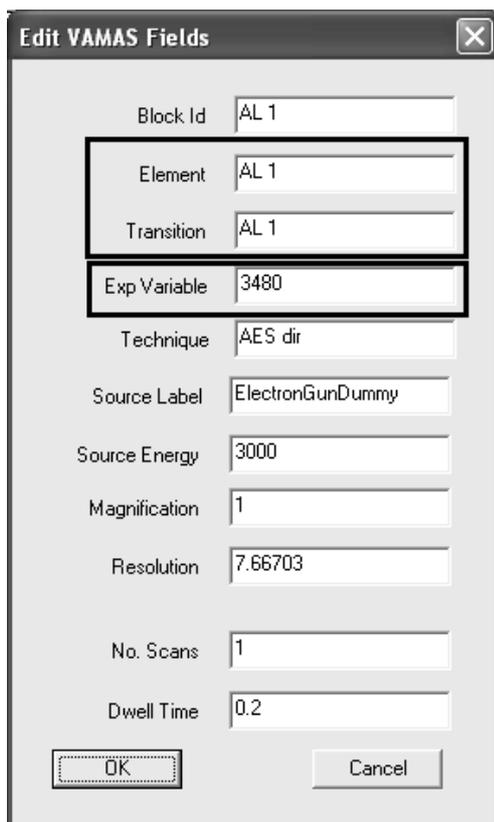


The Report Spec property page offers the means of quantifying data acquired as separate narrow scan spectra. The spectra used to quantify a surface composition must be displayed in the same row as viewed via the right-hand pane of the experiment frame.

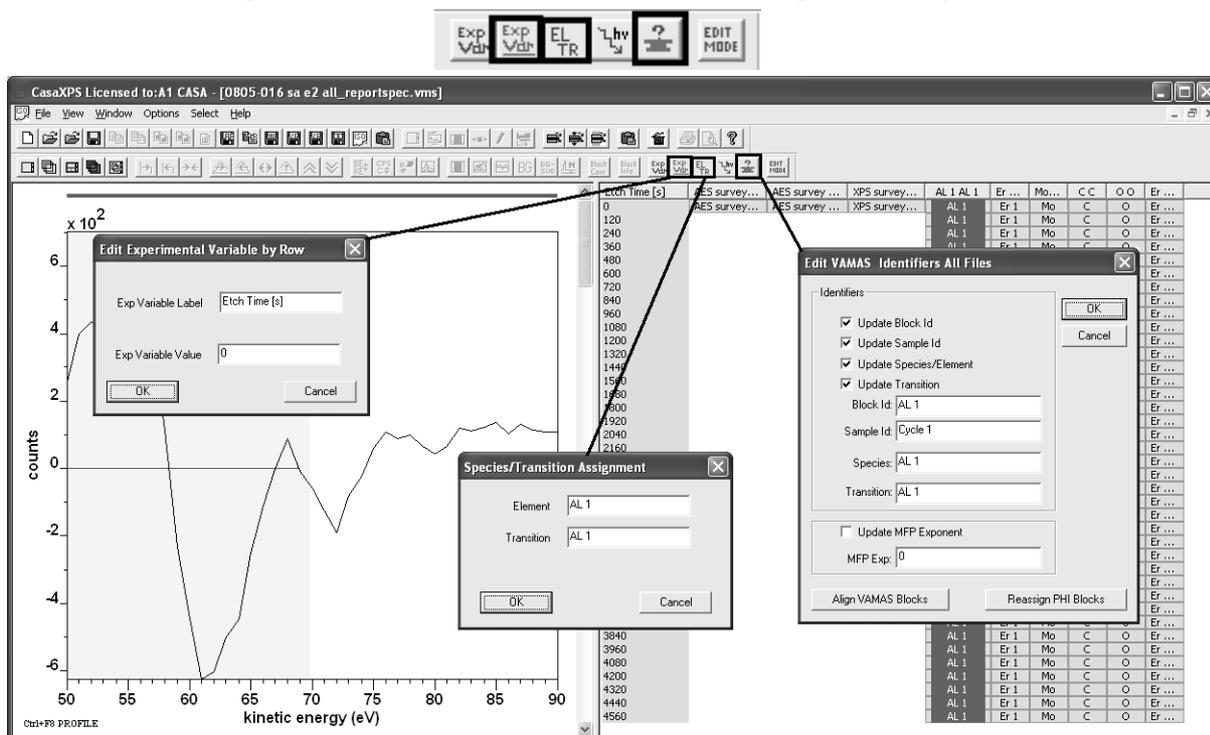
AL ...	Er ...	Mo...	CC	OO	Er ...
AL 1	Er 1	Mo	C	O	Er ...
AL 1	Er 1	Mo	C	O	Er ...
AL 1	Er 1	Mo	C	O	Er ...

The organisation of the VAMAS blocks in the right-hand pane is based on the element (species)/transition VAMAS fields in the data blocks and the experimental variable assigned to the VAMAS block. The values for these VAMAS block parameters may be altered using several toolbar options.





The Edit VAMAS fields dialog window acts on the data displayed in the active tile. Other dialog windows act on selections in the right-hand pane.

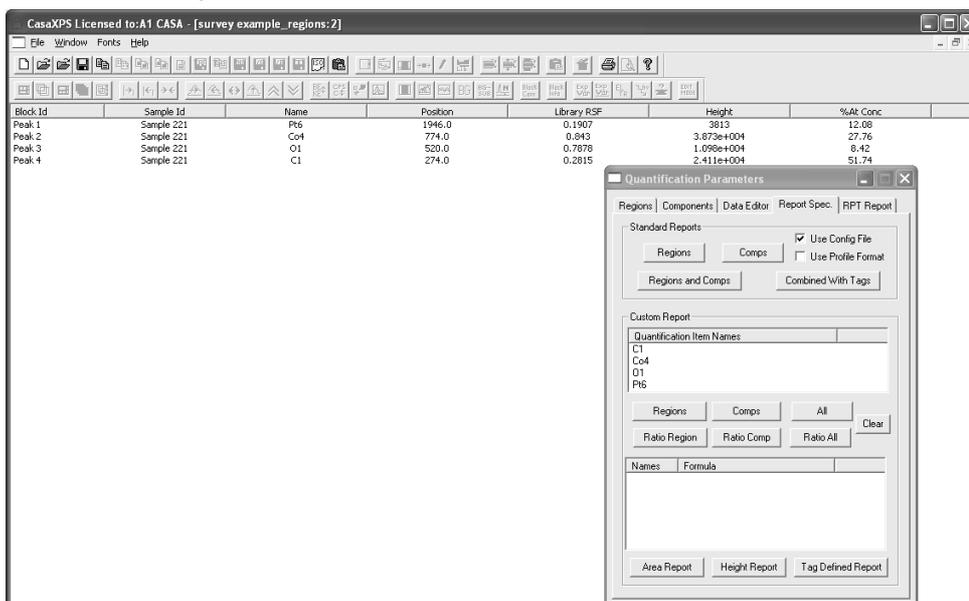


VAMAS blocks with the same element/transition fields appear in the same column in the right-hand pane, while VAMAS blocks with the same experimental variable appear, where possible, in the same row.

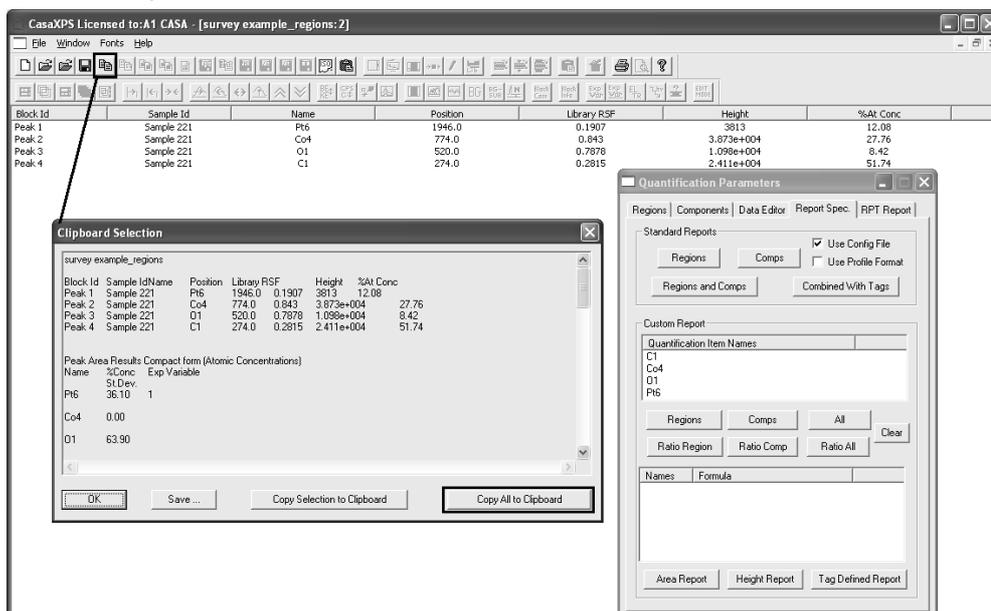


3. Invoking the Quantification Parameters dialog window and selecting the Report Spec property page.
4. Pressing the button labelled Regions in the Standard Report Section on the Report Spec property page.

When the Regions button is pressed, if the Use Config File tick-box is ticked a configuration file is used to define the information appearing in the text report. A detailed discussion regarding these configuration files is presented in a later section. The report generated from one specific configuration file appears as a text report in CasaXPS.



A quantification report generated from the standard report options is copied through the clipboard by pressing the Copy toolbar button or Control-C at the time the text report window has focus in CasaXPS.



Any program capable of accepting text via the clipboard can be used to further manipulate the data. The data placed on the clipboard includes a variety of tabulation formats, not all applicable to peak-to-peak data.

The screenshot shows a Microsoft Excel spreadsheet titled 'survey example\_regions'. The data is organized into two main sections. The first section, starting at row 3, contains a table of peak data with columns: Block Id, Sample Id, Name, Position, Library RS, Height, and %At Conc. The second section, starting at row 10, is titled 'Peak Area Results Compact form (Atomic Concentrations)' and contains a table with columns: Name, %Conc, and Exp Variable.

Block Id	Sample Id	Name	Position	Library RS	Height	%At Conc
Peak 1	Sample 221	Pt6	1946	0.1907	3813	12.08
Peak 2	Sample 221	Co4	774	0.843	3.87E+04	27.76
Peak 3	Sample 221	O1	520	0.7878	1.10E+04	8.42
Peak 4	Sample 221	C1	274	0.2815	2.41E+04	51.74

Name	%Conc	Exp Variable
Pt6	36.1	1
Co4	0	
O1	63.9	
C1	0	

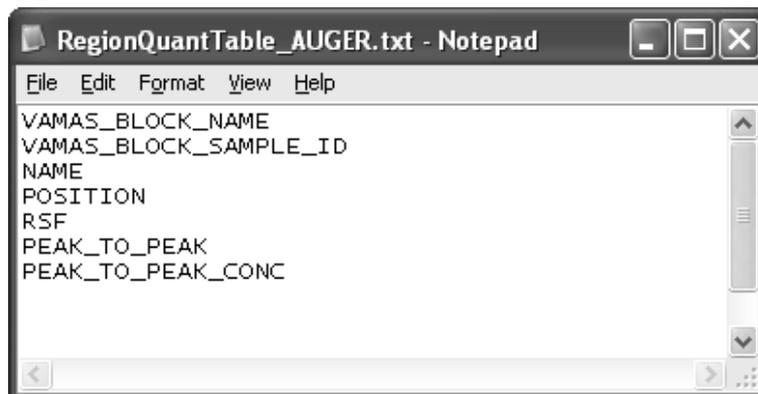
### ***Configuration Files for Standard Reports***

The configuration files for the standard report are constructed from a set of keywords entered into an ASCII file one keyword per line. The keywords are:

Keyword	Description
VARIABLE	Experimental Variable value from the VAMAS block or Row Label when in Edit Mode
NAME	Region or component name.
POSITION	Peak position.
FWHM	Peak full width at half maximum
AREA	Peak area correct for transmission and energy dependence but not RSF
RSF	Relative Sensitivity Factor
CONCENTRATION	% Atomic Concentration
ERROR_BAR	Std Deviation in % atomic concentration for regions
START	Quantification region lower limit
END	Quantification region upper limit
PEAK_TO_PEAK	Intensity for peak to peak Auger Peak intensity maximum to minimum XPS/SIMS peak height above background
PEAK_TO_PEAK_CONC	% Concentration measured using peak to peak intensity
LINE_SHAPE	Synthetic line-shape for a component
AREA_ERROR_BAR	Std Deviation in peak area measured using a quantification region.
TRANSITION_TAG	Tag string from region or component
POSITION_CONST	Component position constraint string
AREA_CONST	Component area constraint string
FWHM_CONST	Component FWHM constraint string

COLUMN_LABEL	Column character appearing above a region or component on the respective property page
DEGREES_OF_FREEDOM	Degrees of freedom used to compute the figure of merit from least squares fit.
VAMAS_BLOCK_NAME	VAMAS block identifier
CENTROID	Position of the centroid of a peak
MASS	Mass assigned to a region or component
MASS_CONC	% Mass Concentration
SIGNAL_TO_NOISE	Std Dev for noise distribution
CORRECTED_AREA	Peak area corrected by the total sensitivity factor
TOTAL_SENSITIVITY_FACTOR	Combined factor from RSF, Transmission and energy dependence factors
TRANSMISSION	Transmission function value at peak maximum
MEAN_FREE_PATH	Kinetic energy dependence factor
RAW_AREA	Uncorrected integral of background subtracted signal
PEAK_PLUS	Peak intensity above background
PEAK_MINUS	Peak intensity below background
SIMS_PEAK_AREA	Summation of data channel
VAMAS_BLOCK_SAMPLE_ID	VAMAS Sample Identifier string

Notepad or any other means of creating an ASCII file can be employed to create the configuration files.

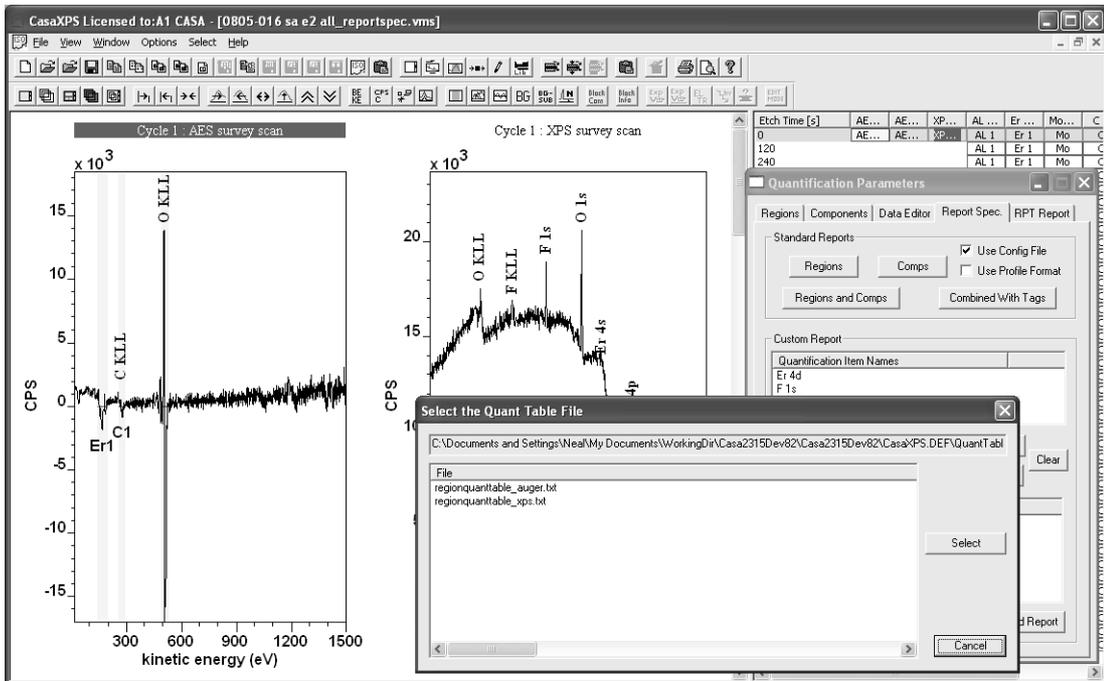


The configuration file used to generate the standard report is located on the disk relative to the directory containing the CasaXPS.exe executable file. Within the same directory as the CasaXPS.exe executable file is a directory called CasaXPS.DEF. Default settings enabled on starting a new CasaXPS session are also saved in the CasaXPS.DEF directory.

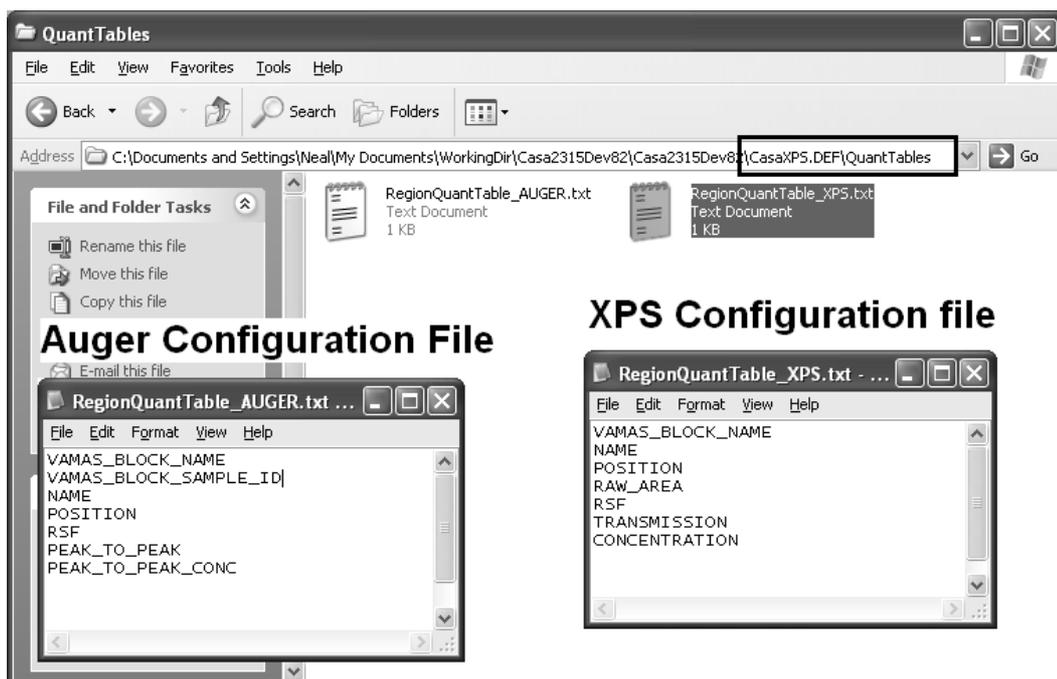
Each type of configuration file for the standard report options is identified by key names; specifically, the file called RegionQuantTable.txt provides the configuration information for the columns in the standard report generated when the Regions button in the standard report section is pressed. Similarly, other configuration files with key names are associated with the other reporting options in the standard report section. These configuration files are used by default each time a standard report is requested and are most

appropriate for those users requiring a fixed format for each report generated.

A further feature allows a choice of configuration files. If a directory exists in the CasaXPS.DEF directory by the name of QuantTables, then on pressing a standard report button the user is offered a list of configuration file. The report format is dependent on the choice made from the list.

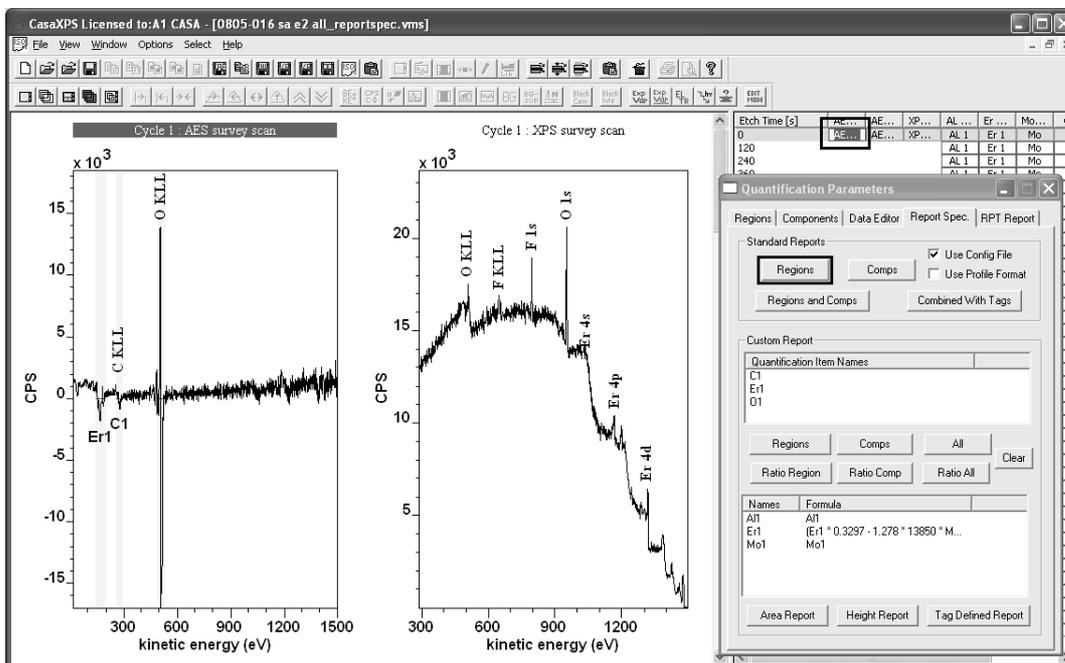


Since all files in the directory CasaXPS.DEF/QuantTables are offered in the dialog window, the names of the files within the QuantTables directory are unimportant and therefore the correct configuration file for the type of data must be selected.

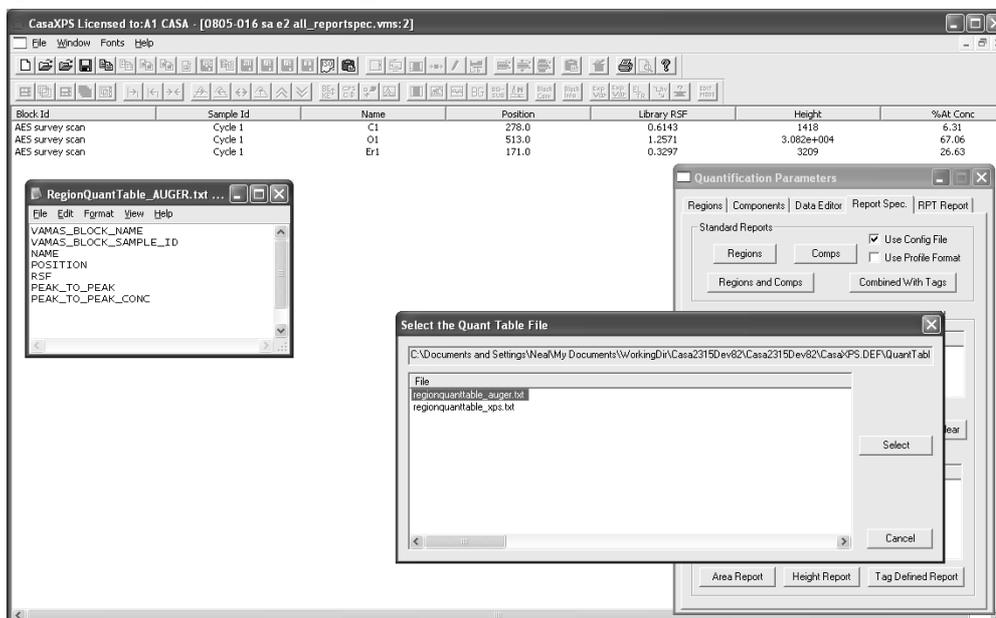


To quantify the Auger survey:

Select in the right-hand pane the VAMAS block containing the AES survey spectrum and press the Regions button from the Standard Report section.

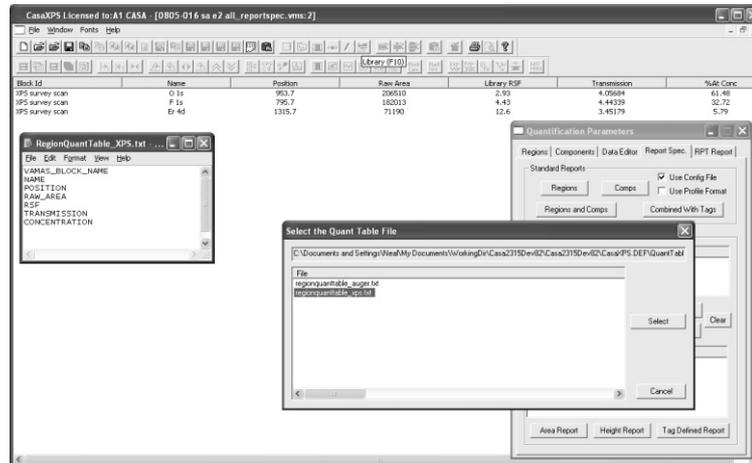


On the resulting dialog window, select the configuration file from the list and press the Select button. The quantification table appears with column headings defined by the configuration file.

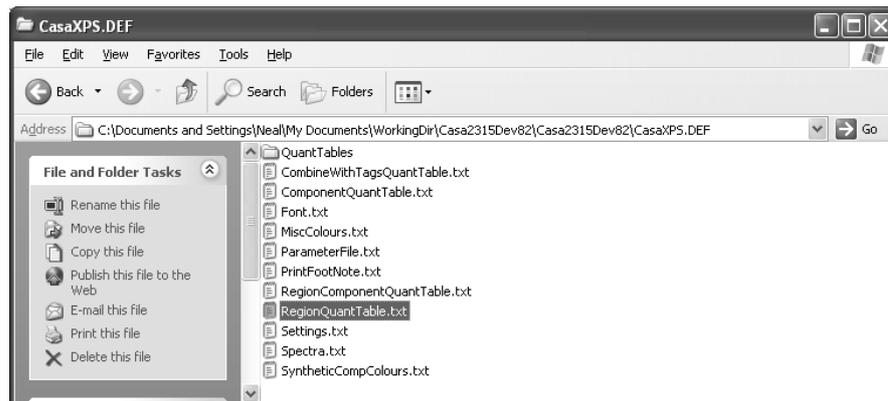


A different report is obtained from a similar sequence of steps for the XPS survey spectrum recorded from the same sample and located in the same VAMAS file. By selecting the configuration file prepared for XPS data an appropriate report is selectively produced; XPS spectra are typically

quantified using peak area after background subtraction rather than the peak-to-peak approach of Auger spectra.



In the event no selection is made from the dialog window invoked by pressing the Regions button, the default configuration file for the Regions button is used to generate the report. The default configuration file for the Regions button on the Standard report is located in the CasaXPS.DEF directory with the key name RegionQuantTable.txt.



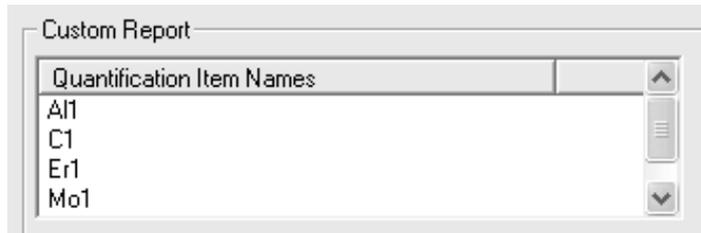
The selection dialog window only appears if the QuantTables directory exists in the CasaXPS.DEF directory. The default configuration file for the Regions button is automatically used if the CasaXPS.DEF directory is prepared *without* the QuantTables subdirectory.

## Custom Reports

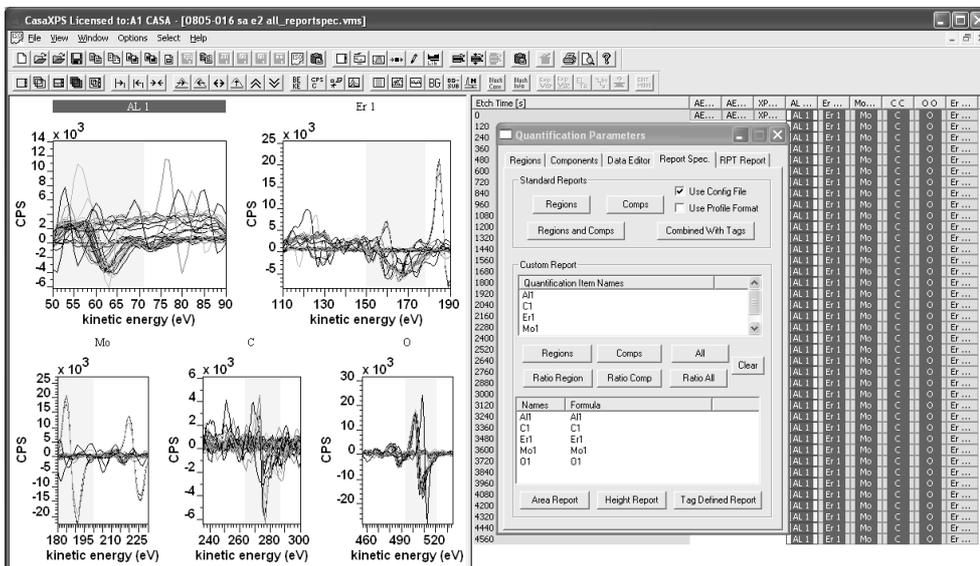
Custom reports are not configurable and data are presented in columns with each row of the table associated with an experimental variable. The intention is to provide a means of profiling changes in spectra with respect to etch time or angle or any parameter that varies through the course of an experiment.

The Custom Report, like the Standard Report, only applies to the current selection in the right-hand pane of the experiment frame. Regions and

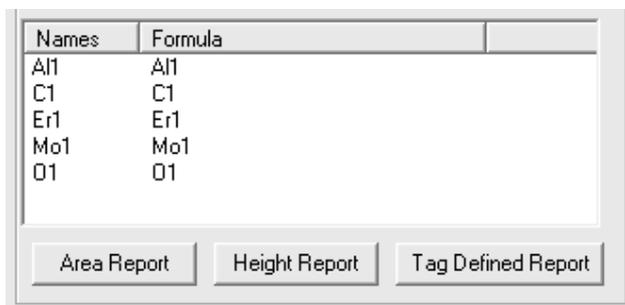
components are treated identically within the custom report and are referred to as quantification items, where both forms of these quantification items are identified by the name fields used in the definition of the regions and components. When a VAMAS block is selected in the right-hand pane, all the region names and component names are collected into a list displayed under the heading Quantification Item Names.



Only quantification item names appearing in the Quantification Item Names list are used in the custom report.

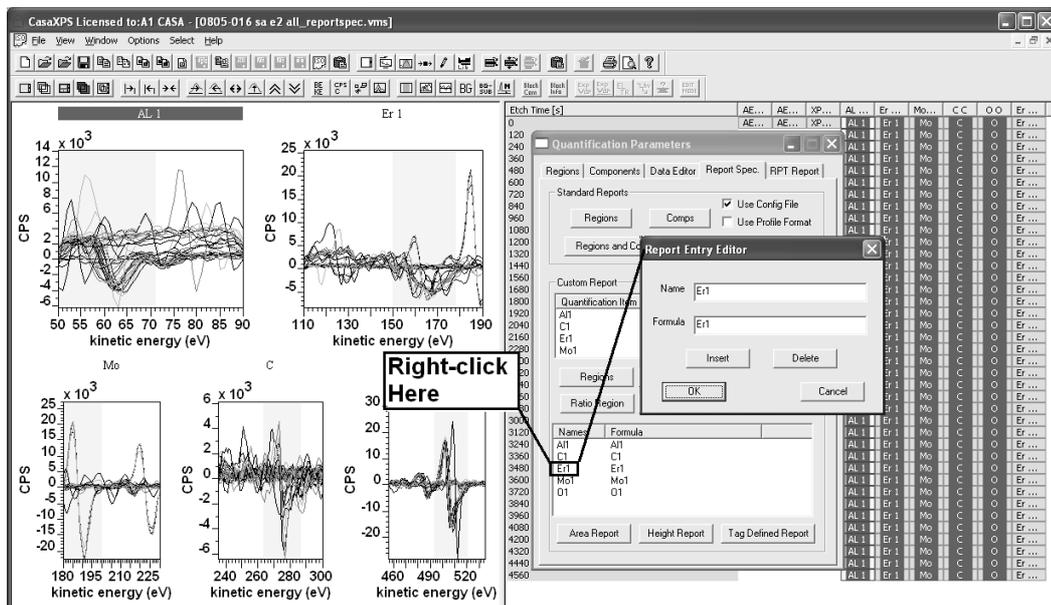


A custom report is defined in terms of the currently active quantification item names using the Name and Formula table.



The Names and Formula table can be initially populated using the set of buttons between the two tables. Pressing the Regions button between the Quantification Item Names table and the Names and Formula table causes the set of unique region names currently displayed in the Quantification Item Names table to be transferred to the Names and Formula table. The Names

and Formula entries can be edited by right-clicking the mouse with the cursor over a name entry in the lower table.

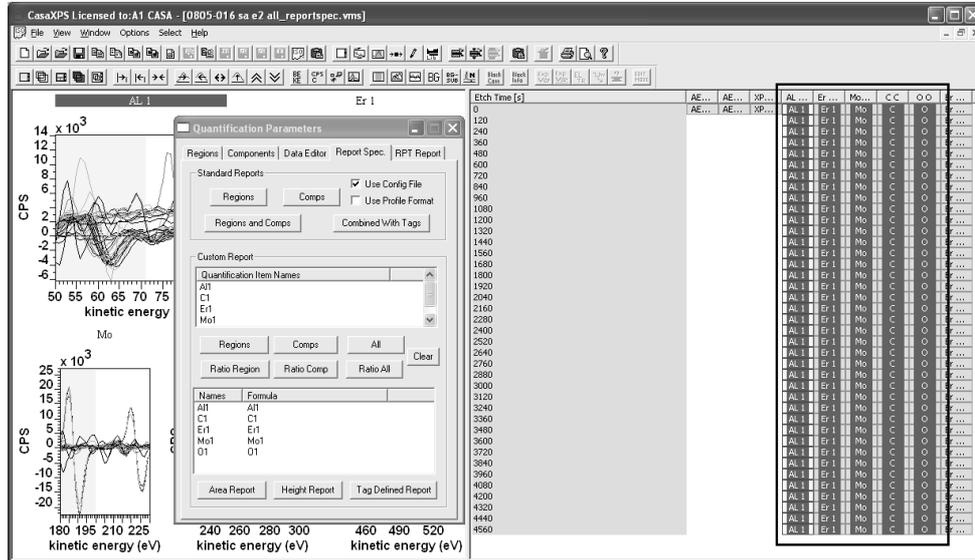


The function of the buttons between the two tables is to provide an initial state for the Names and Formula table. Although the action apparently loads the Names and Formula table using information from Regions, for example, it is important to note that any component with the same name as a region will also be included in the custom quantification report regardless of whether the Region button was initially pressed. The objective for the custom report is to provide a flexible means of combining intensities from both regions and components, so to differentiate between regions and components different name should be used.

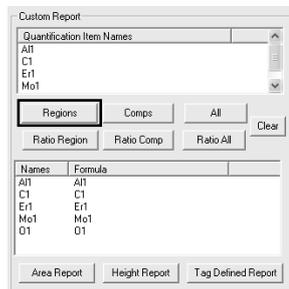
A further word of warning is that any quantification item with identical names will be summed together. This feature makes it doubly important that regions and components should be assigned different names. The consequence of not using unique names for regions and components is the intensities will effectively be doubled for any spectrum for which a region defines the background for a component. Peak fitting with components is rarely performed for Auger spectra, so this warning is less important for Auger as for those using XPS, but nevertheless, custom reports will sum regions with identical names therefore an awareness of the mechanism is important.

For the purposes of profiling the data being used as an example, initially a custom report simply based on the region names is sufficient. To create the Names and Formula entries:

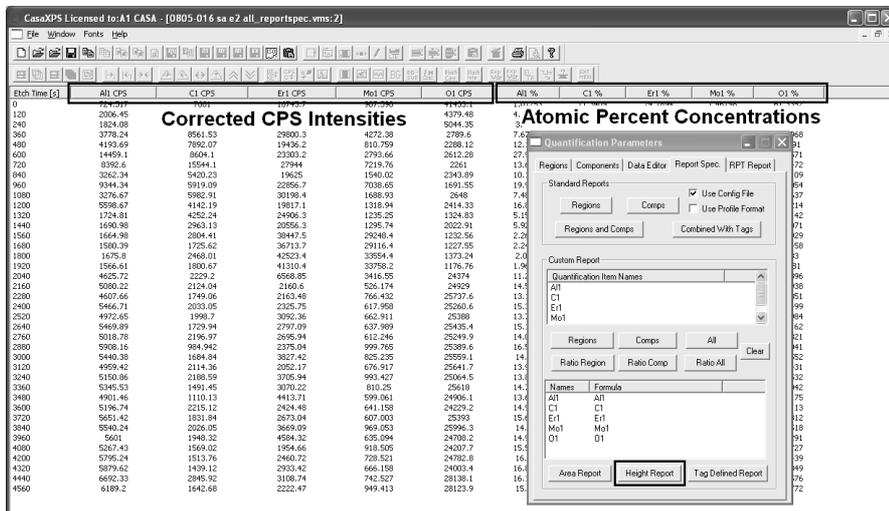
1. Select the VAMAS blocks containing the quantification regions previously prepared.



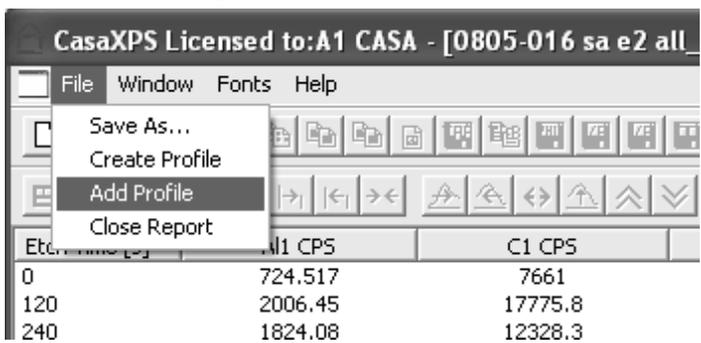
2. Press the Regions button between the two tables in the custom report section.



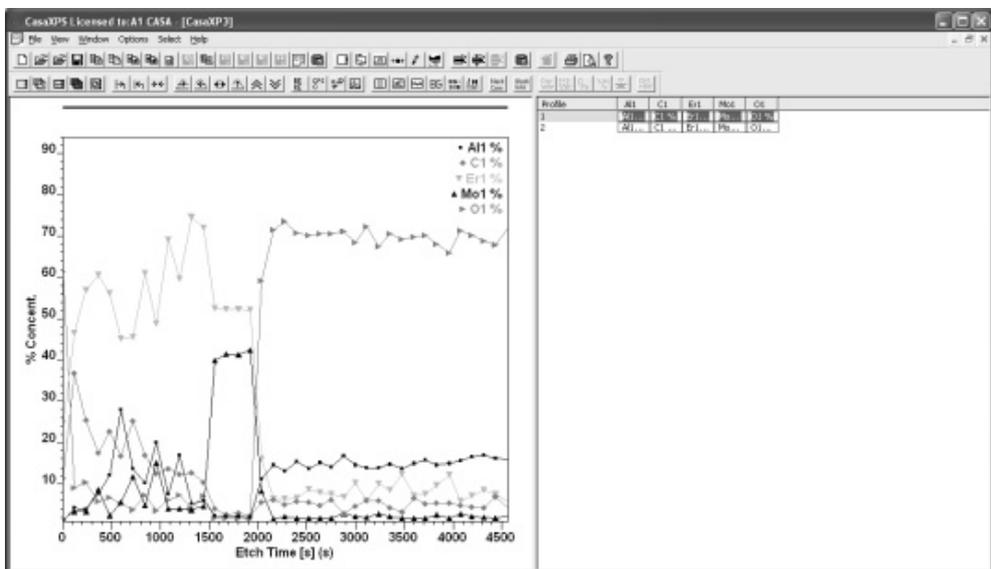
3. Since the data are in derivative form and therefore peak-to-peak intensities and RSFs are in use, press the Height Report button in the custom report section.



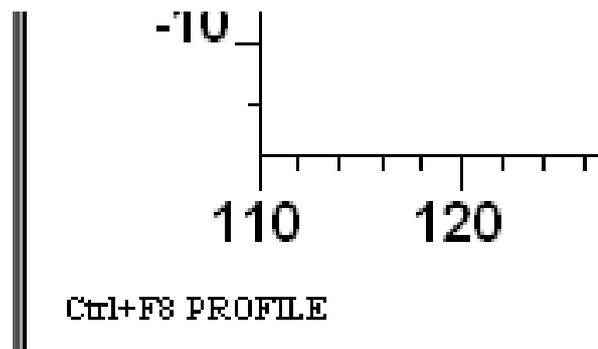
The resulting quantification table represents two sets of traces, namely, a set of corrected peak intensities in CPS and a set of atomic concentrations expressed as a percentage. These data may be placed on the clipboard using the Copy toolbar button (or Control-C) and pasted into plotting software or further manipulated in CasaXPS. A VAMAS view of the profiles is obtained either as a separate VAMAS file or within the current spectrum file using the File menu offered while the report window has focus.



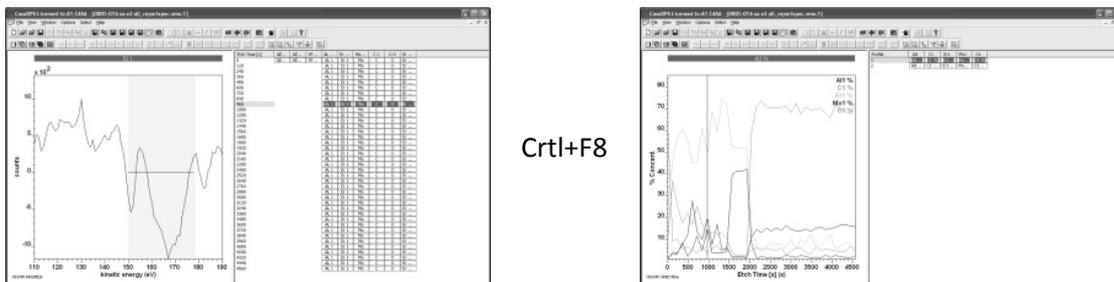
The Create Profile menu option causes a new experiment frame to appear containing two rows of VAMAS blocks. The top row corresponds to the atomic percentage columns in the quantification report, while the second row in the new experiment frame corresponds to the RSF corrected peak-to-peak intensities.



The second option for displaying the profile data allows the features in the profile to be correlated with the spectra from which the profile is derived. Selecting the Add Profile menu option from the File menu causes the profile data to be added to the original VAMAS file containing the spectra. When a profile is added to the spectral data, a string is added to the display of the spectra in the active tile.



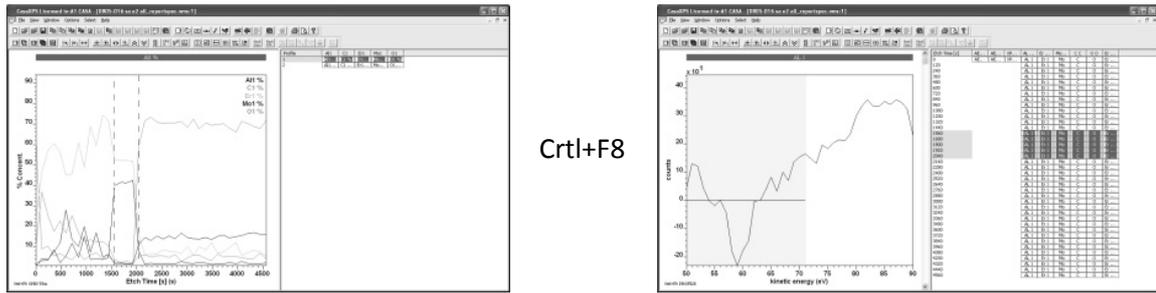
The string Ctrl+F8 Profile indicates that holding down the Control key on the keyboard and pressing the F8 function key cause the display to switch from spectra to the most recently added profile data.



A raw Auger depth profile may therefore be viewed in spectrum format, where rows of spectra ordered with respect to etch-time, and processed profile format, where traces computed from the spectra are plotted against etch-time. The Control+F8 key stroke not only switches between the two perspectives of the data, but also changes the display of the spectra based on the position of the cursor when viewed in profile format, or the displayed position of the cursor in the profile format based on the selection in the right-hand pane when viewed in spectrum format. The row currently selected in the spectrum format of the profile, and therefore the etch time, translates into to position of the cursor on the profile format of the data. Similarly, a cursor placed on the profile format of the data becomes a selected row of spectra when the Control+F8 action is pressed causing the display to revert back to the spectrum format.

It is also possible to indicate a range of spectra via the normal selection mechanism in the right-hand pane of the experiment frame displaying the spectra. On pressing Ctrl+F8, a pair of vertical cursors indicates where in the profile the selected spectra correspond in the profile. Again, if a pair of vertical cursors is placed on the profile trace, on switching back to the spectrum form of the data, the range of spectra indicated by the cursors on

the profile becomes selected in the right-hand pane of the spectrum form of the data.

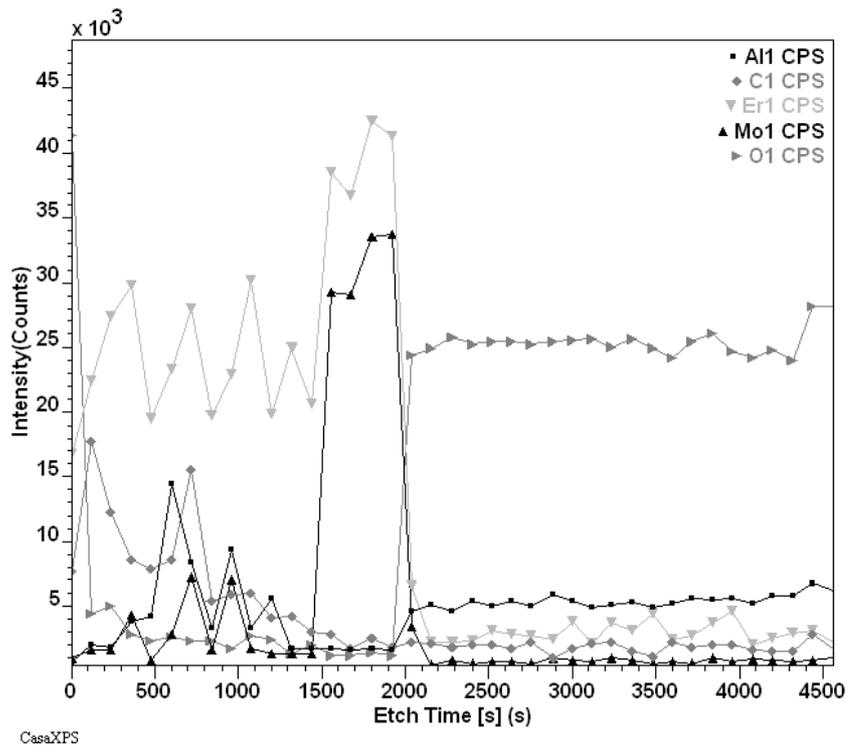


Ctrl+F8

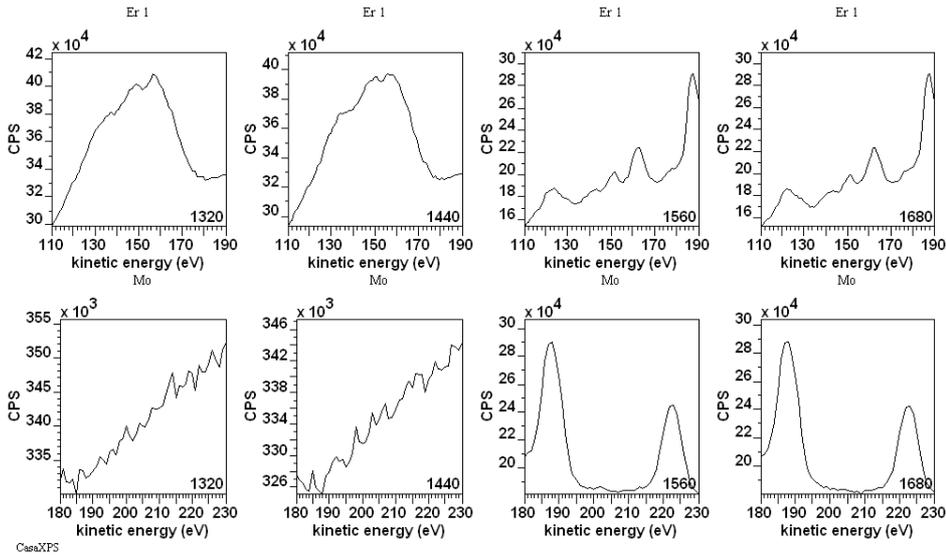
To mark the profile with a pair of cursors, hold the Shift key down while dragging the cursor across the active tile displaying the profile. On releasing the mouse button, the drag box marks the position of the two cursors.

**An Advanced use of the Custom Report**

The profile used to illustrate the custom report involves erbium and molybdenum. The basic profile created using region intensities suggests a correlation between the molybdenum layer and the erbium surface layer.



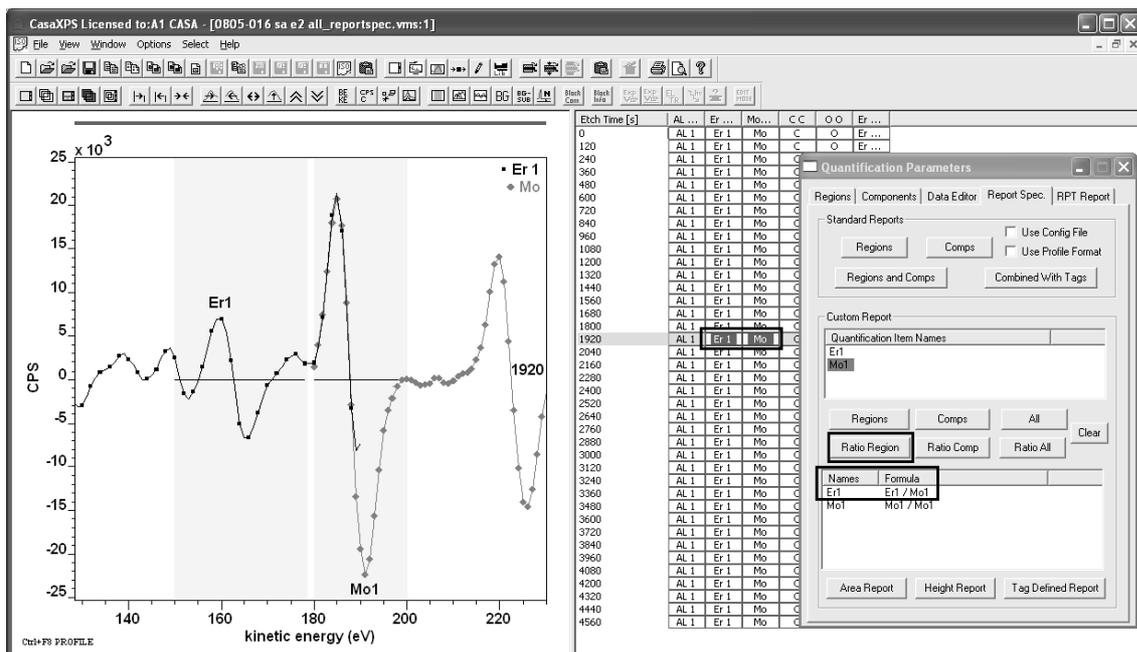
Since the erbium Auger peak used in the profile is located near a molybdenum peak, examining the intensity of the erbium will require a more detailed analysis than simply following the profiles of region intensities. Examining the direct spectra at etch-times close to the molybdenum interface confirms the influence of the molybdenum Auger line on the intensity measured for erbium.



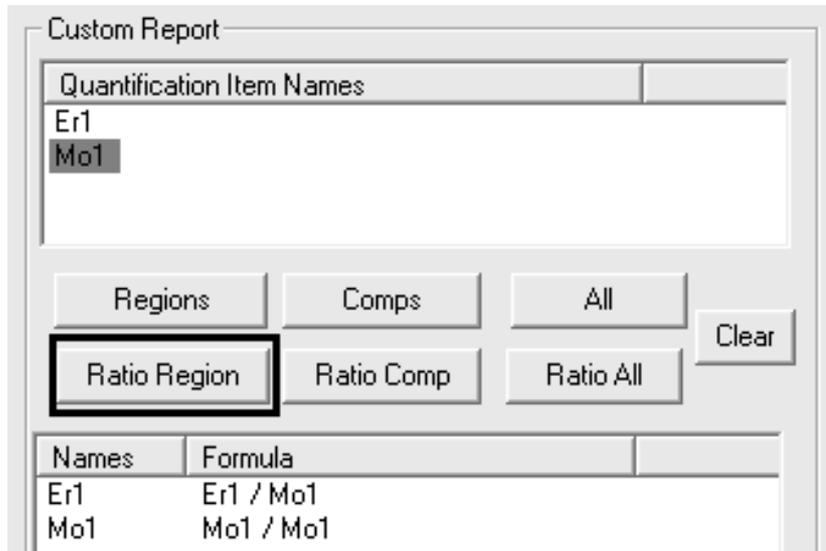
It is therefore proposed to calculate the erbium intensity using the molybdenum region to remove the molybdenum peak-to-peak intensity contribution from the erbium region. To estimate the relationship between the peak-to-peak intensity for the molybdenum interference and the Mo1 Auger transition, a representative pair of spectra is selected and used to measure the intensity ratio of the Er1 region to the Mo1 region, where it is assumed the Er1 region is at a point in the profile such that the erbium signal is negligible compared to molybdenum.

Measuring the ratio of these molybdenum peaks can be performed using the custom report:

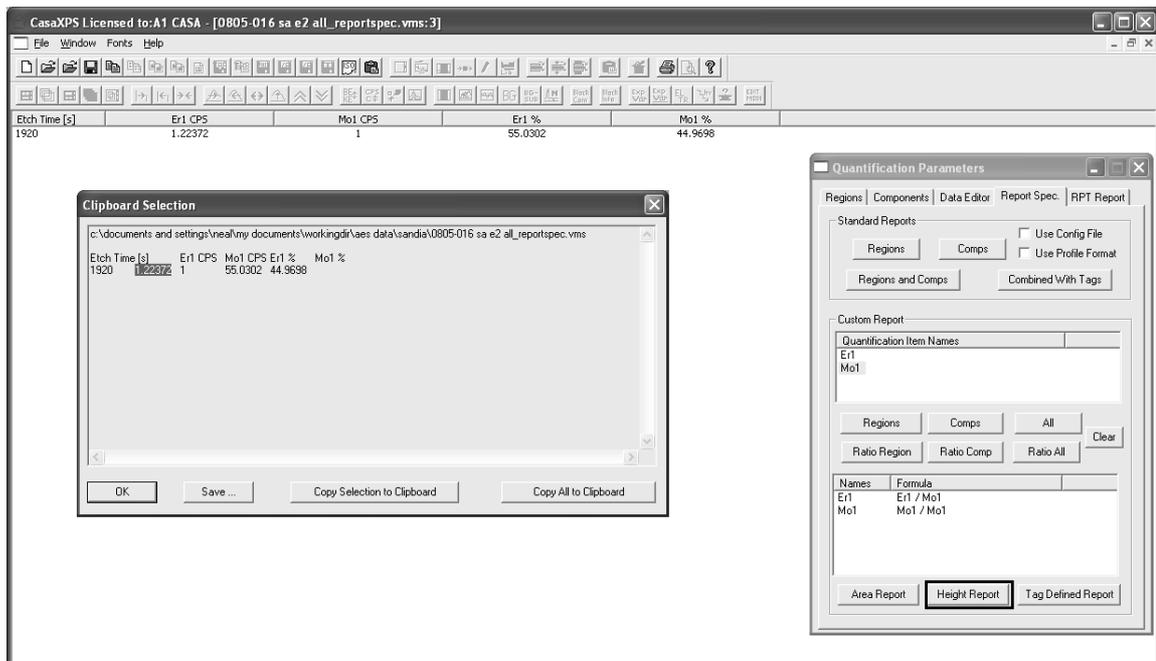
1. Select the two VAMAS blocks containing the erbium and molybdenum data for an etch-time where erbium is not significant.



2. Select the Mo1 name in the Quantification Item Names table on the Custom Report section of the Report Spec property page before pressing the Ratio Region button.

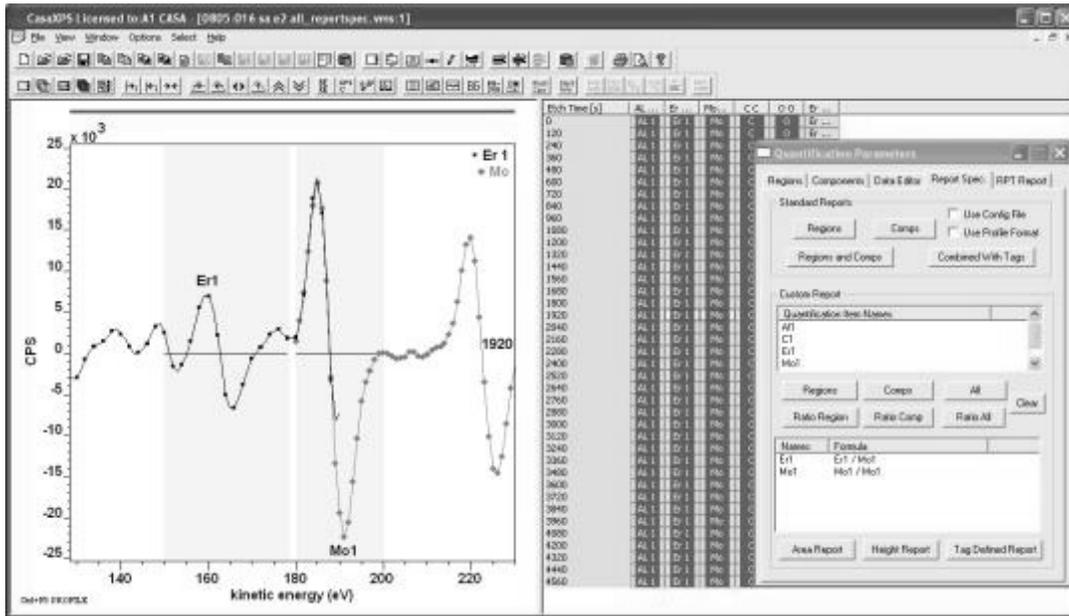


The Names and Formula table is populated with formulae involving a simple division with respect to the Mo1 quantification items selected in the table above. Pressing the Height Report button followed by the Copy toolbar button results in a dialog window from which the ratio can be selected, copied, and then pasted into a new set of formulae for profiling the full experiment.

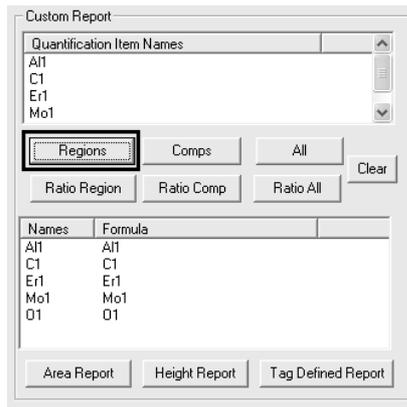


To profile the full experiment:

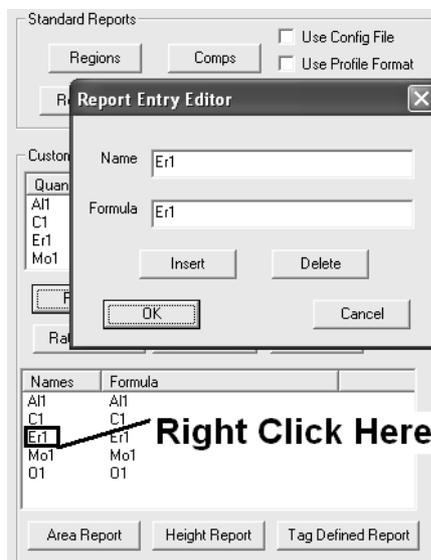
1. Select all the VAMAS blocks for which regions are defined.



2. Press the Regions button between the Quantification Item Names table and the Names and Formula table.



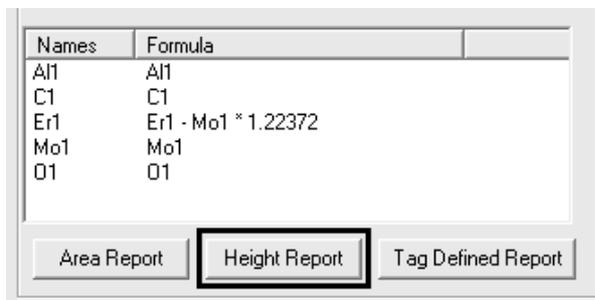
3. Right-click with the cursor over the name field for the Er1 entry in the Names and Formula table.



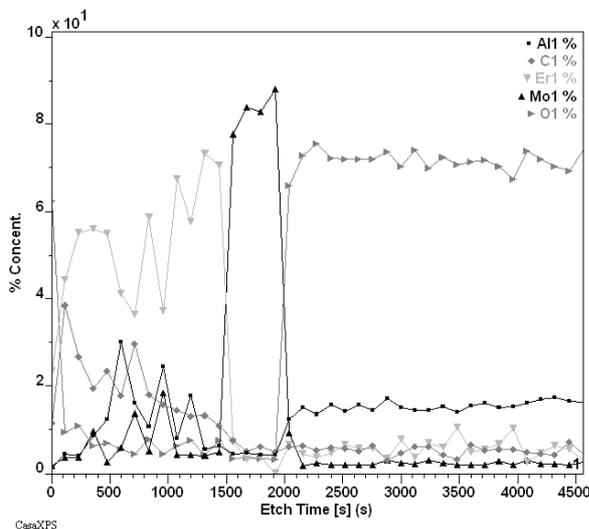
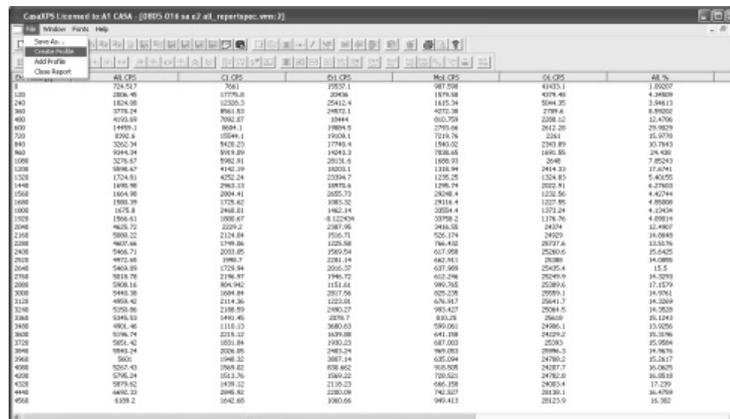
- Enter the formula for the modification to the erbium intensity based on the ratio previously determined.



- Press the Height Report button on the Custom Report Section.



The custom report table can again be exported using the Copy toolbar button, or a VAMAS form of the profile can be created using the File menu.



Ideally, the relative intensity of the Mo1 peak to the molybdenum peak measured at the same energy as the erbium should have been measured using a molybdenum standard rather than assuming a value computed from the profile data.

An alternative to manipulating the peak intensities via the custom report is to use a least squares approach to separate the erbium from molybdenum interference.

### ***Least Squares Approach to Depth Profile Interpretation***

A least squares procedure offers a means of partitioning a spectrum into component spectra. The component spectra are chosen to embody the transitions responsible for the measured data. Once these component spectra are determined in a least squares sense, the relative contributions of these underlying transitions to the measured data can be identified using quantification regions in exactly the same way any spectrum in the profile is quantified.

The least squares procedure is described in the context of the Savitzky Golay algorithm for differentiating the Auger direct spectra. The essential difference in the least squares decomposition of spectra compared to the Savitzky Golay algorithm is the basis functions are now spectra rather than terms  $(1, x, x^2, \dots)$  in a polynomial. The net result is the same in the sense that a spectrum  $\underline{s}$  is expressed as a linear combination of a set of  $n$  component spectra  $\underline{c}_j$ .

$$\underline{s} \cong \sum_{i=1}^n a_i \underline{c}_i$$

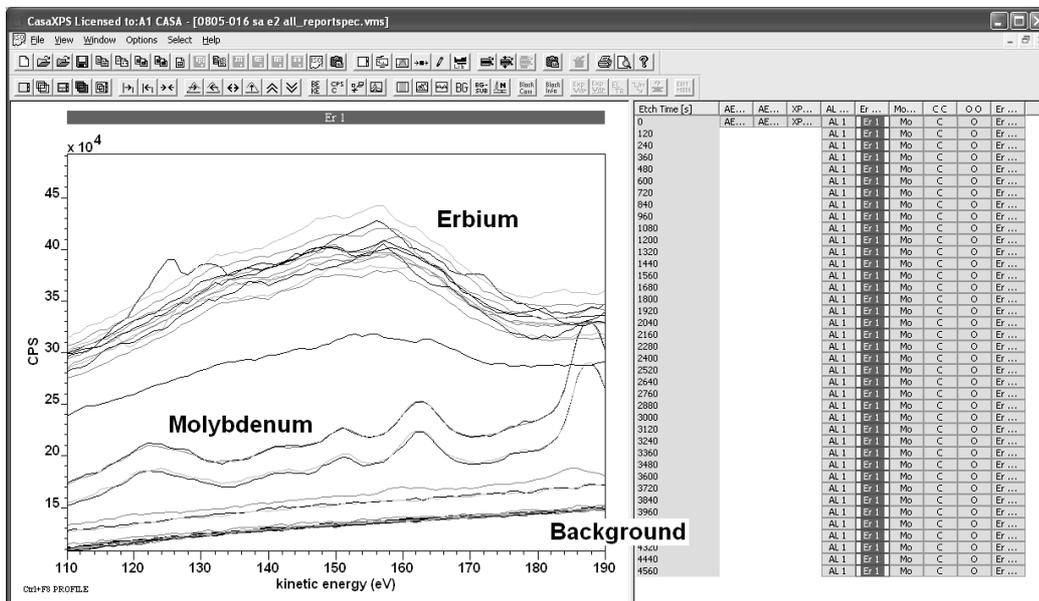
The coefficients  $a_i$  are determined in a least squares sense and the spectrum  $\underline{s}$  is therefore decomposed into component spectra  $a_i \underline{c}_i$ .

By way of example, the erbium/molybdenum problem will now be addressed using a least squares decomposition.

### ***Least Squares Example***

While the data in the Auger depth profile will be quantified using the differentiated spectra, since the act of differentiation involves a Savitzky-Golay operation which effectively smoothes the data, the least squares analysis will be performed on the raw direct spectra rather than working with already processed differentiated data.

The first step is to identify the component spectra for use in the least squares decomposition. Overlaying the Er1 VAMAS blocks in the active tile offers an easy partition of the data into three forms: pure erbium, predominantly molybdenum, and background signal measured at depths below either the erbium and molybdenum layers.



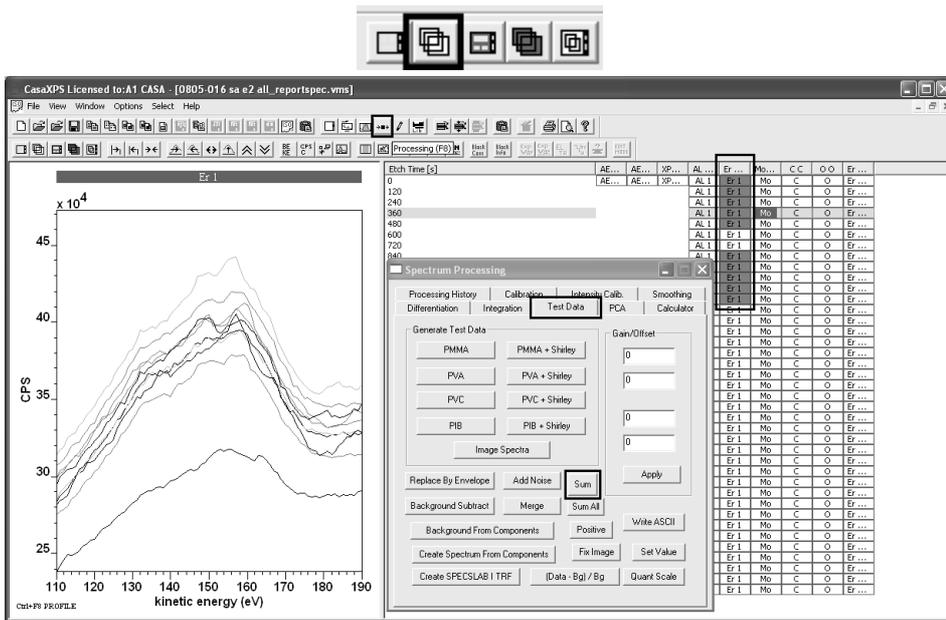
In general it is good practice to improve the signal to noise ratio in the component spectra by adding together appropriate sets of spectra from the three zones identified. While the Calculator property page on the Spectrum Processing dialog window provides a means of combining spectra acquired under varying conditions, the data from the depth profile are very uniform in the acquisition parameters; therefore, summing a set of spectra such as these is achieved in a simple fashion using the Test Data property page on the Spectrum processing dialog window.

The Test Data dialog window offers a range of miscellaneous processing options, two of which permit data to be summed without regard to acquisition conditions. That is, these options are only appropriate for very specific cases in which all the spectra have identical numbers of data channels. To sum data from a set of VAMAS blocks:

1. Select an appropriate set of spectra over which a summation can be performed.
2. Invoke the Spectrum Processing Dialog window and select the Test Data property page.



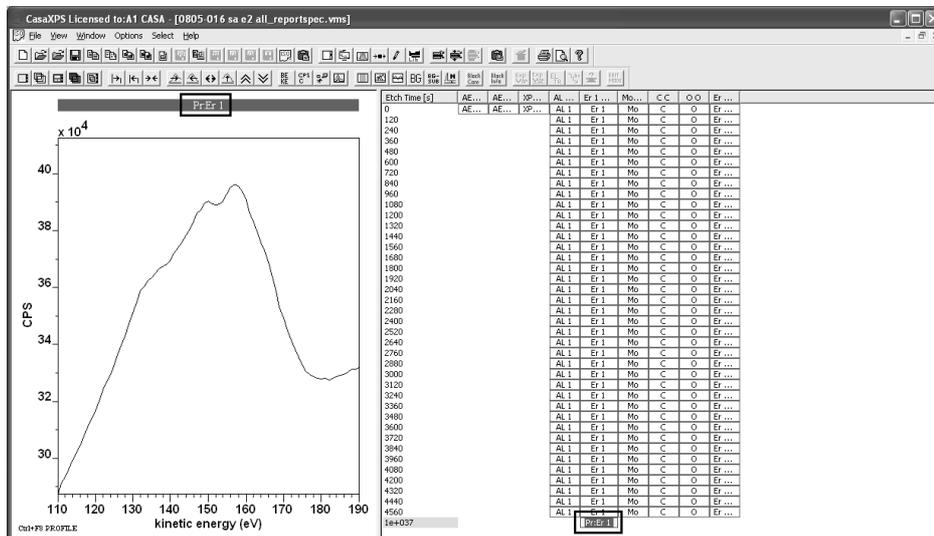
### 3. Overlay the selected VAMAS blocks in the active tile.



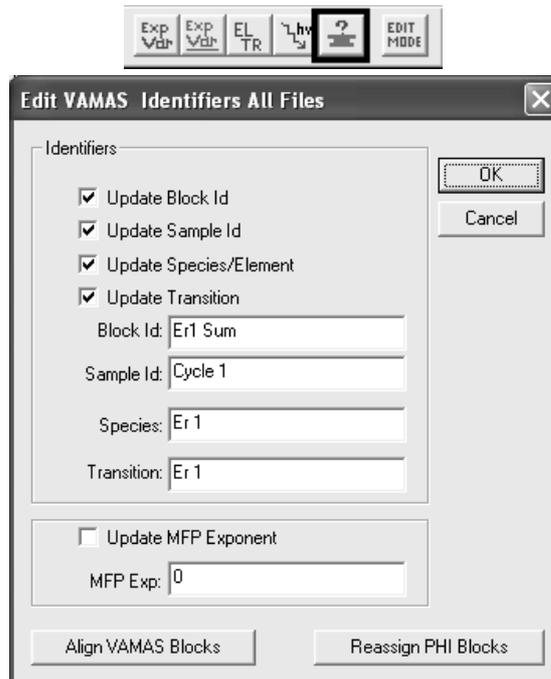
### 4. Press the SUM button on the Test data property page.

Note: the SUM All button should **not** be used as the SUM All button includes each corresponding variable in each VAMAS block in the summation. Most spectra include transmission function information as a corresponding variable; therefore, the resulting spectrum would be incorrect if the SUM All button were used. The SUM All button is used for imaging data sets where spectra-at-pixels appear in the VAMAS file as corresponding variables in VAMAS blocks.

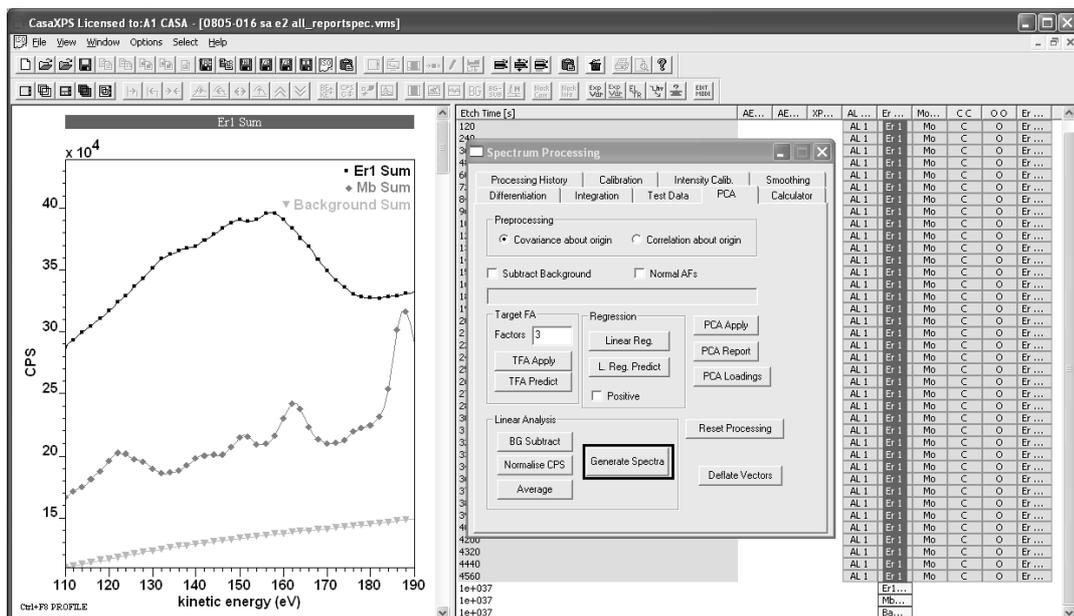
Following the use of the SUM button acting on the spectra overlaid in the active tile, a new VAMAS block appears in the right-hand pane which contains the sum of the spectra appearing in the active tile.



For the current example where three zones within the profile are identified, the summation steps need to be repeated for the molybdenum layers and also the layers beneath both the erbium and molybdenum layers. The resulting experiment frame now contains three additional VAMAS blocks appended to the column headed Er1. Adjusting the VAMAS block identifiers for these three summed spectra helps to understand the context of these data in the experiment frame created by the linear least squares procedure. The toolbar option for editing the block identifier applies to the VAMAS blocks selected in the right-hand pane.

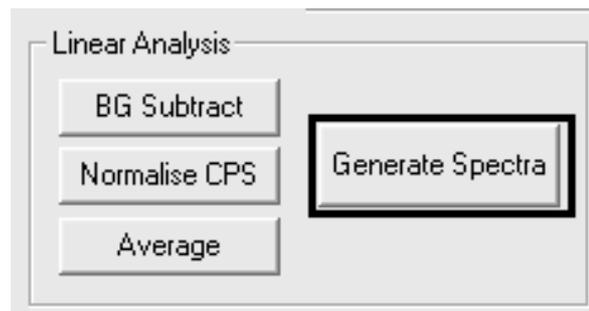


Having created the three component spectra, select and overlay the component spectra in the active tile.

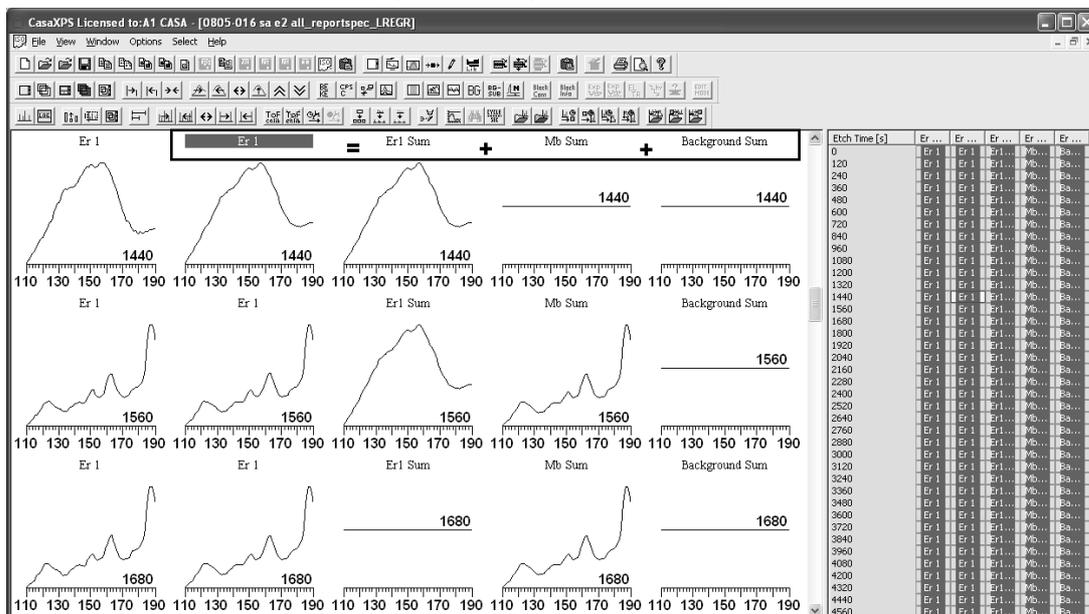


The component spectra overlaid in the active tile are used to fit the spectra selected in the right-hand pane. To create an experiment frame containing the least squares decomposition of the erbium spectra:

1. Select the column of erbium spectra.
2. Invoke the Spectrum Processing dialog window and select the PCA property page.
3. Press the Generate Spectra button in the Linear Analysis section of the property page.



A new experiment frame opens containing a row for each VAMAS block selected in the original experiment frame containing the depth profile. Each row includes the original VAMAS block followed by the least squares approximation to the original spectrum based on the component spectra, followed by each scaled component spectrum.

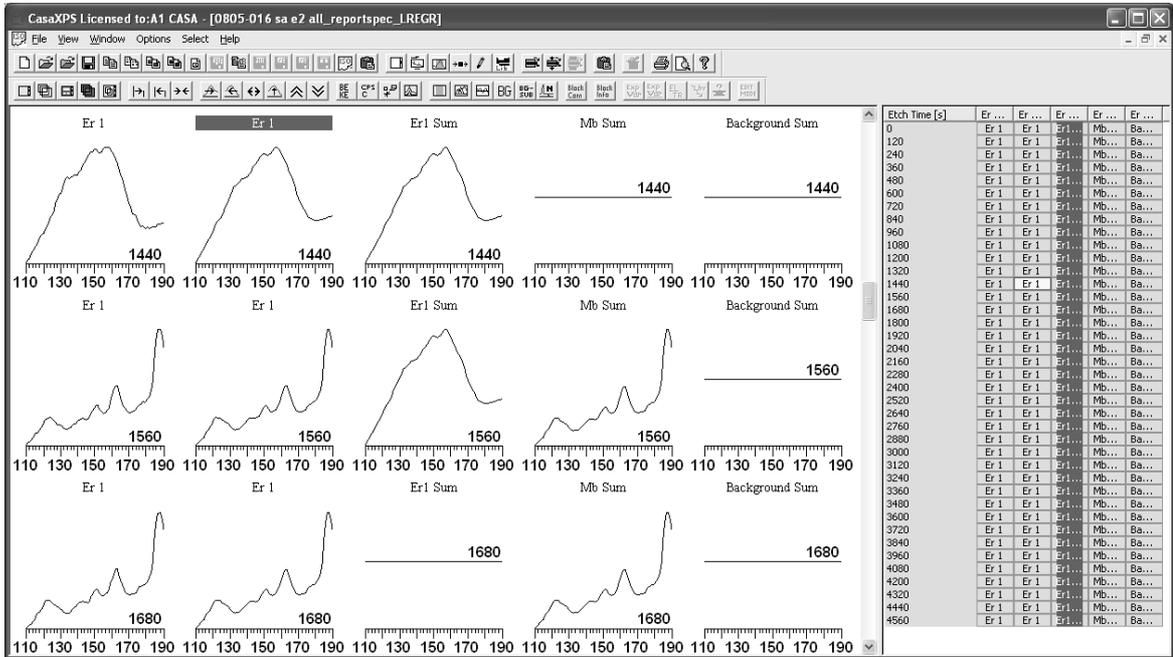


In order to profile the erbium signal, the column in the new experiment frame corresponding to the scaled erbium component from the least squares decomposition must be copied back to the original depth profile experiment frame. Once the erbium component is returned to the originating data file,

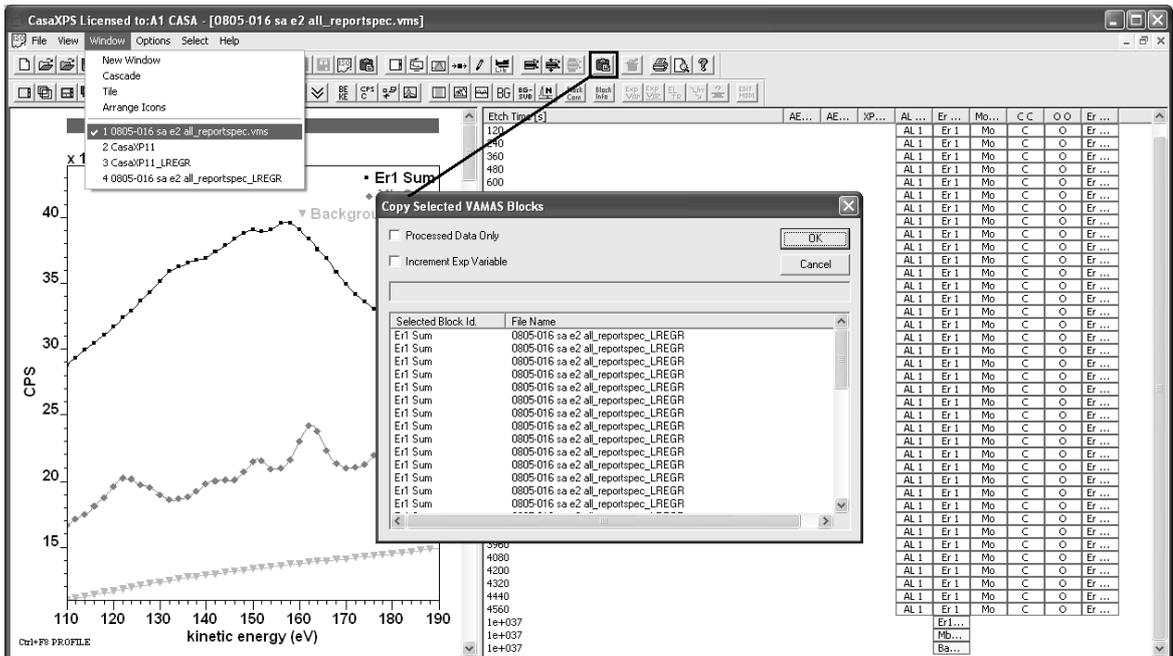
the profiling steps can be followed where the unprocessed erbium spectra are replaced in the profile by the new least squares component data.

To copy the erbium components:

1. Select the column of VAMAS blocks representing the erbium component spectra.

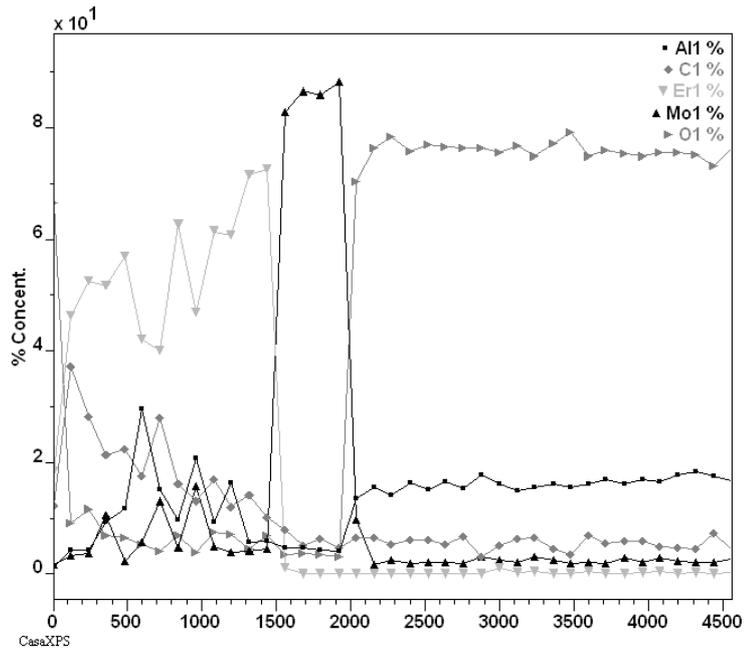


2. Switch focus to the original experiment frame and press the Copy/Paste toolbar button.



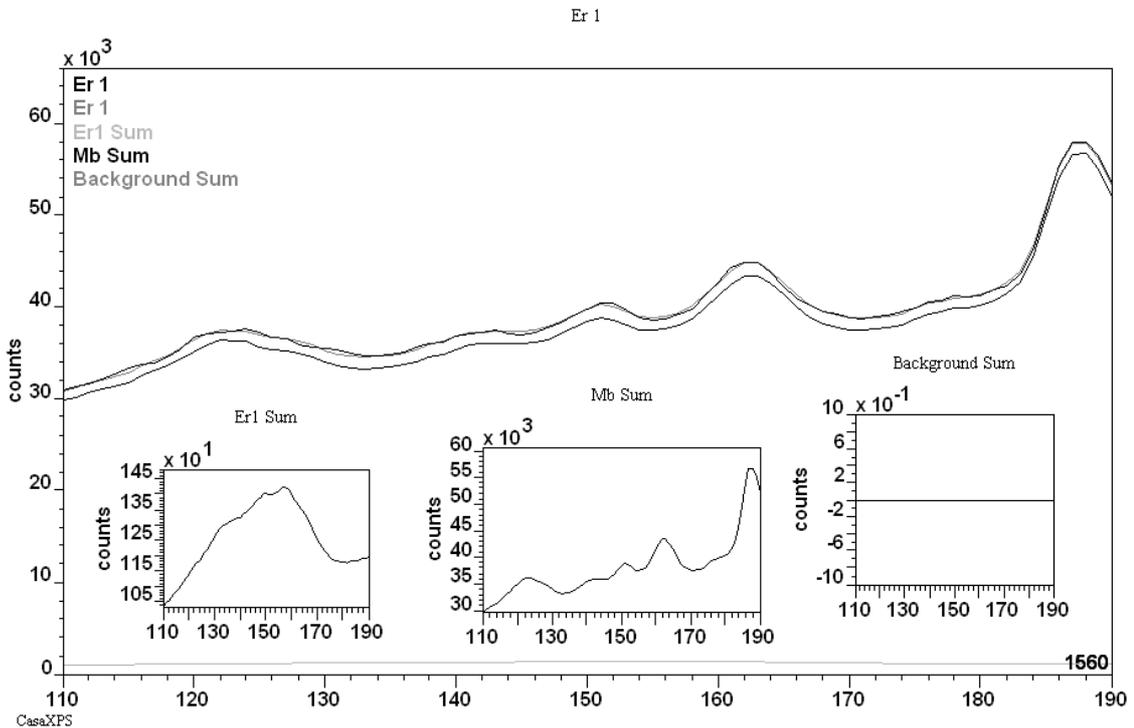
The VAMAS blocks corresponding to the components are now moved to the original experiment frame.





### Linear Least Squares

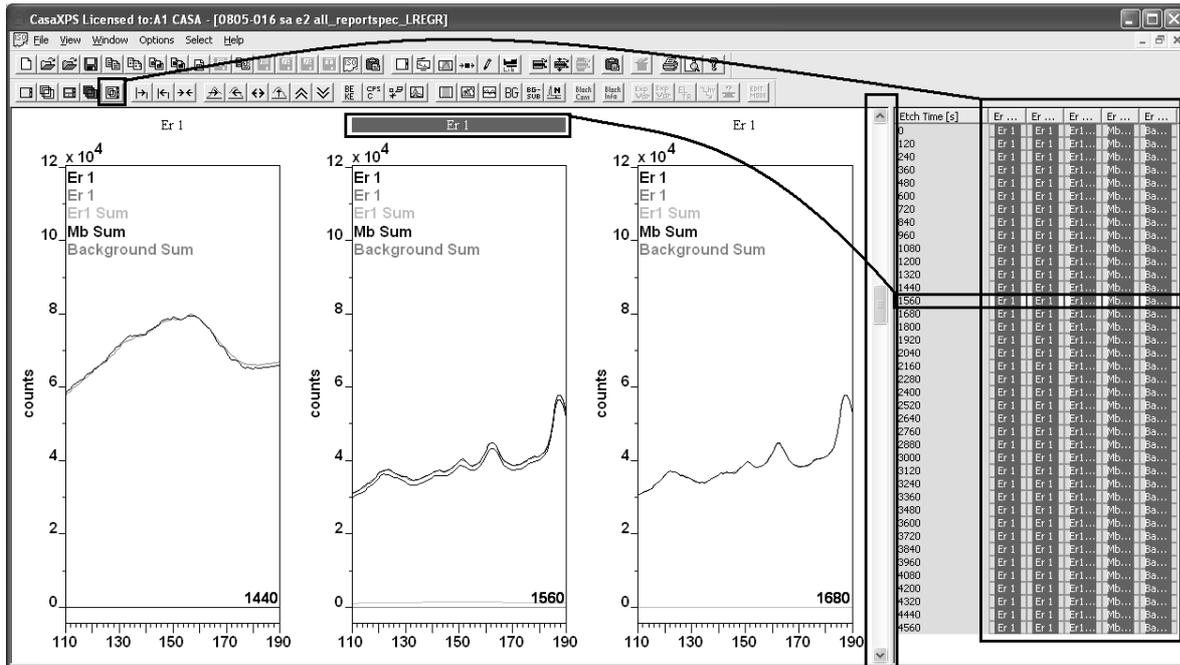
While the linear least squares approach is a powerful tool when used correctly, the least squares criterion may produce poor representations of the original spectra due to an incomplete set of component spectra. For this reason, the results of a linear least squares decomposition are offered in a new experiment frame with the view to assessing the validity of the decomposition. Overlaying the raw spectrum together with the least squares solutions provides a visual feedback of how well the procedure applied to the profile data.



A useful option for displaying the spectra generated from the least squares procedure is the Tile by Row toolbar button.



Selecting a set of rows in the right-hand pane before pressing the toolbar button causes the creation of one display tile per row of selected VAMAS blocks in the right-hand pane where each tile appearing in the left-hand pane displays an overlay of spectra from a row of selected VAMAS blocks.



## CasaXPS Element Library

Elemental identification and quantification using XPS/AES spectra rely on the maintenance of libraries containing peak positions and relative sensitivity factors. The default CasaXPS element library is compiled using rough peak positions and Scofield cross-sections for aluminium and magnesium X-ray anodes to represent the corresponding relative sensitivity of the photoelectric peaks relative to the C 1s transition. While appropriate for some, these peak energies and relative sensitivity factors will not satisfy all and therefore the CasaXPS system offers mechanisms for user, technique and sample specific element library creation. This section describes the means for modifying the element library in CasaXPS.

### Element Library Format

The CasaXPS element library is an ASCII file. The first line in the file is a version number, which may be 0, 1 or 2. Library files updated from version

2.3.15 of CasaXPS are written in version 2 format. The format for version 1 and version 2 files is TAB spaced ASCII organised so that the data are easily edited in a spreadsheet program such as Excel. The difference between version 2 and version 1 formatted files is simply the ability of the version 2 format to include additional user-defined TAB spaced fields appended to the end of the standard set of fields defined for version 1 library files. Each entry within an element library file consists of the following standard fields:

1. Element
2. Transition
3. Label/Name
4. Mass (Daltons)
5. Energy Type (BE or KE)
6. Energy (eV)
7. F.W.H.M.
8. Line shape (e.g. GL(30))
9. Relative Sensitivity Factor
10. Excitation source string

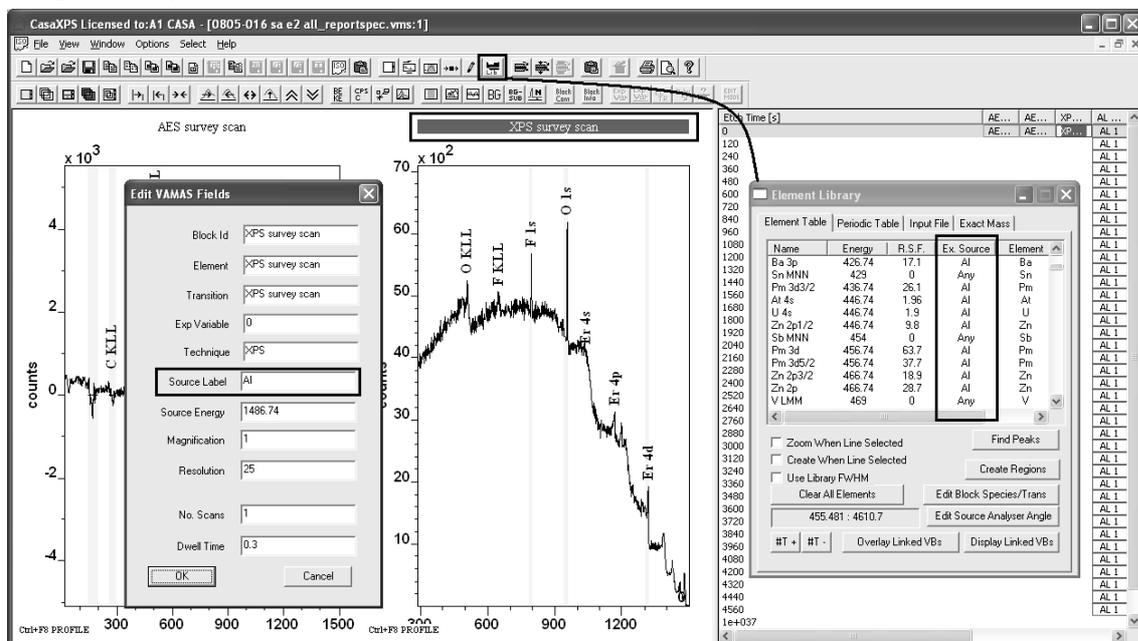
These standard fields when viewed via a spreadsheet appear as follows:

	A	B	C	D	E	F	G	H	I	J	K
1		1									
2	Bi	6p	Bi 6p	0.00E+00	BE	3.00E+00	1.00E+00	GL(30)	8.41E-02	Al	
3	Po	6p	Po 6p	0.00E+00	BE	5.00E+00	1.00E+00	GL(30)	1.36E-01	Al	
4	At	6p	At 6p	0.00E+00	BE	8.00E+00	1.00E+00	GL(30)	1.98E-01	Al	
5	Rn	6p	Rn 6p	0.00E+00	BE	1.10E+01	1.00E+00	GL(30)	2.72E-01	Al	
6	Fr	6p	Fr 6p	0.00E+00	BE	1.50E+01	1.00E+00	GL(30)	3.37E-01	Al	
7	Ra	6p	Ra 6p	0.00E+00	BE	1.90E+01	1.00E+00	GL(30)	3.96E-01	Al	
8	Th	6p	Th 6p	0.00E+00	BE	4.30E+01	1.00E+00	GL(30)	4.99E-01	Al	
9	U	6p	U 6p	0.00E+00	BE	1.90E+01	1.00E+00	GL(30)	5.09E-01	Al	
10	Bi	6p3/2	Bi 6p3/2	0.00E+00	BE	3.00E+00	1.00E+00	GL(30)	4.56E-02	Mg	
11	Po	6p3/2	Po 6p3/2	0.00E+00	BE	5.00E+00	1.00E+00	GL(30)	7.45E-02	Mg	
12	At	6p3/2	At 6p3/2	0.00E+00	BE	8.00E+00	1.00E+00	GL(30)	1.10E-01	Mg	
13	Rn	6p3/2	Rn 6p3/2	0.00E+00	BE	1.10E+01	1.00E+00	GL(30)	1.52E-01	Mg	
14	Fr	6p3/2	Fr 6p3/2	0.00E+00	BE	1.50E+01	1.00E+00	GL(30)	1.93E-01	Mg	
15	Ra	6p3/2	Ra 6p3/2	0.00E+00	BE	1.90E+01	1.00E+00	GL(30)	2.30E-01	Mg	
16	Th	6p3/2	Th 6p3/2	0.00E+00	BE	4.30E+01	1.00E+00	GL(30)	2.93E-01	Mg	
17	U	6p3/2	U 6p3/2	0.00E+00	BE	1.90E+01	1.00E+00	GL(30)	3.01E-01	Mg	
18	Pb	6p	Pb 6p	0.00E+00	BE	1.00E+00	1.00E+00	GL(30)	3.48E-02	Mg	

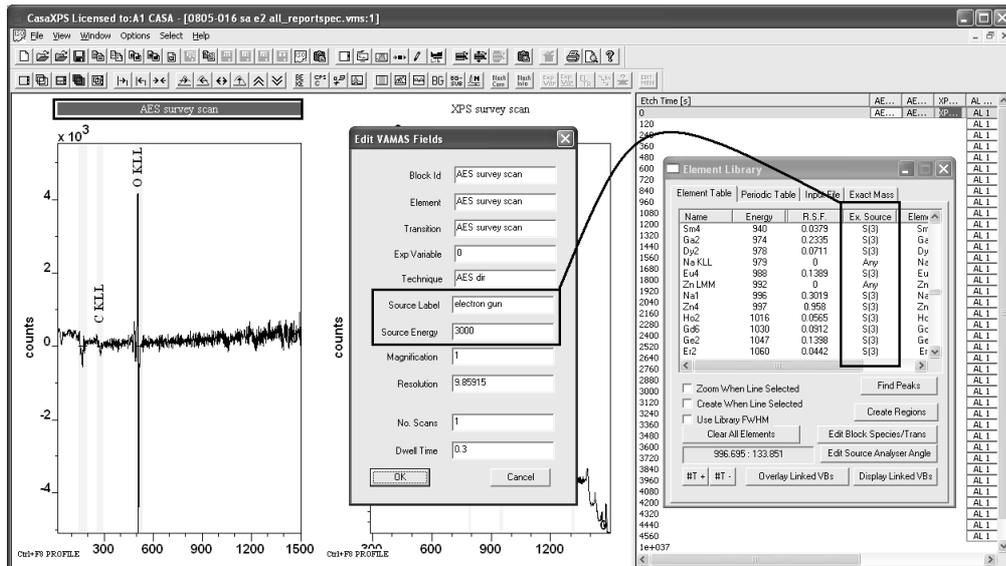
For a large number of changes, using a spreadsheet is the best means of constructing a CasaXPS library; however, for small alterations the Element Library property page offers dialog-window-based adjustments of the library.

Note how the library entries visible in the spreadsheet include two different excitation source strings, namely Al and Mg. A single library file may contain any number of entries corresponding to different excitation source strings; however, when used in CasaXPS these strings are matched to the excitation source string in the displayed VAMAS block in the active tile. Only those library entries for which a match occurs are displayed on the Element Table property page of the Element Library dialog window. Thus, an XPS spectrum displayed in the active tile measured with an Al anode, and therefore assigned a source label of Al, will cause the Element Table property page to list only those element library entries with matching excitation source strings.

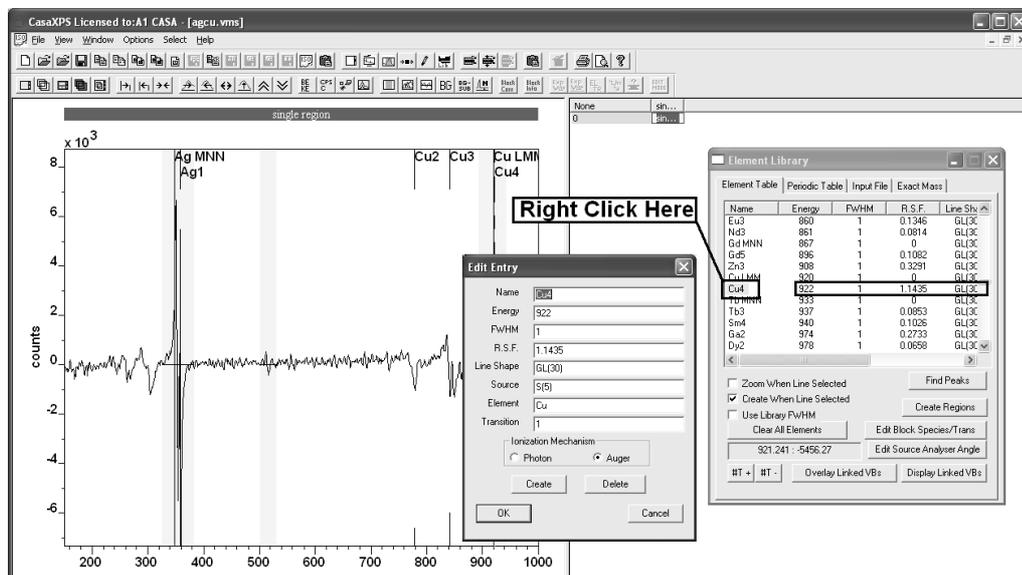
The transitions listed because of a match between the excitation source string and the VAMAS block source label field are supplemented by transitions with excitation source entries identified using the string Any. These additional element library entries with excitation source string Any are for XPS induced Auger transitions, the function of which is to simply mark the position of Auger lines in any XPS spectrum. Since these Auger lines do not specify lines used in quantification, the RSF for these Auger lines is typically zero. An XPS induced Auger line for which an RSF has been established may be entered into the library using an Energy Type of KE and excitation source string appropriate for the data.



The element table offered for the XPS spectrum should be compared to the entries displayed from the same element library file when the data in the active tile is an Auger spectrum.



The transitions offered in the element table are specific to the Auger data in the active tile. When the Source Label field for the data includes the string *electron gun*, the string used to match the entries in the element library is constructed from the electron gun energy parameter in the VAMAS block. Hence, in the current example data, since the electron gun energy is 3000 eV, the string used to display the Auger transitions in the element table is S(3). Although version 2 of the library format is aimed at editing library files within a spreadsheet program, a mechanism exists within CasaXPS for making occasional changes and additions to the currently loaded library file. The Edit Entry dialog window is invoked by placing the cursor over the Name field for an entry in the element table before right-clicking the mouse button. The current set of library fields for the selected peak is displayed on the dialog window. These fields can be adjusted, then either updated or a new entry created.



The Edit Entry dialog window allows the library entry to be altered and then updated using the OK button. Alternatively, pressing the Create button causes a new library entry to be added to the element library based on the parameters defined on the dialog window. The Delete button will remove the entry used to invoke the dialog window.

Any modifications to the element library within CasaXPS are only written back to disk once the current session of CasaXPS is ended. On exiting CasaXPS, a File dialog window presents the opportunity to save the changes to a new filename.

On starting CasaXPS, the library file CasaXPS.lib located in the same directory as the executable file CasaXPS.exe is loaded as the default element library. In general, when a spectrum is displayed in the active tile, on invoking the Element library dialog window, the Element Table property page displays those entries for which the excitation source string from the entry matches the corresponding field in the VAMAS block holding the spectrum. The exception to this rule occurs for AES data. If the excitation source field in the VAMAS block is set to a string including the key words **electron** and **gun**, then for Auger spectra the electron gun energy is used to construct the string used to match an excitation source in the element library. For example, an AES element library might include relative sensitivity factors for electron beam energies 3 keV, 5 keV and 10 keV, and therefore should have entries with excitation source strings S(3), S(5) and S(10).

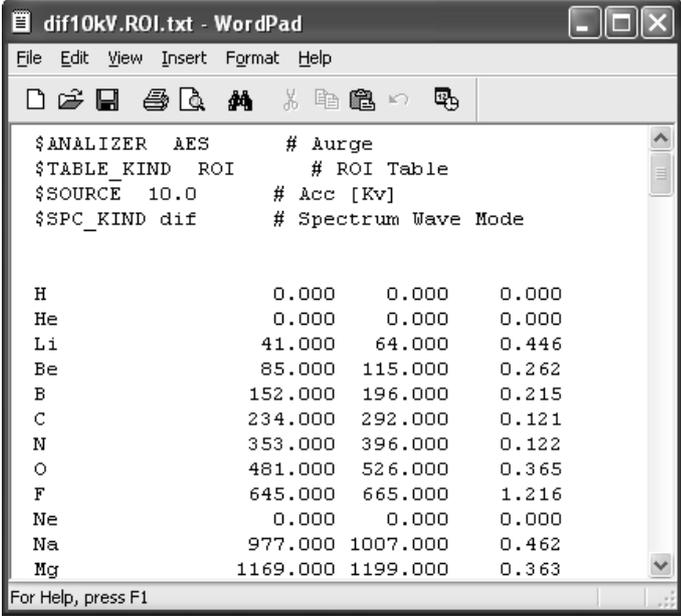
	A	B	C	D	E	F	G	H	I	J	K	L
1		2										
2	Cu	1 Cu 1	0 KE		916		1 GL(30)		0 S(3)			
3	Cu	1 Cu 1	0 KE		916		1 GL(30)		1.1435 S(5)			
4	Cu	1 Cu 1	0 KE		916		1 GL(30)		0 S(10)			
5	Cu	2 Cu 2	0 KE		837		1 GL(30)		0 S(3)			
6	Cu	2 Cu 2	0 KE		837		1 GL(30)		0.3473 S(5)			
7	Cu	2 Cu 2	0 KE		837		1 GL(30)		0 S(10)			
8	Cu	3 Cu 3	0 KE		766		1 GL(30)		0 S(3)			
9	Cu	3 Cu 3	0 KE		766		1 GL(30)		0.1899 S(5)			
10	Cu	3 Cu 3	0 KE		766		1 GL(30)		0 S(10)			
11	Ag	1 Ag 1	0 KE		357		1 GL(30)		0 S(3)			
12	Ag	1 Ag 1	0 KE		357		1 GL(30)		3.2713 S(5)			
13	Ag	1 Ag 1	0 KE		357		1 GL(30)		0 S(10)			
14	Ag	2 Ag 2	0 KE		351		1 GL(30)		0 S(3)			
15	Ag	2 Ag 2	0 KE		351		1 GL(30)		0 S(5)			
16	Ag	2 Ag 2	0 KE		351		1 GL(30)		0 S(10)			

A set of sensitivity factors for AES are published in the book edited by Briggs and Grant (ISBN 1 901019 047); different instrument manufacturers

recommend different sensitivity factors for specific instruments, so an appropriate library for a given instrument should be prepared.

## ***Importing a JEOL Element Library***

A file format used by JEOL Auger instruments is supported in CasaXPS as a means of importing transition and RSF information into the CasaXPS element library. The file format is a relatively simple format.



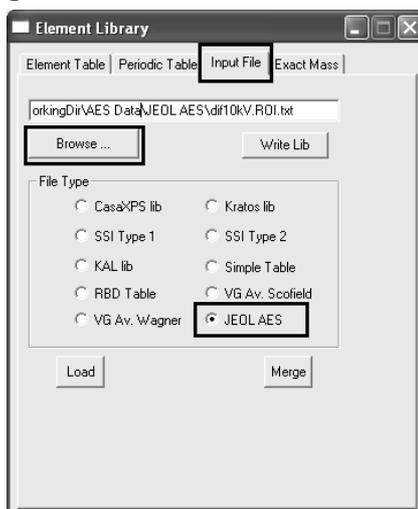
```

$ANALIZER AES          # Auger
$TABLE_KIND ROI       # ROI Table
$SOURCE 10.0          # Acc [Kv]
$SPC_KIND dif         # Spectrum Wave Mode

H           0.000    0.000    0.000
He          0.000    0.000    0.000
Li          41.000   64.000    0.446
Be          85.000  115.000   0.262
B           152.000  196.000   0.215
C           234.000  292.000   0.121
N           353.000  396.000   0.122
O           481.000  526.000   0.365
F           645.000  665.000   1.216
Ne          0.000    0.000    0.000
Na          977.000 1007.000   0.462
Mg         1169.000 1199.000   0.363

```

Importing these files into CasaXPS involves the Input File property page on the Element Library dialog window.



To import a JEOL formatted file:

1. Using the File dialog invoked by the Browse button, browse for the ASCII file. Select the file and press the Open button on the File dialog. The selected file is entered onto the Input File property page.
2. Select the radio button labelled JEOL AES.

3. Enter the information into the element library by pressing either the Load button to overwrite the existing element library or Merge button to add the new entries to the current element library.

The JEOL library files include an entry specifying the electron gun energy; therefore a JOEL formatted file is required for each electron-gun energy. In addition, the JEOL library files are either for differentiated spectra peak-to-peak measurements or direct spectra measurements. The two different files contain different RSF values depending on the type of spectra analysed during quantification.

## Concentration Calculation

The principal means of comparing XPS/AES samples in CasaXPS is via percentage concentration values. The names assigned to these quantities are an indication of the source for the values rather than an assertion that the tables necessarily contain atomic or mass concentration for the surface material. The accuracy of these concentration values depends on appropriate transition and instrumental specific corrections as well as matrix context for the material analysed. The objective in using concentration values to characterise a sample is to reduce the intensity values to a set of normalised quantities in the hope that some of the measurement artefacts are removed from consideration when different samples are compared.

A concentration calculation consists of determining intensities for the transitions computed from the raw data  $I_i$ , followed by a correction based on the transition, encapsulated in the RSF  $R_i$  and, where available transmission correction  $T(E)$  accommodating instrumental intensity variations. The concentration  $X_i$  for an element is given by

$$X_i = 100 \frac{A_i}{\sum_{i=1}^m A_i}$$

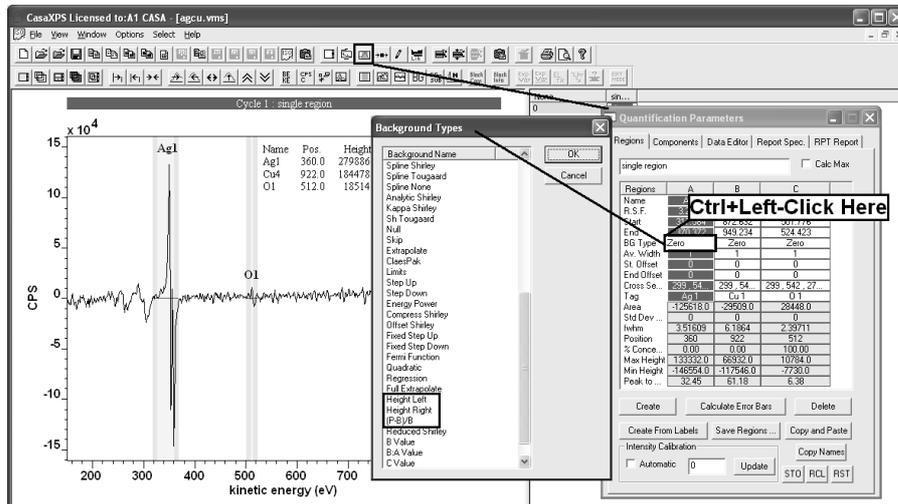
$$A_i = \frac{I_i}{T(E)R_i}$$

The intensity  $I_i$  may be measured using peak height above background, peak-to-peak or peak area. For mass concentration the raw intensity is multiplied by the mass for the element. The essential feature for these quantities is the normalisation to the total signal measured.

While the standard method for measuring intensity for Auger spectra is based on peak maximum to peak minimum (peak-to-peak) within a

quantification region, other methods are possible within CasaXPS. Extracting these alternative intensity values is dependent on the background type used within the quantification region.

To reveal the set of possible background types, hold the Control Key down and left-click the mouse with the cursor over a background type string on the Regions property page of the Quantification Parameters dialog window.

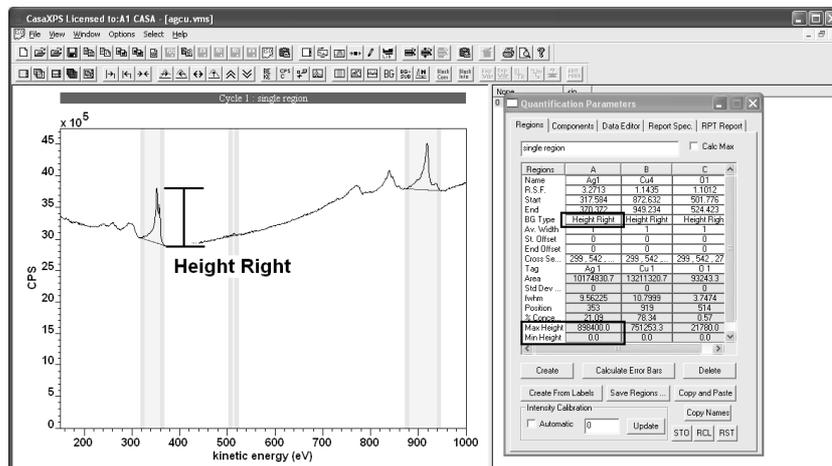


The alternative methods from peak-to-peak for computing peak intensities are for spectra in direct mode:

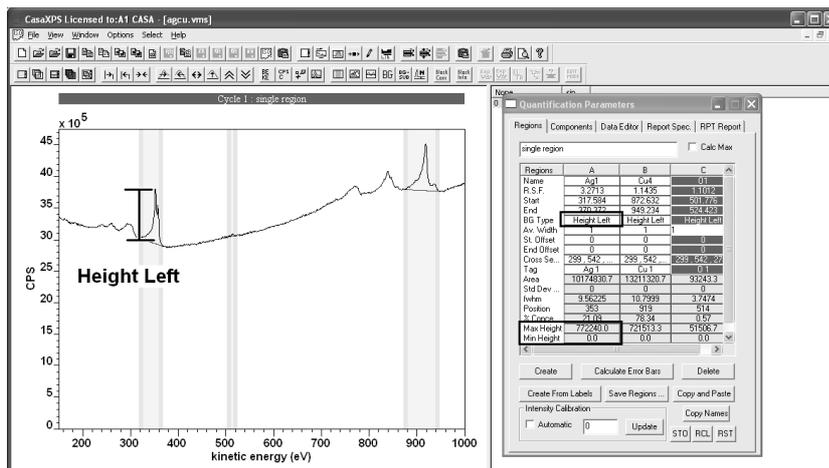
1. Peak height above background, where the background intensity is measured at the left hand side of the quantification region.
2. Peak height above background, where the background intensity is measured at the right hand side of the quantification region.
3. The ratio of the Peak height above background to the background intensity.

The background types corresponding to these options are Height Left, Height Right and (P-B)/B.

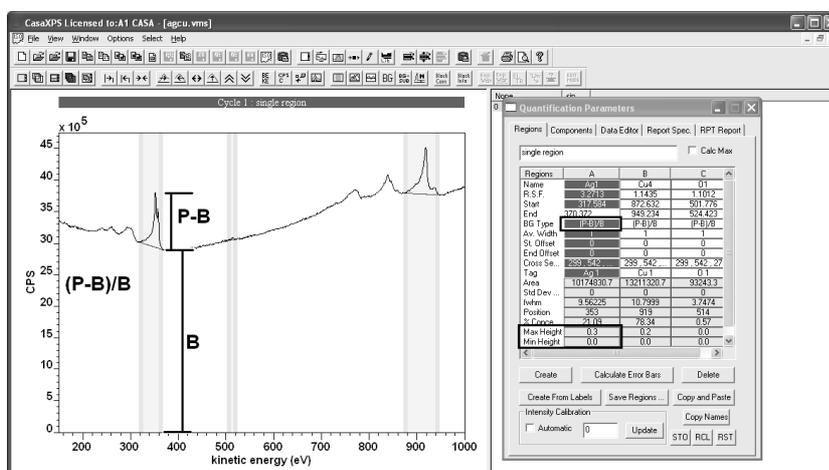
Height Right:



Height Left:



(P-B)/B:

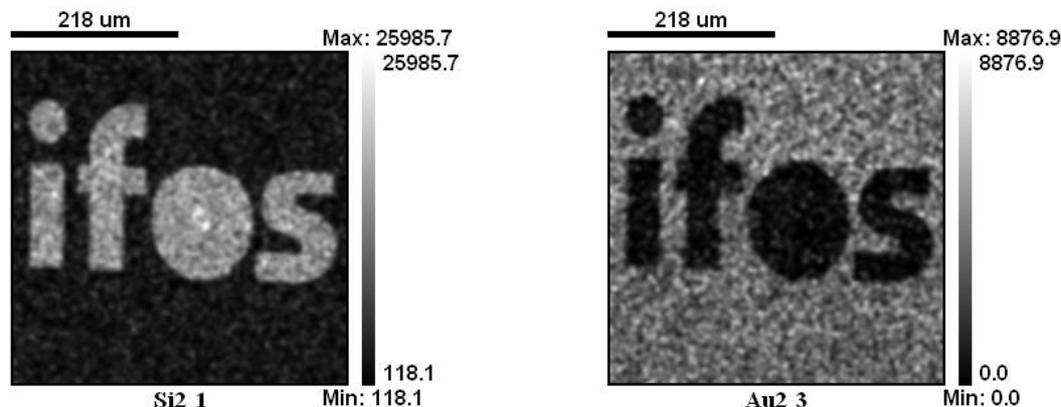


The ratio of peak height above background divided by the background intensity is a means of normalising the peak intensities with respect to background variations. These ratios are sometimes referred to as topographical corrections when used in the context of imaging where peak and background images are measured. Imaging Auger instruments without hardware signal differentiation necessarily measure images in direct mode and therefore these intensity measures provide insight into the quantities exploited by imaging instruments.

## Auger Imaging in CasaXPS

The electron gun technology required for Auger spectroscopy is also capable of generating spatially monitored Auger signal and therefore Auger imaging is often included as an option. Submicron spatial resolution requires vibration isolation and screening of stray electromagnetic fields within the analysis chamber to allow precise scanning Auger microscopy (SAM). Not all Auger

instruments include such additional engineering, but nevertheless imaging is a natural feature of Auger systems.

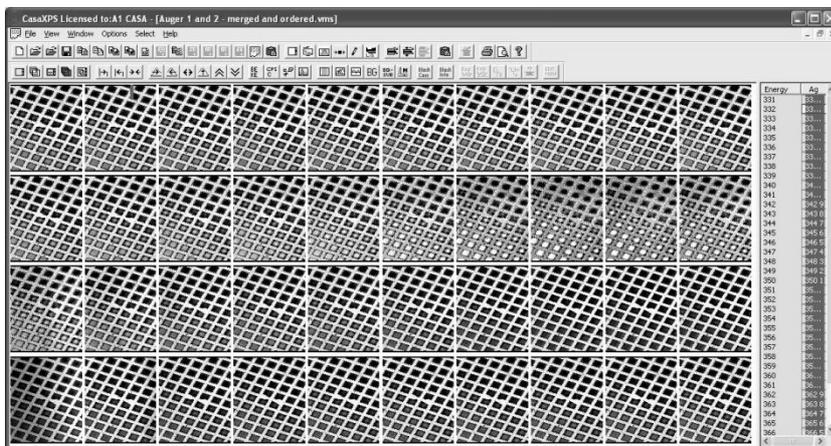


CasaXPS

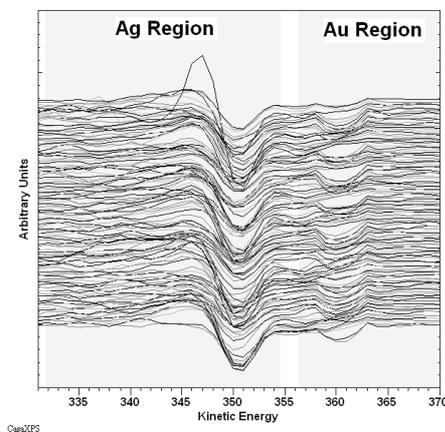
Auger images, when measured at a peak maximum are often difficult to interpret. Fluctuations in the signal as a function of position on the sample causes variation in the pixel intensities independent of the chemical information desired from the surface of the material. The difficulty arises because Auger images are typically collected in direct mode at the peak maximum and unlike spectral measurements, are often taken in isolation; background variations are sufficient to hamper the interpretation of such images. In an attempt to reduce these effects, images are often also acquired at an energy representative of the background and sometimes at a second background energy, with the view to including a contribution from the background to the final image and thereby improving the estimate of the peak height at each pixel. A common calculation for an Auger analysis is the, so called, topographical correction computed from the peak maximum  $N_1$  and a background image  $N_2$ , namely  $(N_1 - N_2) / N_2$ . A variation on a theme is to compute an image from  $(N_1 - N_2) / (N_1 + N_2)$ .

The principal reason for analysing Auger images using peak and background intensities is the time constraint of doing more; however, the benefits of applying spectroscopic techniques to image analysis may, when possible, outweigh the time penalty of performing the extended acquisitions of images and allow spectra at each pixel to be determined. The example examined below (data provided by Pennsylvania State University, USA), is a simple experiment in which a gold grid is placed over a clean silver surface, and a set of Auger images are acquired at unit eV step size across a silver Auger peak. As luck would have it, a weak gold Auger line is also included in the energy range over which the images were recorded and therefore the data set offers

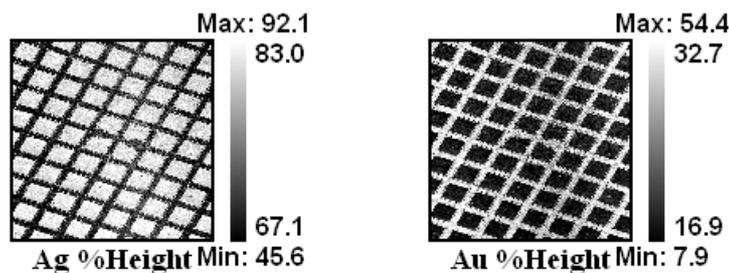
a means of illustrating a simple, yet effective procedure for creating elemental Auger images. Viewing the full set of images in the raw direct mode intensity leaves the impression that the grid is silver rather than gold.



Rather than using the direct spectra, following the conventional wisdom for Auger spectra, the data are differentiated and peak-to-peak measurements made for each pixel in the image. Simple quantification regions are defined on the spectra, one for the silver Auger line and one for the weak gold Auger line.

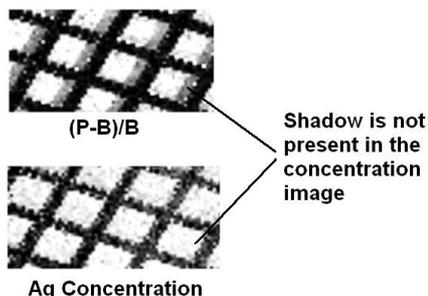


Two images of the peak-to-peak intensities are constructed; these two images in turn are quantified using the standard procedure for quantifying spectra.

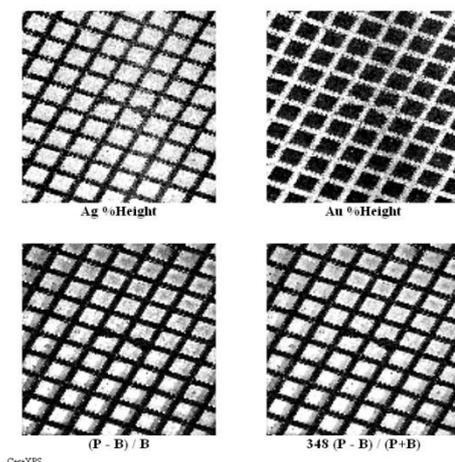


CasaXPS

The results are two images, where the silver image is free from intensity variations other than the elemental surface composition. A comparison with an image obtained from a topographically corrected intensity shows how the normalisation to the total intensity for both Ag and Au regions eliminates to a greater extent the shadowing from the gold grid on the silver.



Regardless of which of the three methods are used to process the raw Auger images, the most striking point is all three methods recover the true composition of the grid, namely, gold rather than silver.



In many ways, the improved quality of the gold and silver images are reassuring, since for years it has been assumed Auger spectra taken from a single point on a sample can be compared by determining atomic concentrations from the relative intensities of differentiated Auger peaks. The images were determined from the peak-to-peak intensities without application of relative sensitivity factors, however provided the appropriate data are available, proper atomic concentration images are possible and these images allow the surface to be viewed using the same regime normally adopted for spectra.

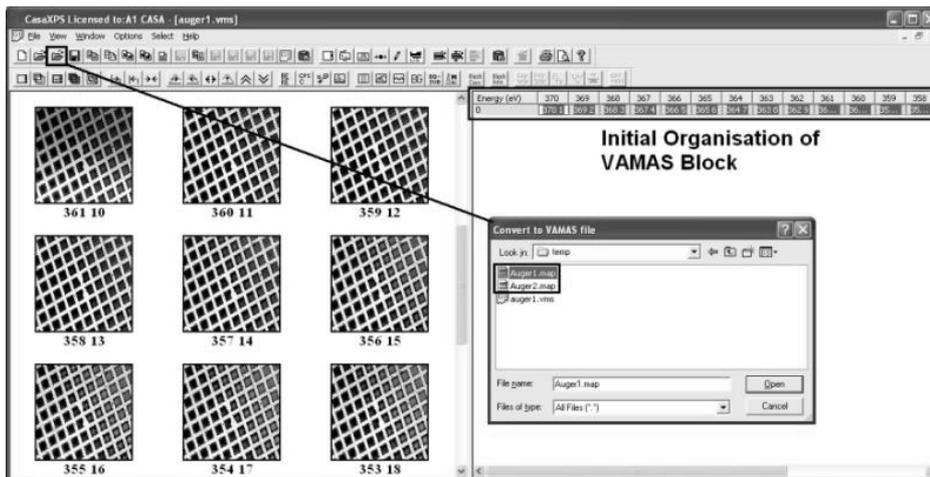
### ***Auger Image Analysis Steps in CasaXPS***

The essential sequence of steps required to process the image data is as follows:

1. Convert the image set to spectra at each pixel.
2. Differentiate all the spectra.
3. Define quantification regions for each transition and propagate these quantification regions to each VAMAS block containing a row of spectra.
4. Convert the region intensities to images.

Within these steps there are potentially sub-steps and these sub-steps are detailed below based on the original data for the given example.

The Auger images were acquired on a PHI Auger system, in this particular case, using two data files in which the saved images correspond to a sequence of unit energy steps over an interval spanning 370 eV to 331 eV. Since the data are in two separate files, the first job after the data are converted to VAMAS format is to assign the correct energy to the experimental variable for each image and then move the images into a new experiment frame.



### Ordering the Images using the Experimental Variable

Initially, when converted through CasaXPS, the PHI .map files each contain half the images for the entire data set. The images are assigned the same experimental variable and the species/transition VAMAS block fields are all different, therefore the VAMAS blocks appear in the right-hand pane of the experiment frame as a single row.

Energy (eV)	370	369	368	367	366	365	364	363	362	361	360	359	358
0	370 1	369 2	368 3	367 4	366 5	365 6	364 7	363 8	362 9	36...	36...	35...	35...

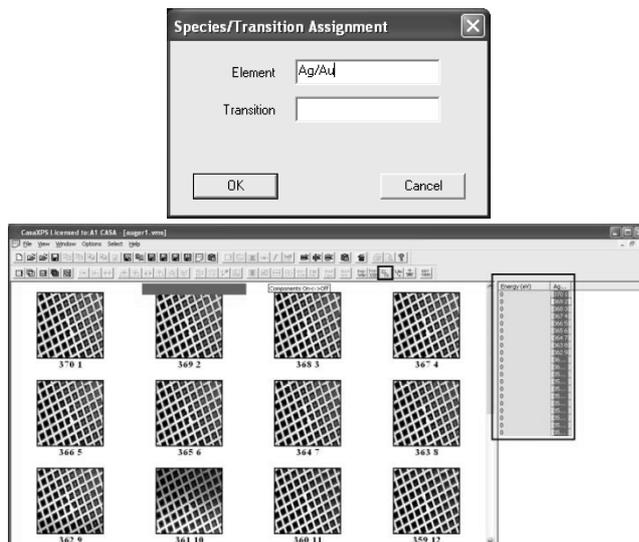
To convert a set of images to spectra at each pixel, the images must appear in the same column and the experimental variable for each image assigned the value for the energy at which the image was acquired. To reorganize the

data as required, the next step is to assign the species/transition fields for each VAMAS block in the file:

1. Select the entire set of VAMAS block in the Experiment Frame.

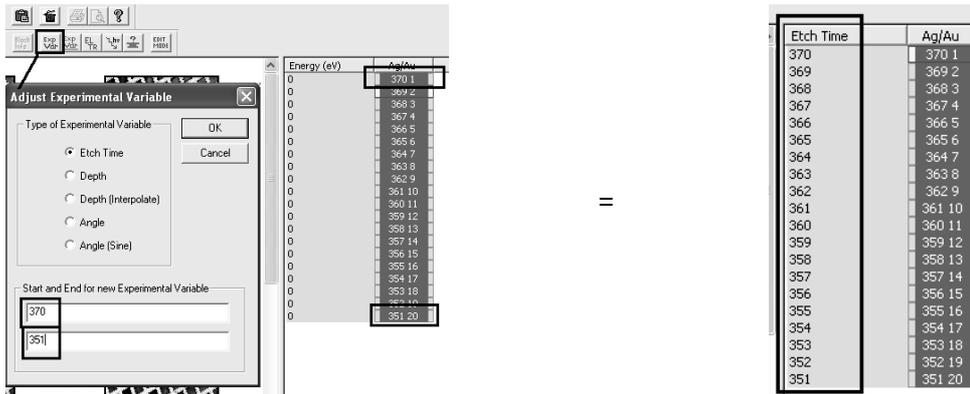
Since the data blocks appear in a single row in the right-hand pane, the entire set of blocks are selected by either left-clicking the mouse with the cursor over experimental variable value; or click once on the button heading the column for the experimental variable values. Both these actions will result in the full set of VAMAS blocks being selected. The former action relies on all the data appearing in a single row, whereas the latter selects the entire set of VAMAS blocks in the experiment frame.

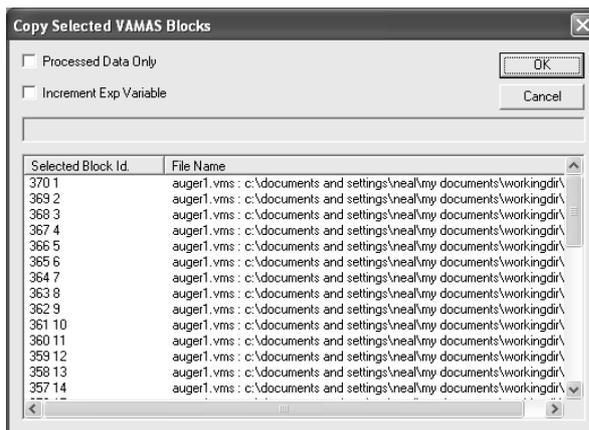
2. Press the  button on the second toolbar and enter new Element/Transition strings on the resulting dialog window. When the OK button is pressed, all the selected VAMAS blocks are assigned the pair of strings entered on the dialog window and as a consequence, the right-hand-side of the Experiment Frame is reordered so that all the VAMAS blocks appear in a single column.



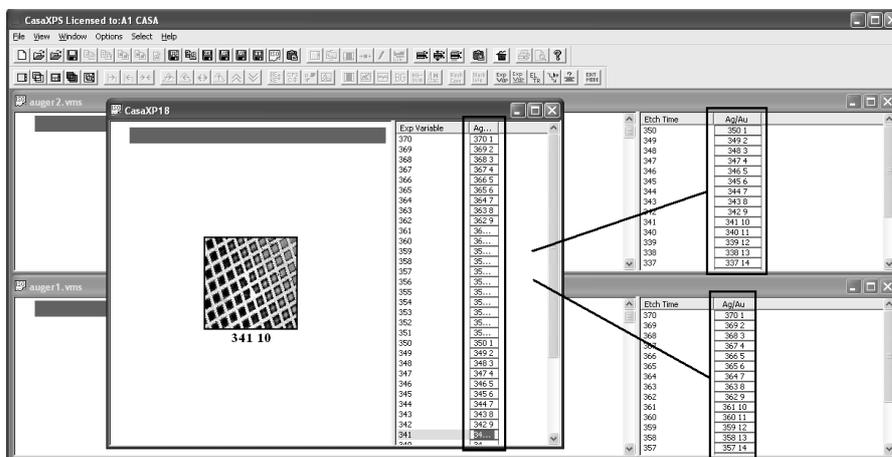
Once the VAMAS blocks appear as a single column in the right-hand pane of the experiment frame, the values for the experimental variable can be adjusted to the energy at which each image was acquired. The two toolbar buttons  provide a means of assigning the experimental variable value on bulk; however the left-most of this pair of buttons offers a means of specifying a range of values for the experimental variable, where each row of VAMAS blocks will be assigned intermediate values. Thus, following rearrangement into a single column, the VAMAS blocks are assigned the

appropriate experimental variable values by specifying the range 370 – 351 eV.

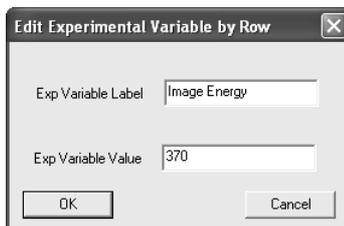




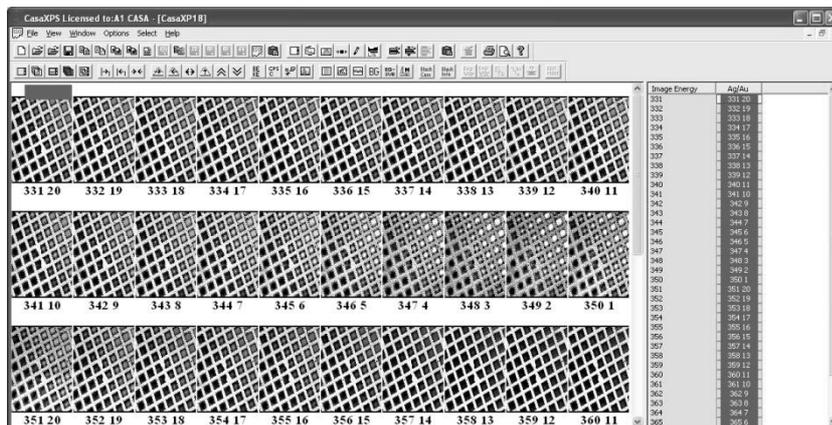
The OK button on the dialog window accepts the selection and results in copies of the selected blocks being merged into the experiment frame with focus.



Although the VAMAS blocks now appear in the same experiment frame all in one column and the map energy is assigned to the experimental variable, there is still one possible problem. The images are ordered from high kinetic energy to low and so the spectra, when generated, will be assumed to be XPS data rather than AES. It is also possible that the merged files appear back to front, from the energy scale perspective, and so the true order of the images, with respect to energy, may yet be realized. The functionality in the second button for assigning the experimental value is required to force the appropriate reordering. The dialog window invoked by the  right of the two toolbar buttons allows the assignment of the experimental variable for a selected set of VAMAS blocks.

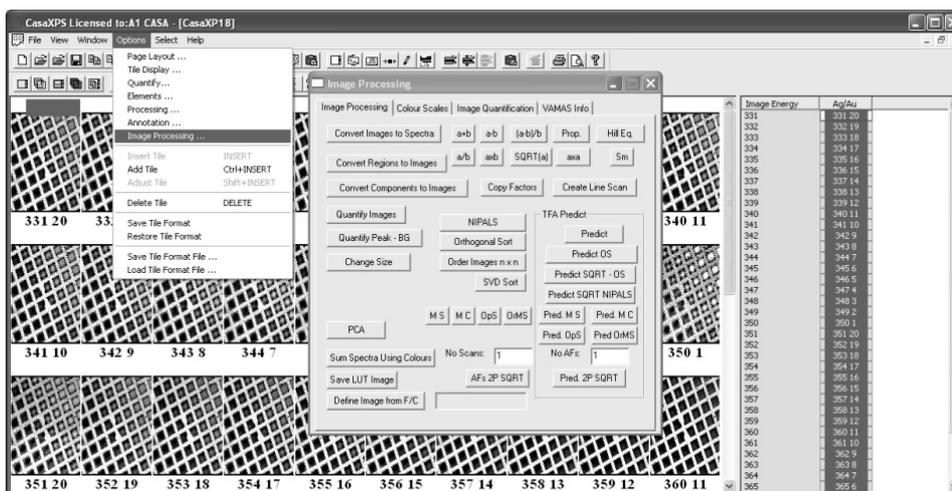


Further, once the assignment for the selection is made, the VAMAS blocks are reordered with respect to the new set of experimental variables. To cause a reordering of the image set, simply select a single VAMAS block and press the OK button on the dialog window. Although no new value was actually assigned, the reordering will still take place and the images then appear in the experiment frame ordered with respect to the map energies.

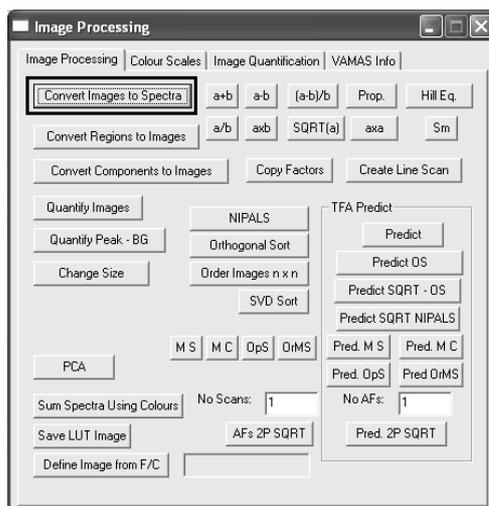


## Converting Images to Differentiated Spectra

Given the set of images, now ordered with respect to energy, the analysis proceeds by converting the image data set into a set of spectra, one spectrum per image pixel. The conversion from images to spectra is achieved using the Image Processing property page on the Image Processing dialog window.

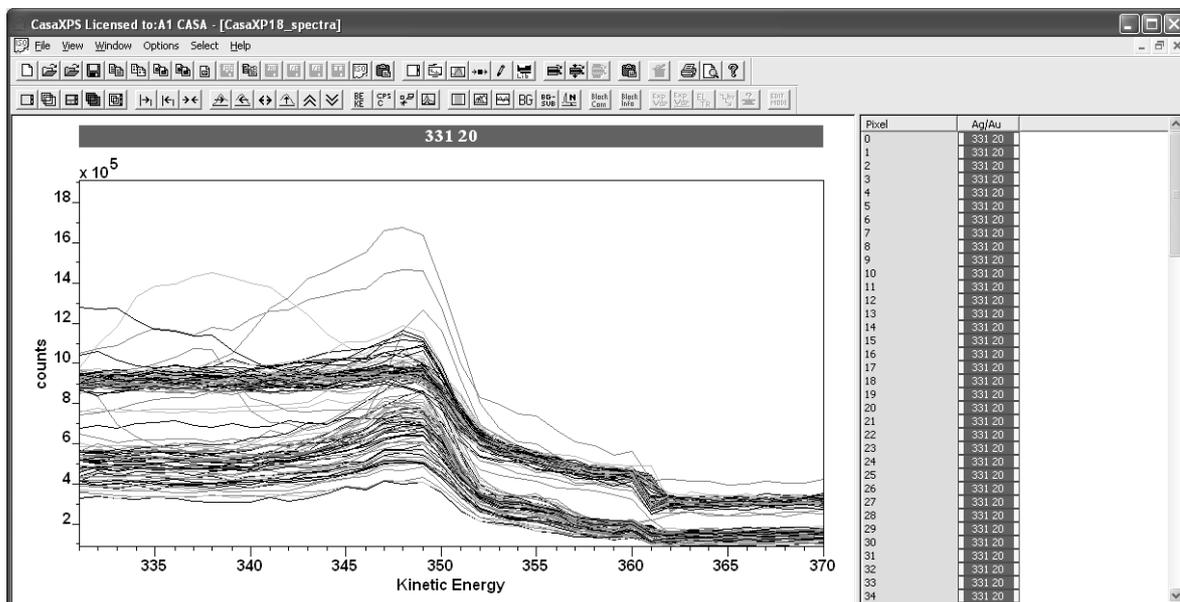


To invoke the Image Processing dialog window, click on the displayed image to ensure the Options menu items are active, and then select the Image Processing menu option. Overlay the images in the Active Tile and press the Convert Images to Spectra button on the Image Processing property page.



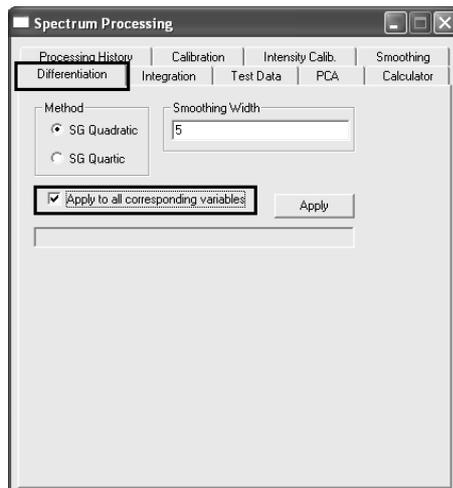
It is important that all the images are acquired using the same acquisition time and the experimental variable represents a sequence of evenly spaced energies. If the step in energy between the images deviates from a constant difference, then an error message will appear and no conversion to spectra takes place.

The converted spectra appear in a new experiment frame, where the experimental variable is labelled pixel and the values for the experimental variables represent row indices of the pixels in the original images.

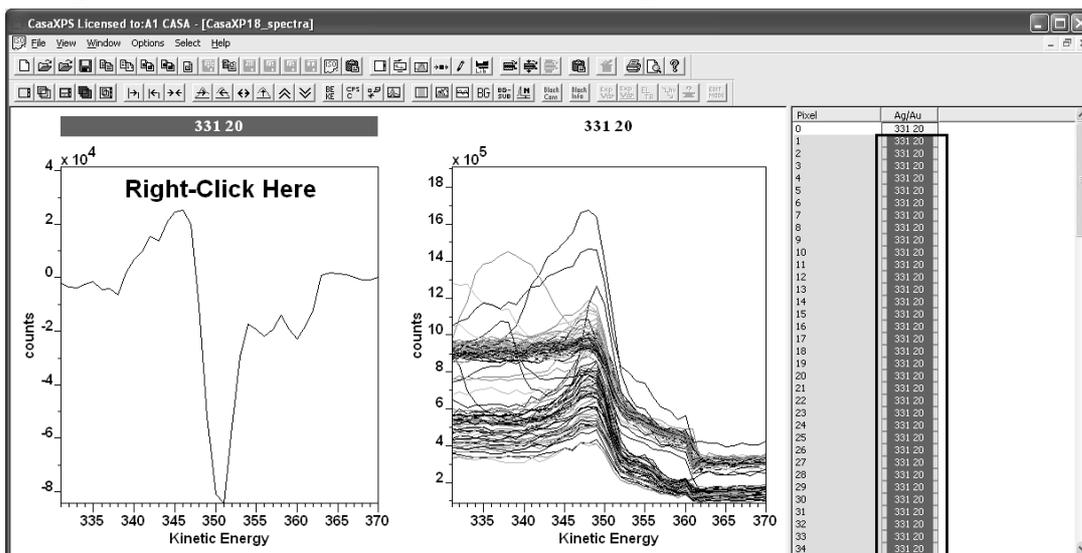


Each VAMAS block contains an entire row of spectra; the spectra are stored as corresponding variables in each VAMAS block and as a result of the method used to store the spectra at pixels, a new processing option on the Differentiation property page of the Spectrum Processing  dialog window specifies that the operation should be applied to all the corresponding

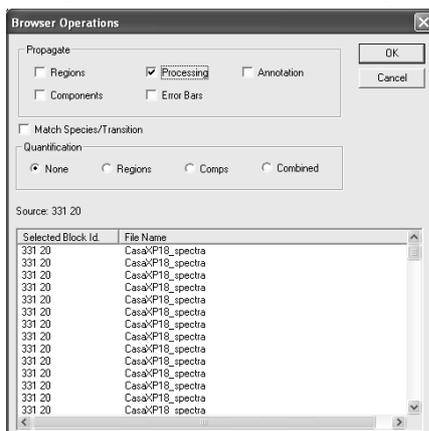
variables in a VAMAS block, rather than simply to the corresponding variable currently displayed in the active tile.



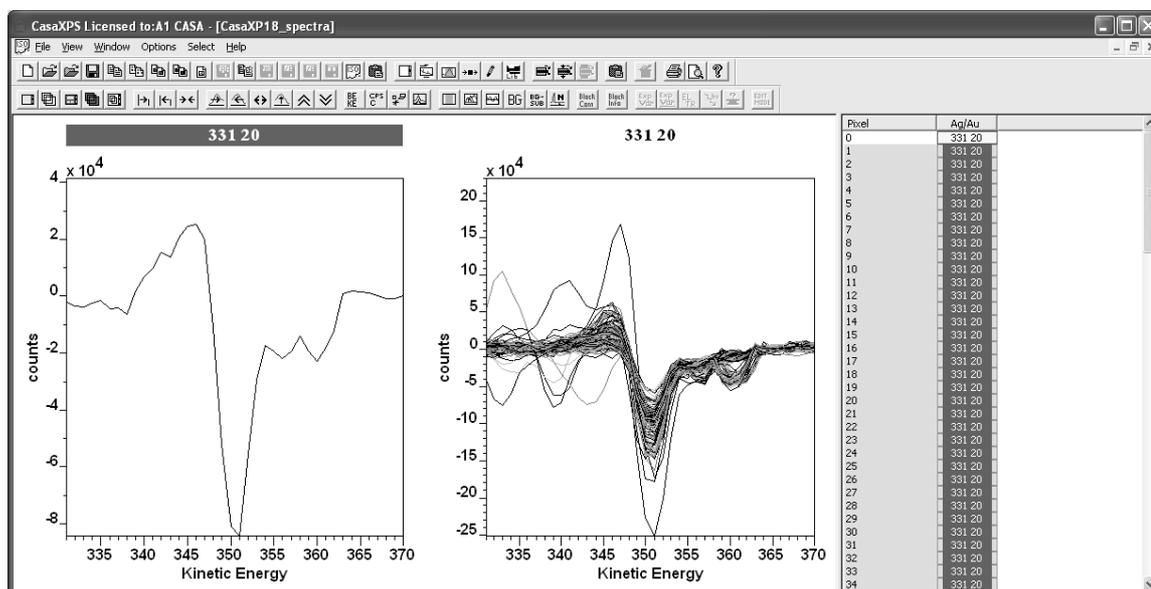
The data in all the VAMAS blocks must be differentiated. Therefore once the data in the active tile is differentiated, the propagate mechanism should be used to process all the VAMAS blocks similarly.



To propagate the differentiation, select the entire set of VAMAS blocks in the right-hand pane of the experiment frame and right-click the mouse button over the active tile containing the differentiated spectrum.



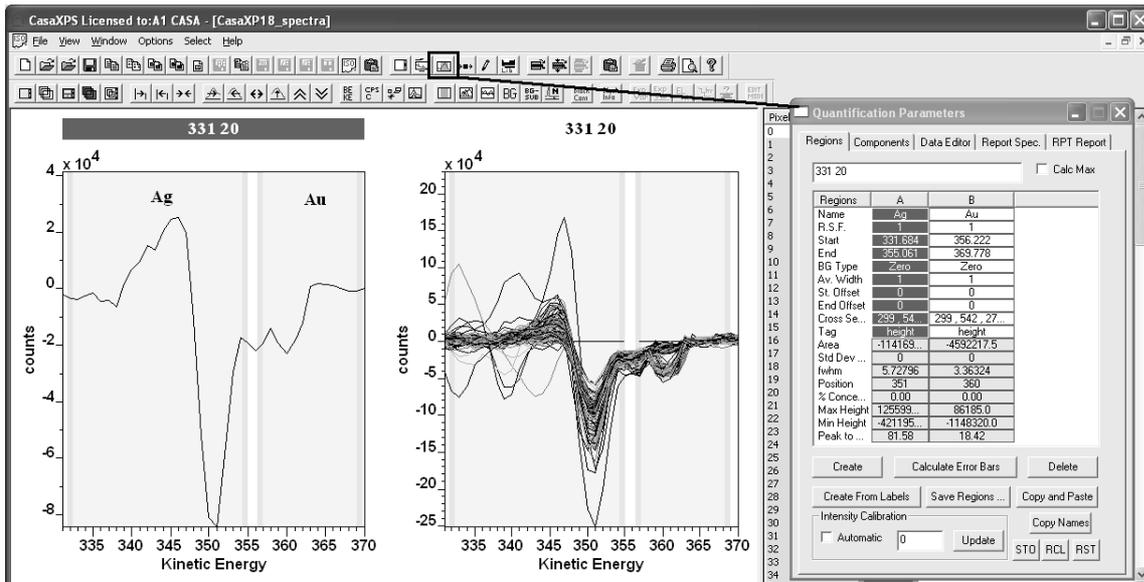
On the Browser Operations dialog window, tick the Processing tick-box within the Propagate section and press the OK button. All the spectra within the targeted VAMAS blocks will be differentiated.



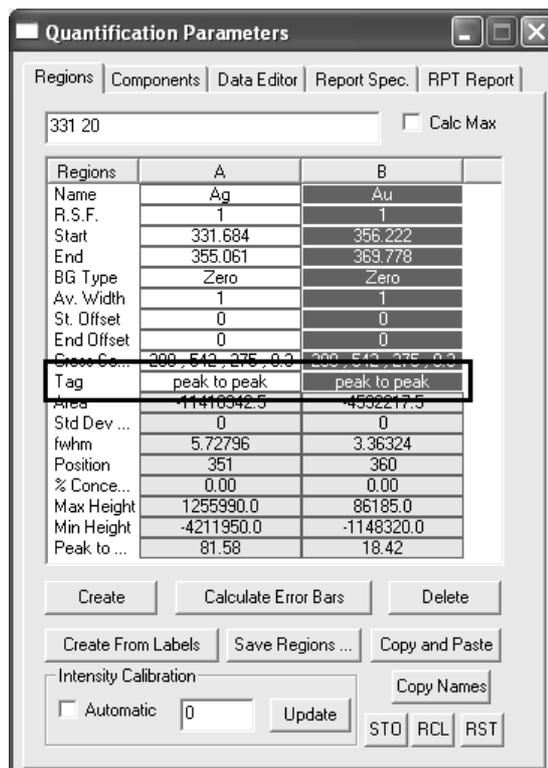
Since the spectra generated from images are stored as multiple corresponding variables and only one corresponding variable from a given VAMAS block can be viewed at a time, it becomes necessary to step through the corresponding variables to inspect the results of the differentiation operation. To step through the corresponding variables in a VAMAS block, the Control + Page-Up and Control + Page-Down keyboard buttons are used. The corresponding variable index in each VAMAS block within an experiment frame is adjusted by the Control + Page-Up and Control + Page-Down keys. Similarly, Control + Home and Control + End move the corresponding variable index to the beginning and end indices for each VAMAS block in the experiment frame. To adjust the index for a corresponding variable on a VAMAS block by VAMAS block basis, using the Page-Up, Page-Down, Home and End keyboard keys whilst holding down the Shift key causes only the VAMAS blocks in the active tile to be adjusted.

### Quantifying the Spectra at Pixels to Produce Images

The quantification of Auger spectra is typically performed using the peak-to-peak metric to measure line intensity. In this example, two Auger lines are evident in the energy range 331 – 370 eV and so two quantification regions can be defined on each spectrum as indicated by the grey bands over the data.

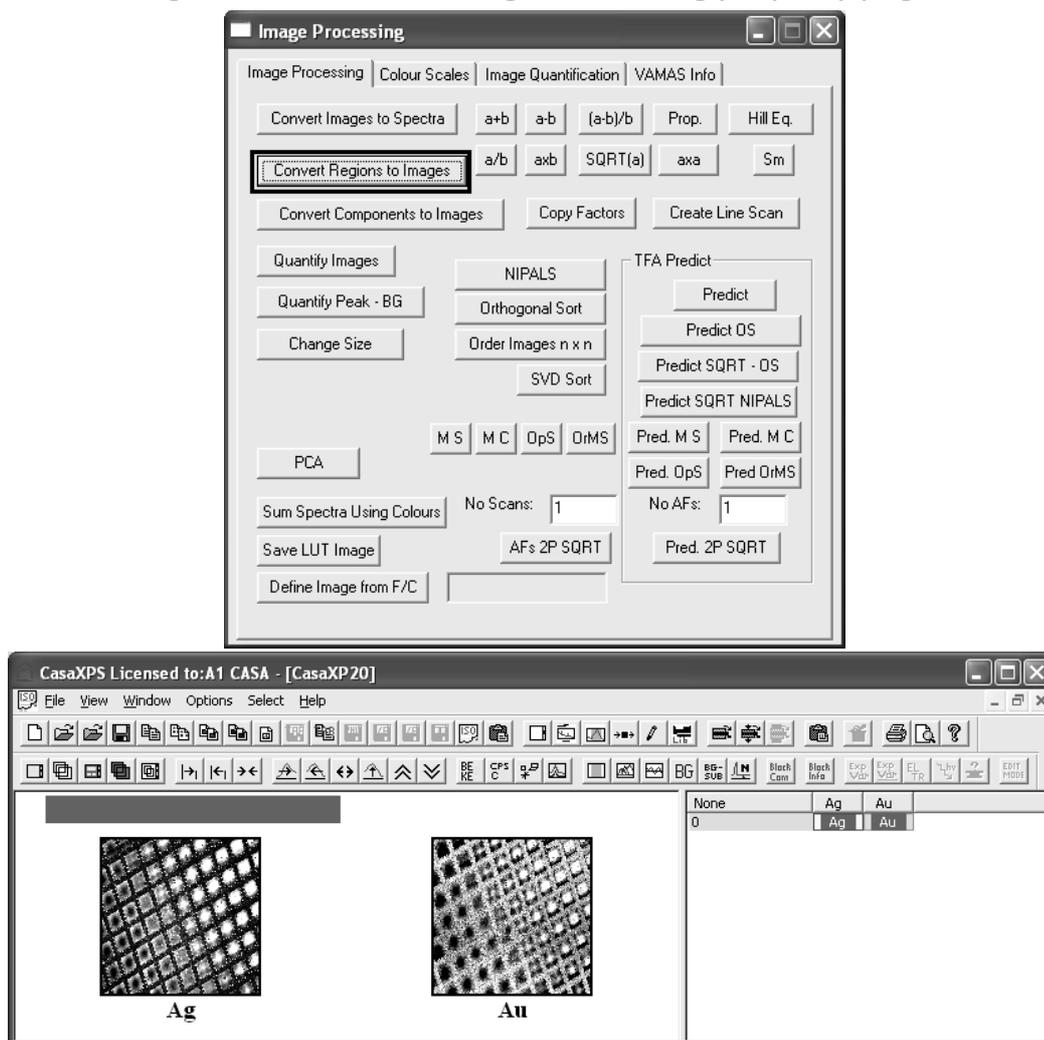


These quantification regions are defined on the Quantification Parameters dialog window via the Regions property page. The regions for use with the spectra-to-images options are identical to those used for general spectral quantification, but with one slight difference. The default action of the **Convert Regions to Images** button on the Image Processing property page is to create images using the integrated intensity based on peak area. For differentiated AES data, the peak-to-peak intensity is required; therefore to create images appropriate for the differentiated data, the Tag field in the region specification table must be assigned a keyword string, namely, *peak to peak*.

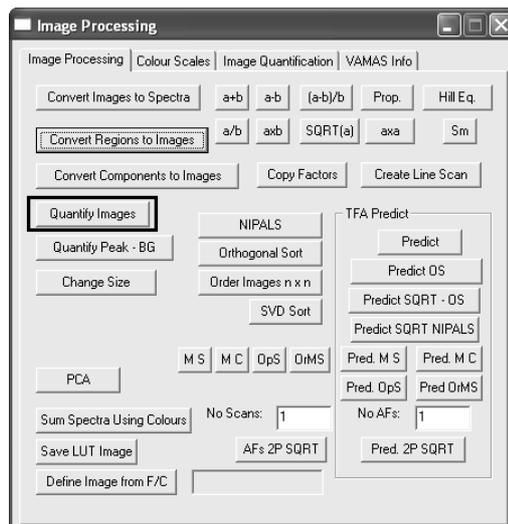


The Tag field is also used to switch between other parameters determined from regions such as fwhm, position and centroid; using these various region outputs, the surface mapped by the images can be viewed with respect to peak broadening or peak shifts. Again the Tag field is entered with the appropriate keyword string e.g. *fwhm*, *position* or *centroid*.

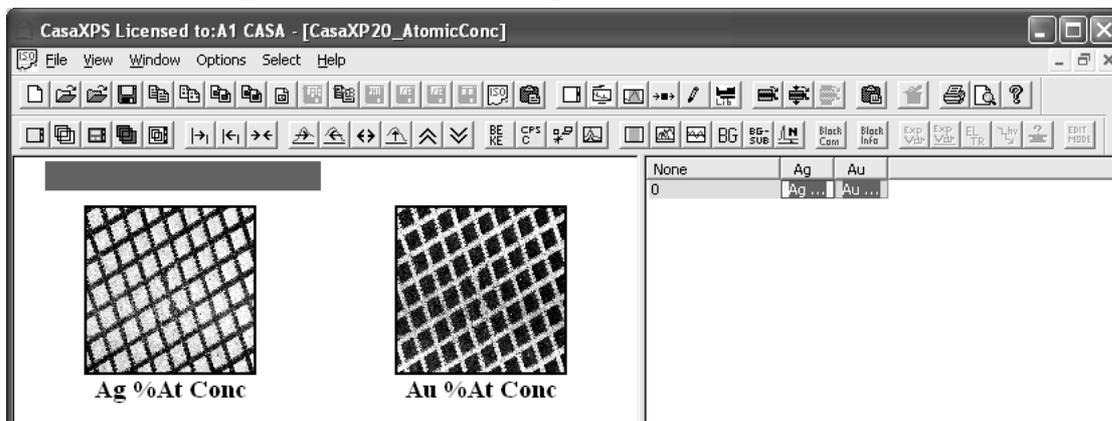
Once quantification regions have been propagated to each VAMAS block in the spectrum file, the corresponding images are generated by overlaying all the spectra from the VAMAS blocks in the active tile and pressing the Convert Regions to Images button on the Image Processing property page.



Ideally, images for each element identifiable on the sample surface should be measured and a similar analysis to the Ag and Au data performed for each element. In this example only two elemental images were recorded, but nevertheless, proceeding to the quantification step based on the two available images has merit in that the resulting images are normalized with respect to each other across the field of view.



The button labelled Quantify Images can be used to perform the operation. The calculation assumes the images are generated from either quantification regions or synthetic components, both of which are in units of CPSeV (for area based intensities) or CPS (for peak-to-peak measurements), therefore the new images are generated simply using the formula  $I_j / (I_0 + I_1 + \dots + I_n)$ . Intensity adjustments for relative sensitivity are accommodated by entering an appropriate value in the RSF field in the quantification regions or components. To perform the quantification step, overlay all the images in the active tile, then press the Quantify Images button. A new experiment frame is created containing the quantified images.



Note, a second button labelled Quantify Peak – BG offers a second means of quantifying a set of images. The procedure in this case does not involve images pre-processed using spectral regions or components and therefore adjustments for time will be included in the calculation. This is neither appropriate nor desirable for data processed as described in this section, but is available for use with raw images, where a less sophisticated approach is adopted.

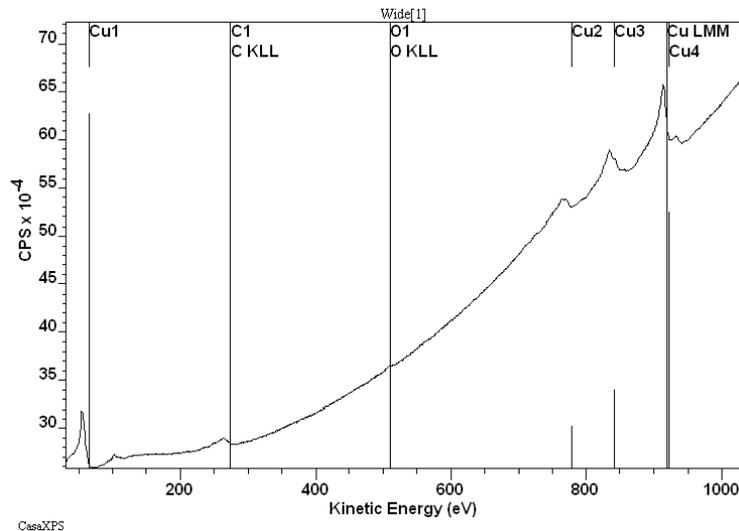
## RBD Instruments Inc. Auger Scan

PHI Auger instruments upgraded by RBD Instruments Inc export data in ASCII files or via the clipboard into CasaXPS. The following are a set of case studies based on data acquired using RBD Auger Scan software.

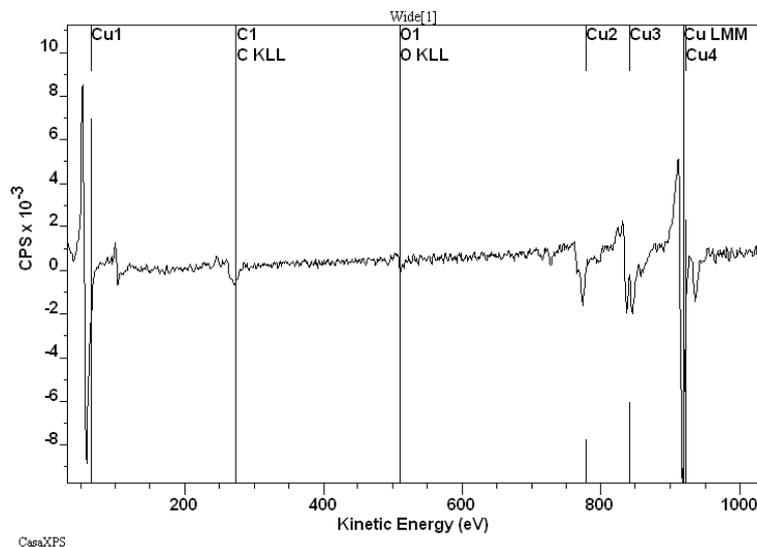
Auger Scan ASCII files include formats suitable for a single survey spectrum, the equivalent of a PHI multiplex acquisition consisting of one or more high resolution spectra or depth profiles relating multiple acquisition cycles to an experimental variable. The data may be acquired in direct  $EN(E)$  mode or as differentiated spectra.

### Survey Spectra

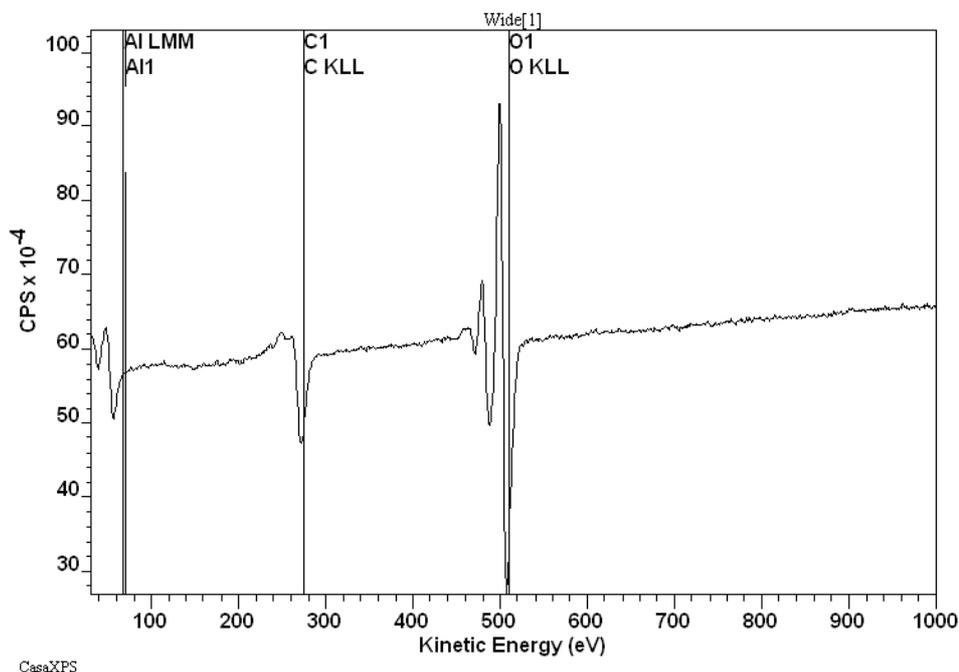
Direct spectra acquired in  $EN(E)$  mode provide an opportunity to visualize the data in the form as acquired:



or numerically differentiated:



Data acquired in differentiated mode differs in the sense that the baseline to the data does not necessarily approximate zero.



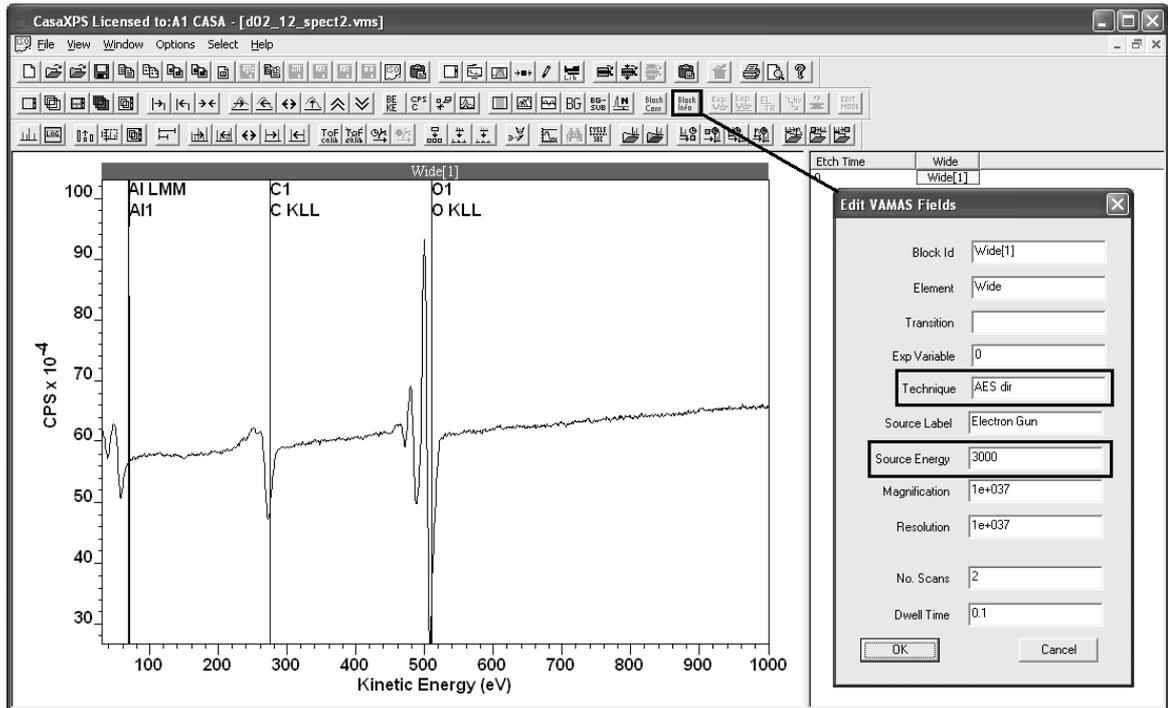
The original form for these data files:

```

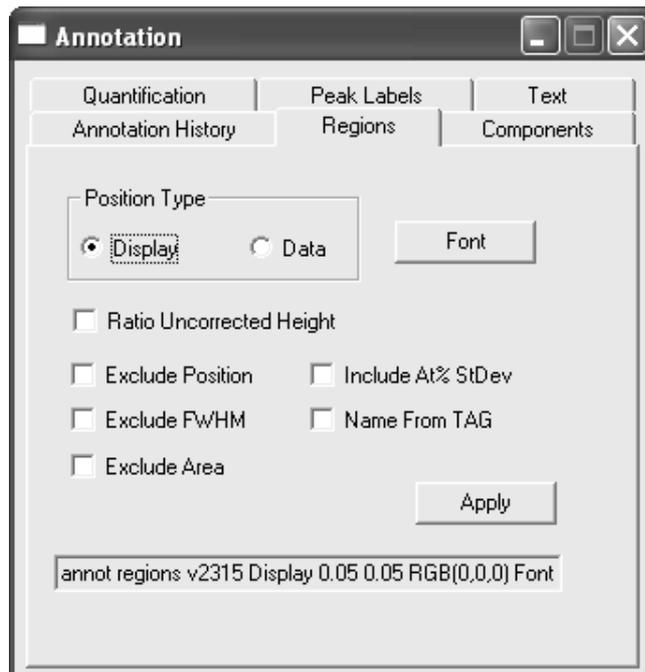
D02_12_spect2.txt - Notepad
File Edit Format View Help
Element ; Region 1 of 1; Depth Cycle 1 of 1; Time Per Step 100; Sweeps 2; AES;
30 123267
31 123450
32 123402
33 122237
34 121699
35 120847
36 118720
37 116815
38 115548
39 114591
40 115197
41 116886
42 118594
43 120076
44 121453
45 122451
46 124376
47 125324
48 125779
49 124622

AES Cu calibration.txt - Notepad
File Edit Format View Help
Element ; Region 1 of 1; Depth Cycle 1 of 1; Time Per Step 50; Sweeps 3; AES;
30 39445
31 39690
32 39823
33 40021
34 40227
35 40376
36 40415
37 40602
38 40732
39 40822
40 40874
41 40932
42 41006
43 41141
44 41223
45 41378
46 41695
47 41857
48 41982
49 42319
50 42723
51 43050
  
```

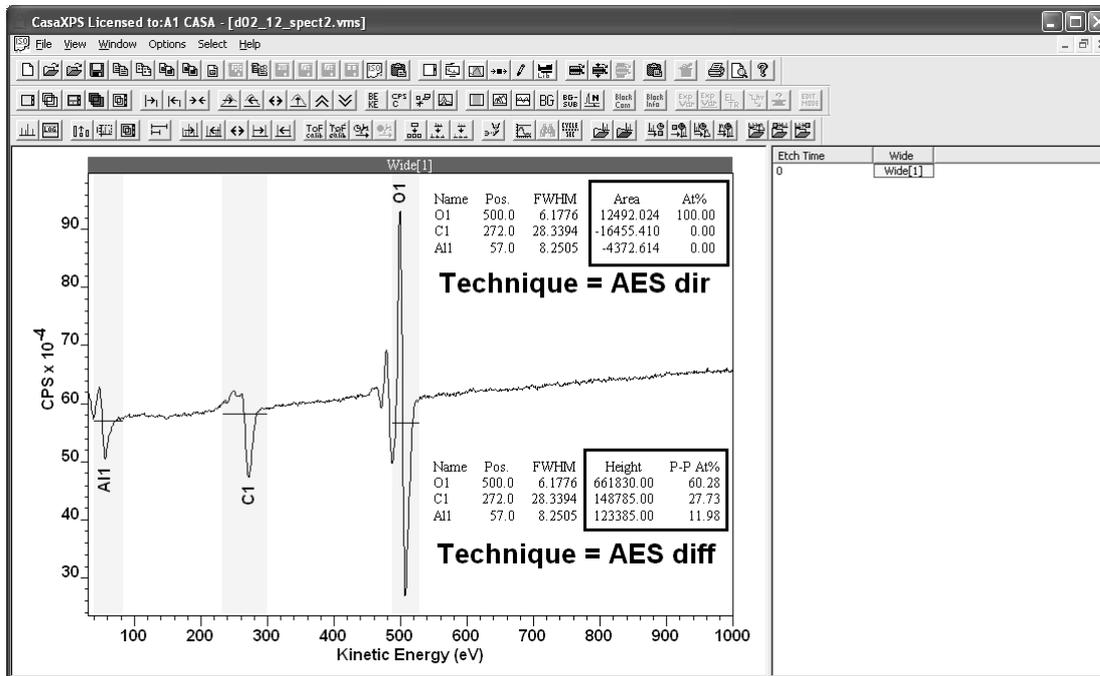
are essentially the same. Since modern instruments typically acquire the Auger spectra in direct mode, the data are assumed to be recorded in direct mode. The implications for the VAMAS file created from these ASCII files are that the VAMAS fields entered by default may need adjusting for the specific data type. The most notable information requiring adjustment is the electron gun energy and the VAMAS technique fields. Both fields influence the ease with which data are quantified.



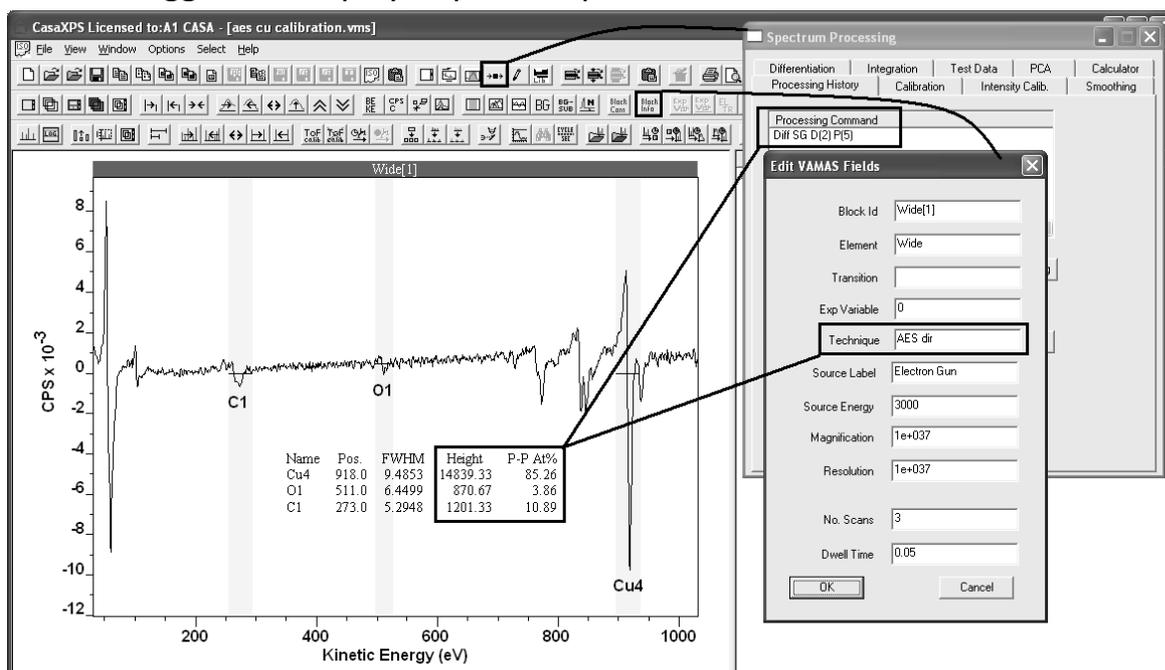
The VAMAS block technique field is assigned by default the value **AES dir**; data acquired as differentiated signal should be assigned the technique **AES diff**. CasaXPS uses the technique field to determine the type of annotation information placed over the display when the Region property page on the Annotation dialog window is applied. For data known to be differentiated, the Region property page creates a table in which peak-to-peak height intensity is reported and used to calculate the atomic concentration. If the data cannot be identified as differentiated, the table offers peak area results.



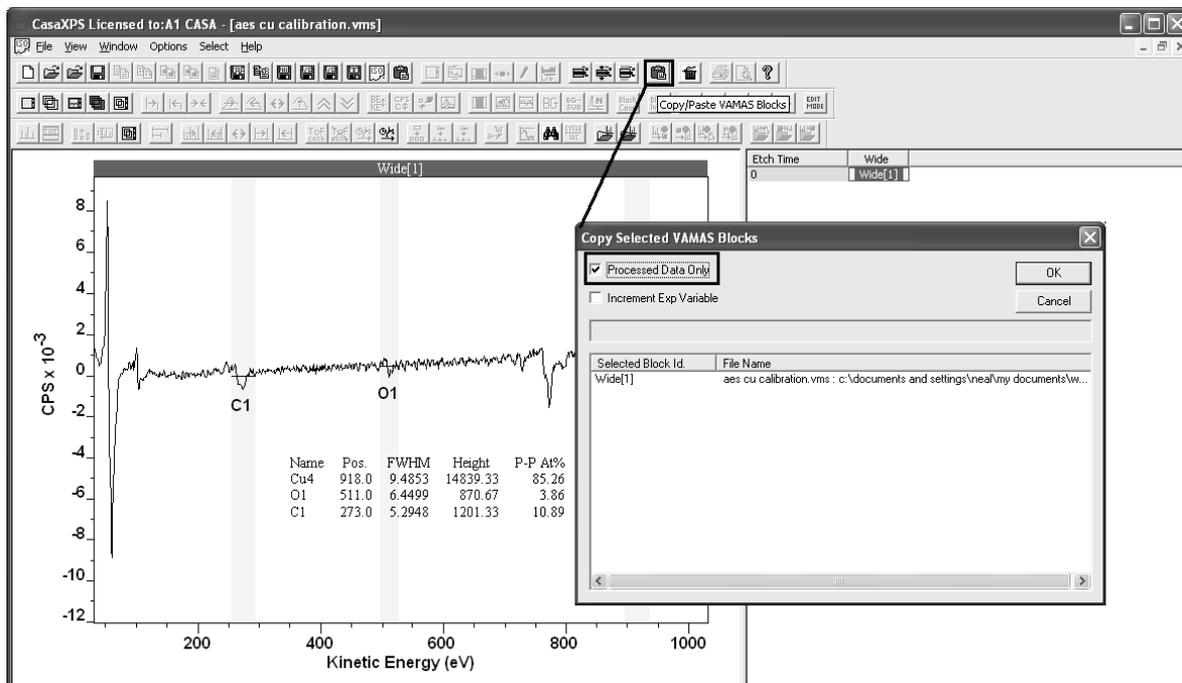
An annotation table created from differentiated data either acquired in that form or externally processed prior to importation into CasaXPS must be assigned a technique type of AES diff.



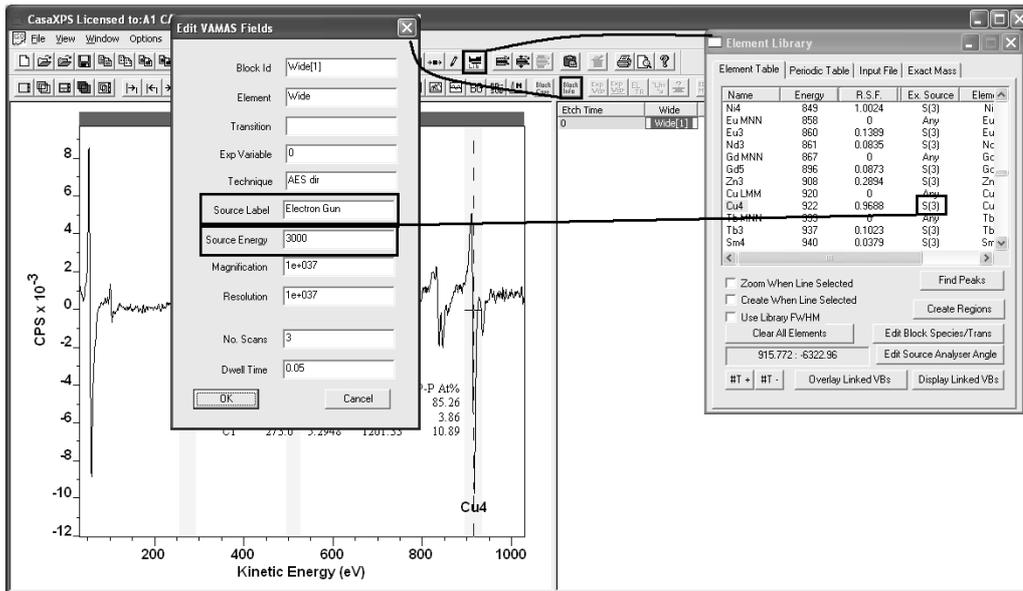
Direct data differentiated within CasaXPS automatically displays the annotation table in terms of peak-to-peak height and peak-to-peak atomic concentrations. The combination of data assigned the technique AES dir and the presence of a processing instruction for differentiating the data displayed via the Processing History property page on the Spectrum Processing dialog window trigger the display of peak-to-peak annotation table.



Note: spectra differentiated in CasaXPS, but copied to a new VAMAS block using the Processed Data Only option will no longer include any processing history and therefore the technique in the copied VAMAS block should be assigned a value of AES diff.



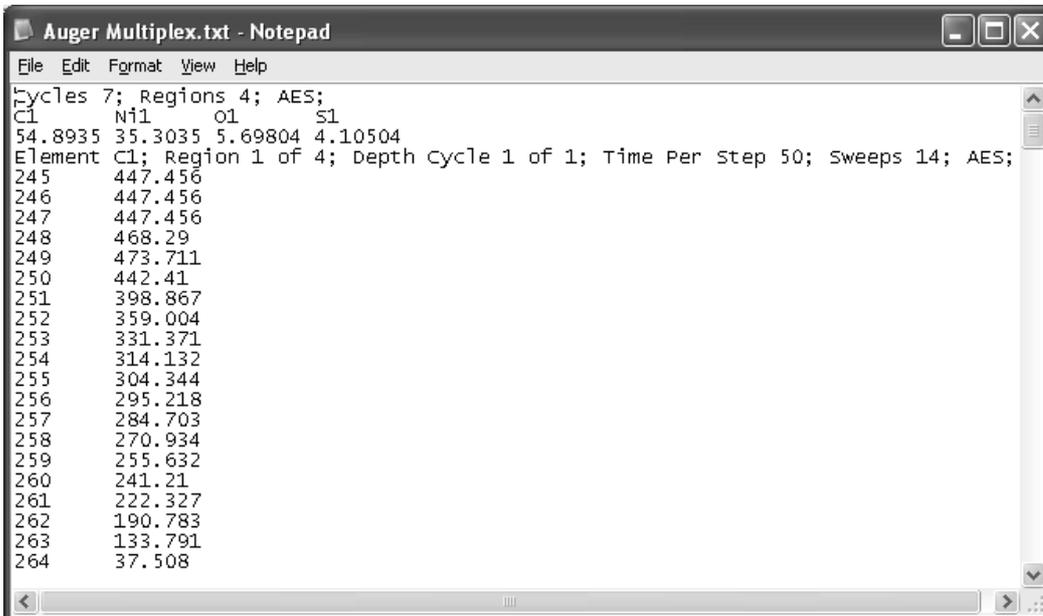
Quantification of spectra involves the correct assignment of an RSF to a transition. RSFs are stored in the element library and to access the appropriate set of transitions for a particular piece of data also requires the correct assignment of the electron gun energy in the VAMAS block containing the data. By default the electron gun energy is assigned a value of 3000 eV. Many older instruments do not have computer control of the electron gun and therefore user intervention is required to specify the actual electron gun energy for the data. The electron gun energy determines the table of RSFs offered via the element library corresponding to the data displayed in the active tile. Quantification regions created via the Element Table property page of the Element Library dialog have RSFs entered into the RSF field based on the table of library entries visible on the property page. It is therefore essential that the correct electron gun energy is assigned prior to the creation of regions.



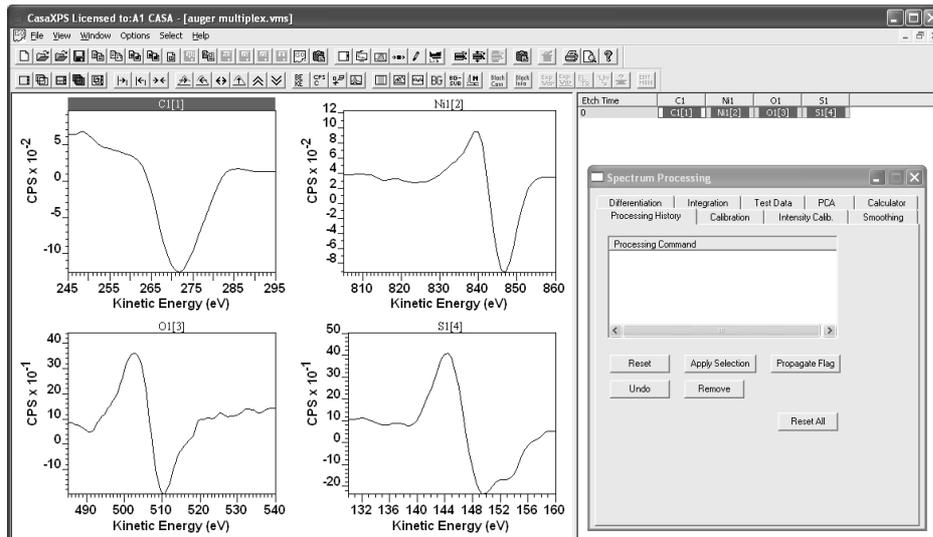
A VAMAS block with Source Energy set to 3000 eV and Source Label set to electron gun results in the Element Table being populated with those library transitions with Excitation Source string S(3). Similarly, a Source Energy of 5000 eV matches to library entries with Excitation Source string S(5).

### Multiplex Auger Spectra

An Auger Scan file may contain more than one spectrum. These spectra typically represent narrow scan data measured for energy intervals in which Auger peaks are expected.



When converted to VAMAS format, each of the narrow scan spectra appear as separate VAMAS blocks.



Note that these narrow scan spectra, for example, have been exported from Auger Scan as processed data, where the processing step was that of numerical differentiation. Data processed externally to CasaXPS are still converted to VAMAS with technique AES dir and so, to be correct, the technique field must be manually adjusted to AES diff. For narrow scan data, the need to set the technique is less important than for survey spectra as quantification of multiple spectra is typically performed using the Report Spec page of the Quantification Parameters dialog window where the nature of the report is specified via configuration files.

In general data exported from Auger Scan may be raw direct spectra, raw differentiated spectra or processed spectra.

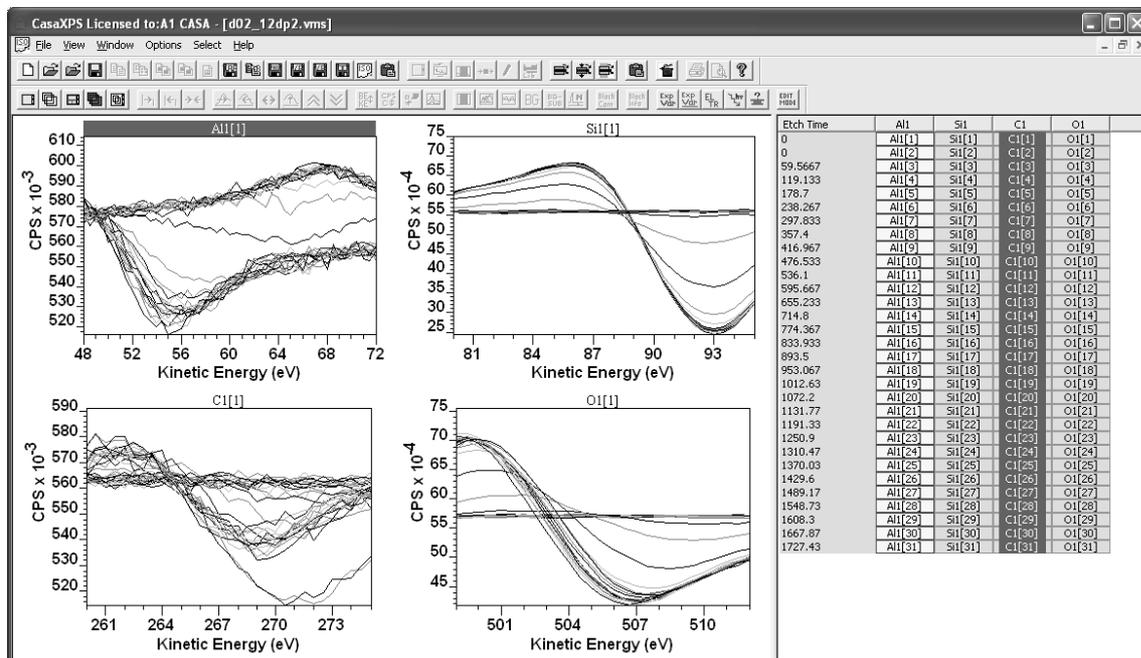
### Depth Profile Data

Auger depth profile data are exported from Auger Scan using a distinct format from data exported as multiplex spectra.

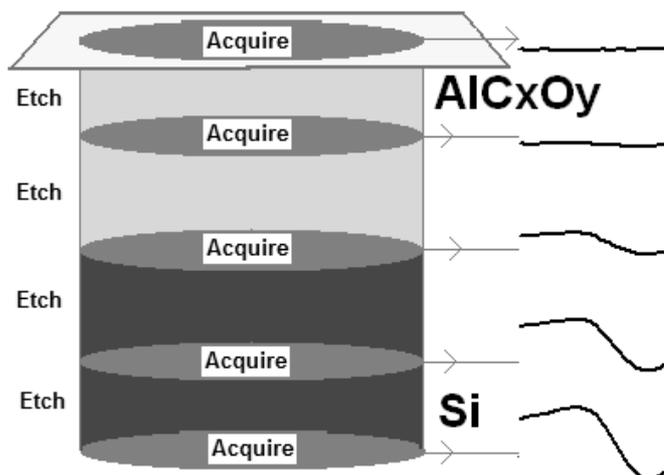
```

D02_12dp2.txt - Notepad
File Edit Format View Help
Depth Cycles 31; Regions 4; SputterTime Continuous 1787; AES;
NumberOfPresputterCycles 1;
Cycle A11 S11 C1 O1
0 50180 5997.5 6684.5 265210
1 49650 5385 65897.5 282835
2 48842.5 4582.5 31220 293640
3 6711.5 6085 31955 287058
4 62097.5 5482.5 34787.5 282353
5 59715 5030 36950 281098
6 63637.5 5752.5 38157.5 278465
7 54930 9882.5 39705 281048
8 51502.5 9152.5 38760 276695
9 54077.5 7490 38347.5 272378
10 54050 5432.5 39035 268598
11 51205 6845 45630 267760
12 49440 4642.5 43630 258308
13 53945 5622.5 42775 236393
14 54555 16865 33505 167483
15 36760 10820 24380 76950
16 20897.5 260503 13137.5 23182.5
17 13257.5 364205 10785 6102.5
18 21510 402188 12055 4240
19 22542.5 417095 6877.5 4135
20 55427.5 420180 6007.5 4797.5
21 27207.5 422708 5932.5 4630
22 26925 430190 8205 4120
23 26025 430338 5320 3637.5
24 24425 431360 6055 5422.5
25 25562.5 431898 7185 4525
26 24700 434015 7967.5 4507.5
27 28335 434770 5160 4895
28 27877.5 437860 4442.5 4502.5
29 26815 433838 7582.5 4332.5
30 28017.5 437365 8297.5 4567.5
Element A11; Region 1 of 4; Depth Cycle 1 of 31; Time Per Step 400; Sweeps 1; AES;
48 233694
48.5 232364
49 230854
49.5 229122
50 230277
    
```

These data are organised into a VAMAS file using the acquisition region labels and etch times. The resulting array of VAMAS blocks as viewed through the right-hand pane of the experiment frame provides the mechanism by which regions are propagated to data from identical transitions.

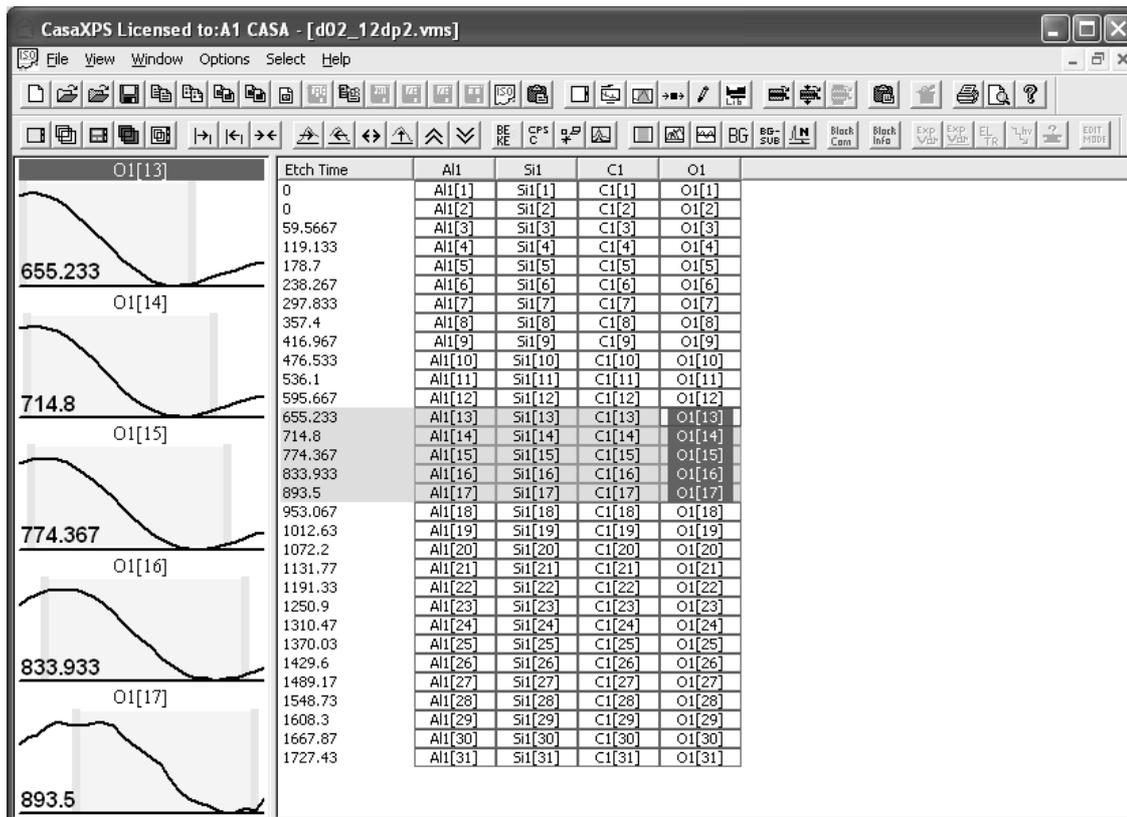


A sputter depth profile involves removing material with an ion-gun interleaved with acquisition cycles where spectra are recorded from each new surface uncovered by the etching process.



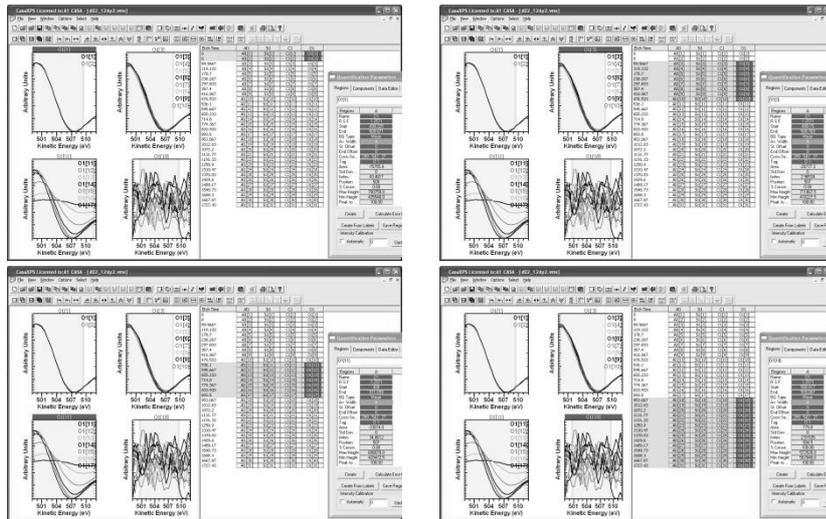
A consequence of etching the material is that the environment for each surface changes with etch time and therefore the nature of the data alters too. An interface between layers may cause a change in chemical state for a transition. For example SiO<sub>2</sub> on elemental Si can cause shifts in peak positions due to charging conditions changing as well as chemical shifts in the peak positions. Differences in the data over the course of a profile are

accommodated in CasaXPS by allowing each VAMAS block to maintain region parameters specific to the spectrum in the VAMAS block.



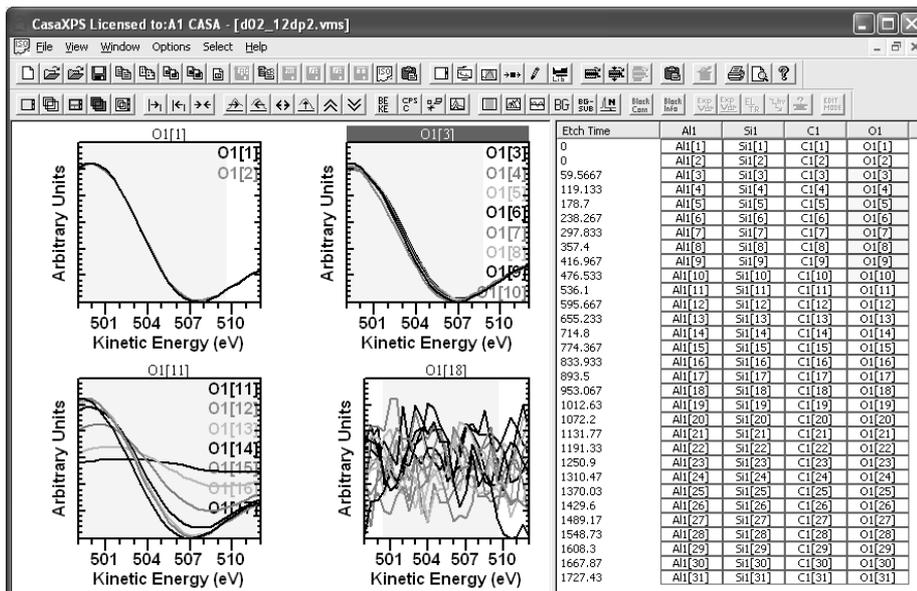
Regions are created using the Regions property page of the Quantification parameters dialog window. The regions displayed on the Regions property page are the regions defined on the VAMAS block displayed in the active tile. If more than one spectrum is displayed overlaid in the active tile then the VAMAS block selected first using the right-hand pane is the active VAMAS block in the active tile. The Regions property page displays the regions defined on the active VAMAS block in the active tile. Any alterations to region parameters only apply to the active VAMAS block in the active tile. It is therefore possible to create regions most appropriate for the individual spectra by displaying the spectra one at a time in the active tile and making adjustments appropriate to the spectrum. Typically, such adjustments are only necessary for a limited number of spectra and the majority of spectra require essentially the same region parameters. The propagate mechanism allows a region defined on a spectrum to be propagated to other spectra based on the selection in the right-hand pane.

For the depth profile under consideration, the oxygen Auger peak is measured from four different environments.



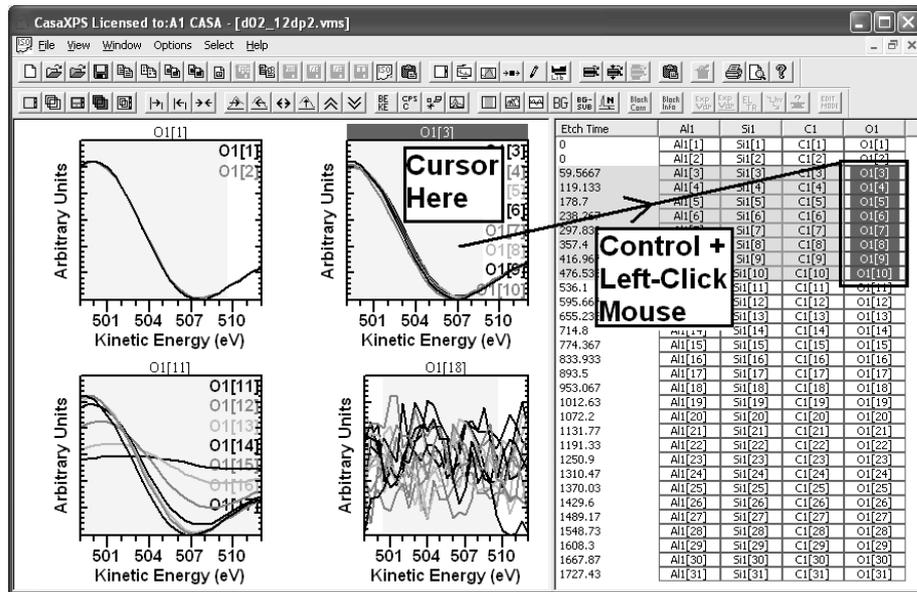
Regions for each of these four environments are specified by, in turn, overlaying the data in the active tile. Creating the first region for the set of VAMAS blocks displayed in the active tile, followed by propagating the region to VAMAS blocks containing similar data.

Since propagation of regions is dependent on the selection in the right-hand pane, options for making selections in the right-hand pane can help target subsets of VAMAS blocks. The display tiles can be used to collect spectra with similar requirements, thus aiding the selection and re-selection of VAMAS blocks in the right-hand pane. The following window illustrates a scenario where the four environments for the oxygen are displayed in four display tiles. No VAMAS blocks are currently selected in the right-hand pane.

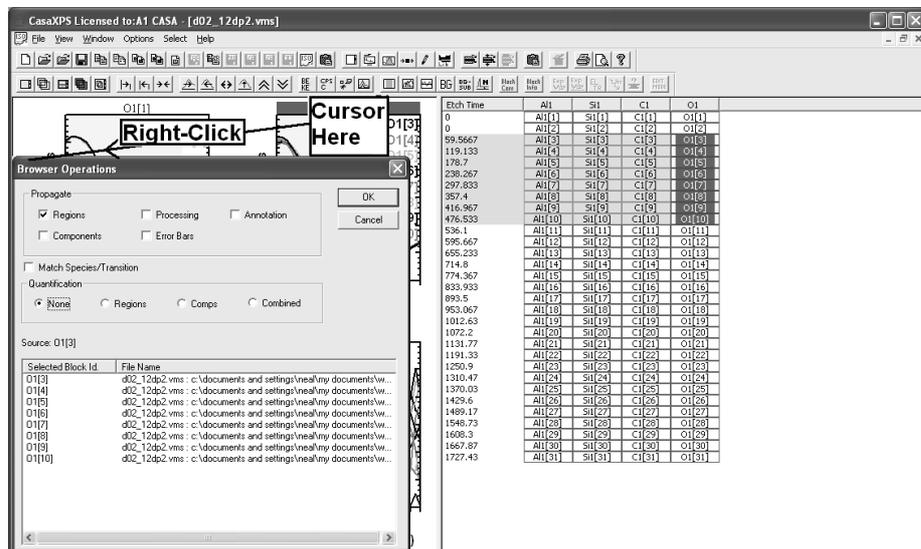


Each display tile represents a subset of VAMAS blocks. If the Control keyboard key is held down and the cursor placed over one of the display tiles, on left clicking the mouse button the VAMAS blocks displayed in the tile over

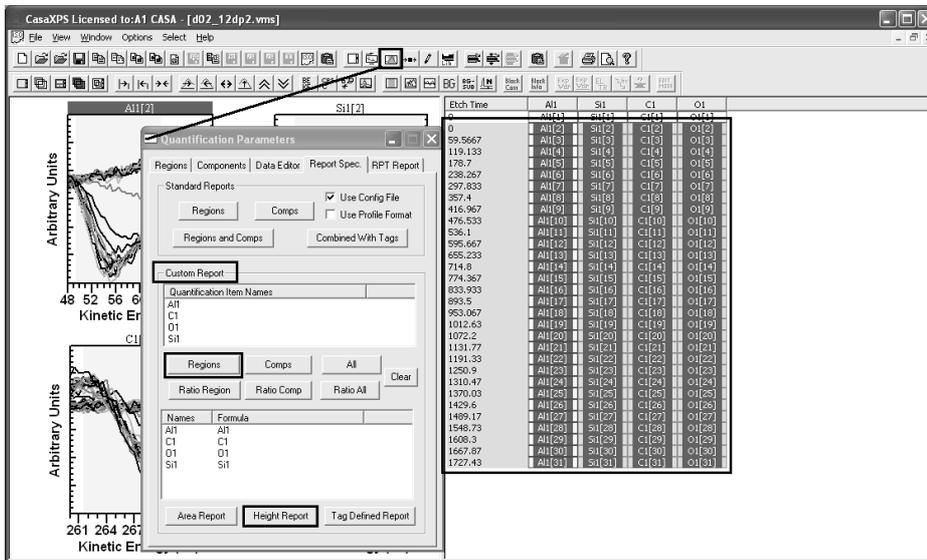
which the cursor resides are toggled into the current selection in the right-hand pane. Thus, the set of VAMAS blocks displayed in the top right-most display tile are reselected as follows:



The VAMAS blocks displayed in the tile over which the cursor is placed are added to the selection such that, if the blocks are already selected, the action deselects the selected blocks while blocks previously not selected become selected. Since the propagate operation transfers regions etc to selected VAMAS blocks, collecting data in display tiles aids the selection and therefore propagation process. Once the subset of VAMAS blocks has been returned to the selection in the right-hand pane, adjusting the region parameters for the block in the active tile naturally leads to the propagation of the changes to the associated data. Right-clicking the mouse with the cursor over the active tile invokes the propagation dialog window, thus facilitating the transfer of changes to all the data displayed in the active tile.

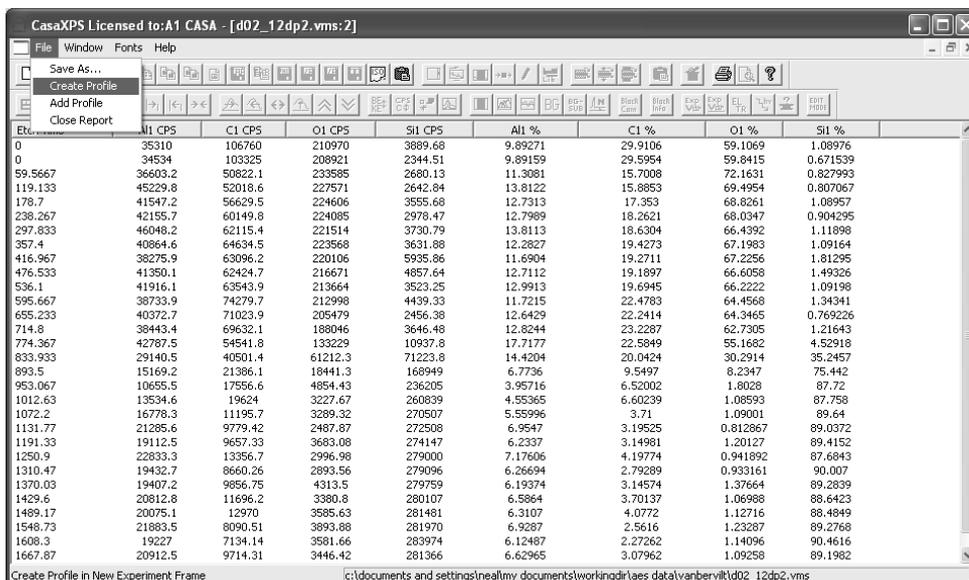


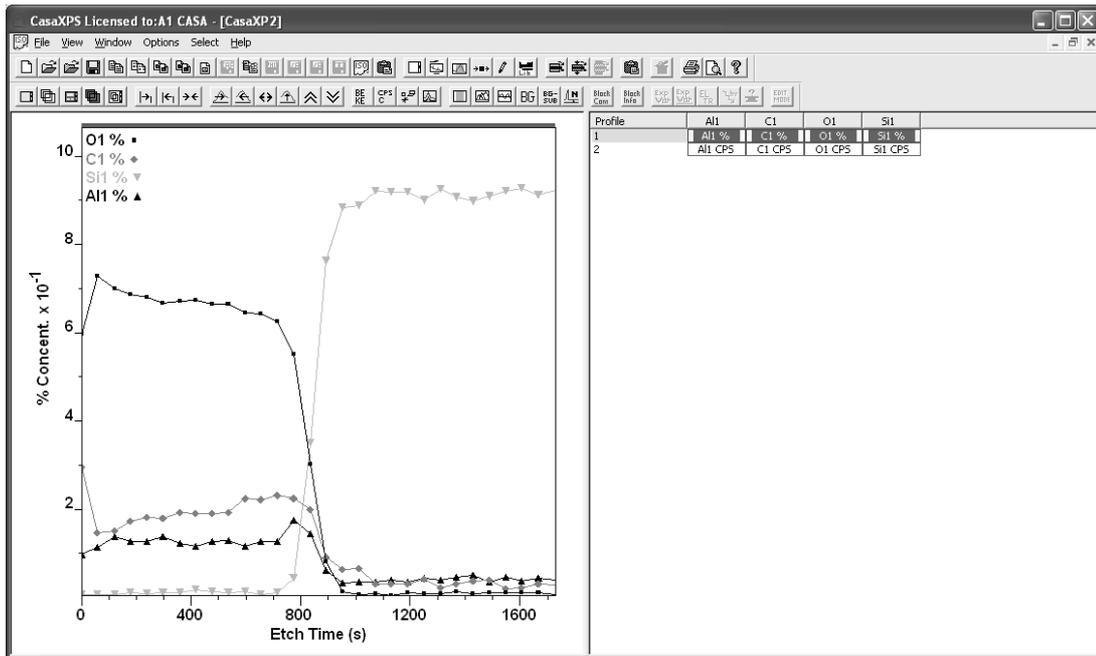
Once regions have been defined for all the spectra in the profile, a plot of atomic concentration against etch time is created via the Report Spec property page.



The Custom Report section on the Report Spec property page offers a means of tabulating intensities and atomic concentrations as a function of etch time. These tables in turn are converted to a VAMAS file or exported via the clipboard to spreadsheet software. The File menu available once the data are tabulated using the Height button on the Custom Report provides a means of generated the VAMAS file, while the copy toolbar button places a text form of the table on the clipboard. These operations are described in earlier sections of the Auger manual.

The following profile plot is an example of a depth profile created via the File menu available when the Custom Report results window is the experiment frame with focus.





# TOF SIMS

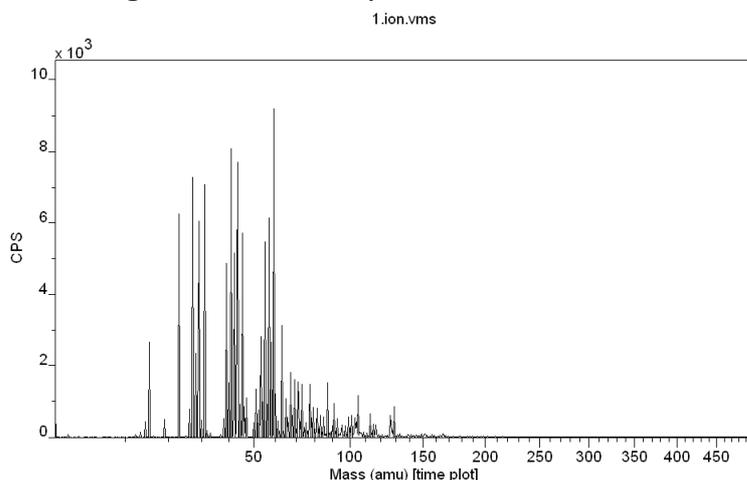
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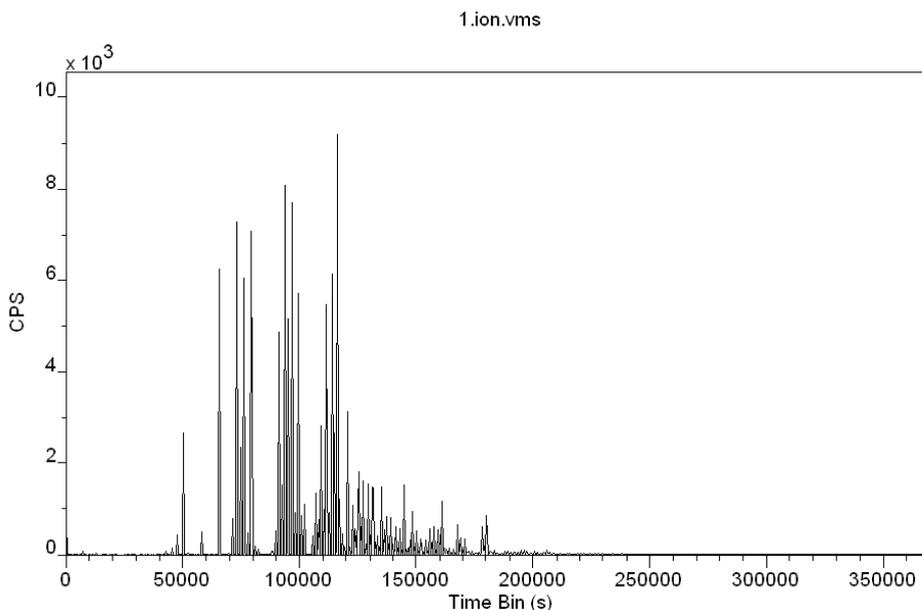
## The Nature of ToF Spectra

Time-of-Flight Mass Spectrometry (ToF MS) is based on the principle that ions created from a sample are accelerated into a flight tube using an electric extraction field resulting in each ion of a given charge acquiring a characteristic energy from a tight distribution of possible energies. Since the kinetic energy of the ions are nearly identical, the velocity attained by ions with differing mass must also differ, thus the time taken for an ion with a given charge to travel a given distance down the flight tube to the detector discriminates between ions of different mass. Specifically, the mass of an ion is proportional to the square of the time taken to travel a fixed distance. Thus, ToF MS works on the basis of a stop-watch; a start event occurs as the extraction voltage is pulsed, followed by a sequence of stop events representing the arrival of ions at the detector. To process a ToF mass spectrum from the raw timing data, a histogram is created from the set of time values, where the time events recorded during an experiment are counted into time-bins. The relationship between the time events and the mass of the ions responsible for the time events allows the time-bin histogram to be viewed using a mass scale.

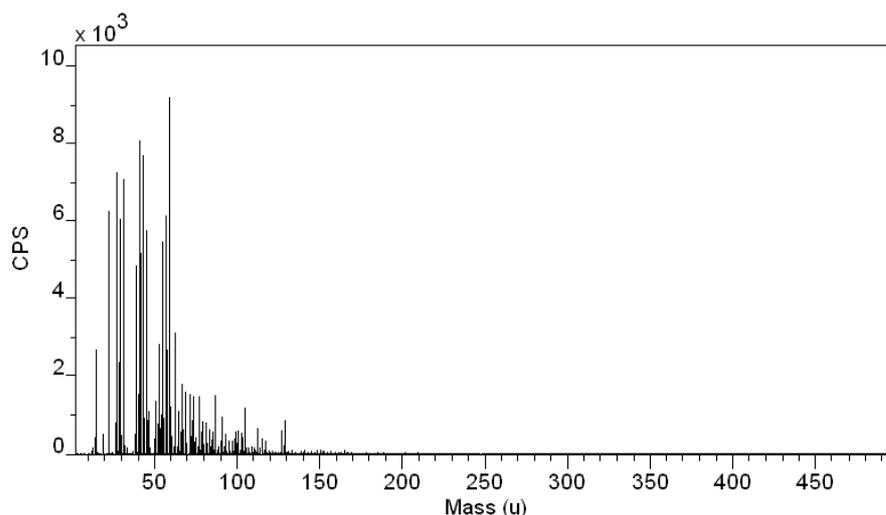
CasaXPS displays the ToF intensities with respect to the time bin indices, even when a mass calibration is available. Converting a spectrum to mass binned intensities involves a mapping which cannot be reversed; explicit steps must be taken to perform the transformation between time and mass.

The following two plots are for the same data, both viewed in the time domain. The mass range in these two plots is identical.



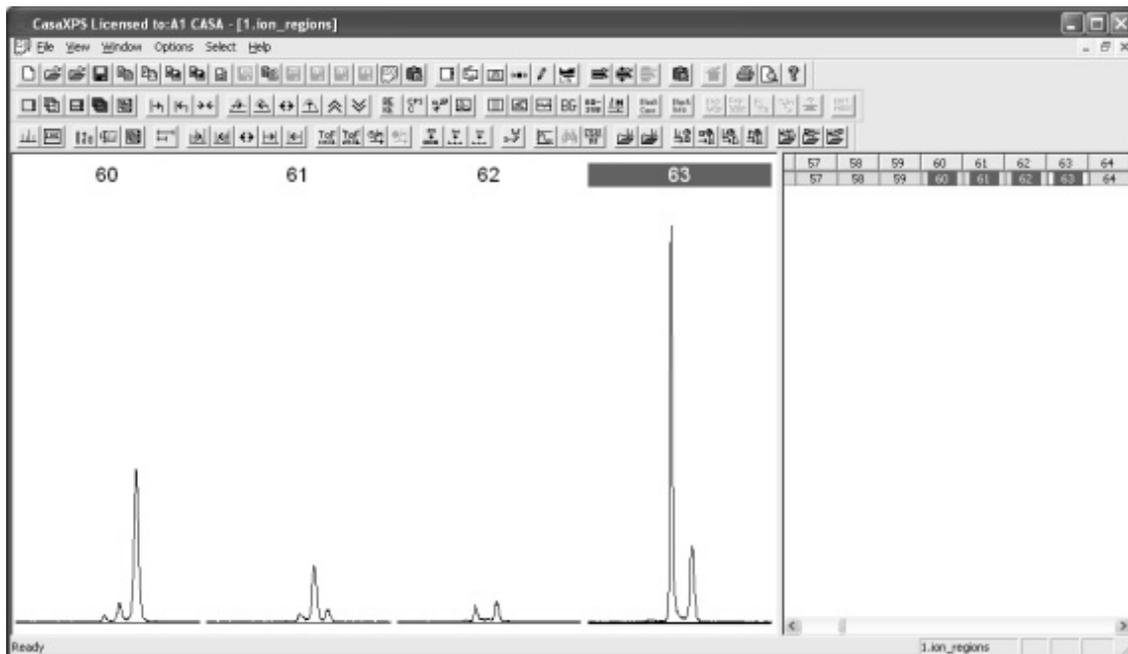


The same spectrum plotted using a linear mass step size changes the perspective of the data as follows.



Spectra from ToF instruments traditionally appear as a single spectrum over a wide range of mass. The spectral display reflects the parallel nature of the technique in the sense that counts are allocated over the entire range of time bins for each pulse of the ion gun. This is in contrast to quadrupole or magnetic sector MS instruments where the signal is only recorded one mass bin at a time. Nevertheless, for high resolution ToF MS the majority of time bins, particularly at low mass, contain little information, therefore CasaXPS offers a means of converting ToF spectra from a single monolithic data set into a set of mass intervals representative of the useful information content. Each nominal mass, based on the current time to mass calibration, is isolated into individual VAMAS blocks. Presenting a ToF spectrum as a set of many

VAMAS blocks favours the tools within CasaXPS providing the basis for data comparison and peak analysis via synthetic peak models.



The partitioning of the time bins into suitable mass ranges around the nominal masses requires a calibration for the mass scale.

## ToF Mass Calibration

The relationship between the mass  $m$  of an ion and the time taken for the ion of a given charge to travel a fixed distance is quadratic in the flight time  $t$ . For an ideal system, the time-to-mass relationship is:

$$m = [(t - t_0) / b]^2$$

where  $t_0$  represents a time offset and  $b$  scales the time values appropriately. Since knowledge of these two parameters  $t_0$  and  $b$  is sufficient to describe the relationship between the mass and time-of-flight, given two mass/time pairs the calibration parameters can be determined from a pair of simultaneous equations. In reality, assigning the mass/time coordinates from the time-binned spectra is not exact and therefore the time-to-mass calibration must be computed in a least-squares sense using multiple mass/time pairs. Further, the choice of mass/time pairs must be carefully made to ensure accuracy of the calibration for both interpolated and extrapolated mass regions. Those mass regions falling within (interpolation) the set of mass/time pairs used to create the calibration will be more accurate with respect to the time-to-mass calibration than those outside (extrapolation) the interval containing the mass/time pairs included in the

least squares fit. It is therefore important to calibrate a spectrum using peaks over as wide a mass range as possible and check that peaks, once calibrated, can be sequentially assigned to nominal masses. The following describes the tools in CasaXPS for calibrating a spectrum of time-bins with respect to mass and how to assess the success of this procedure.

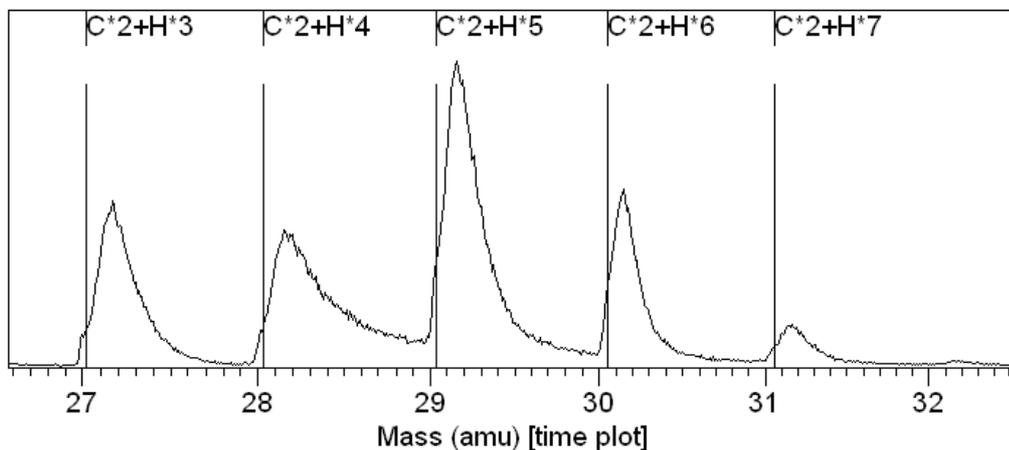


Figure 1

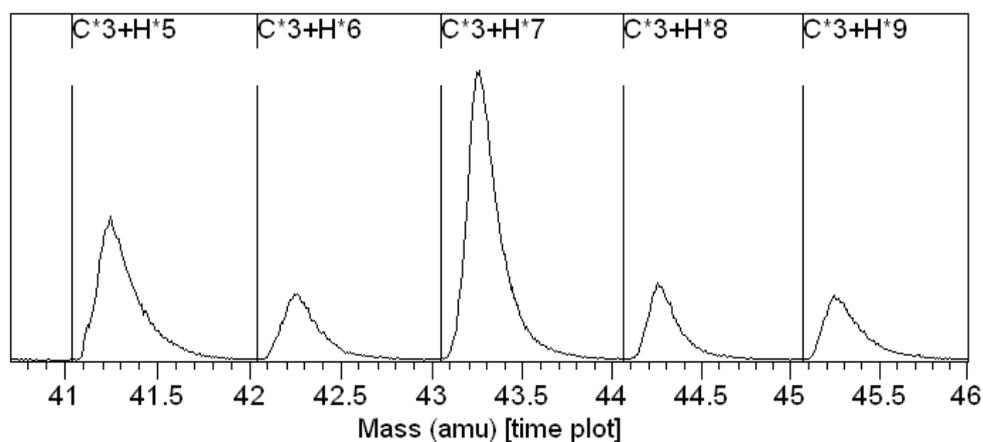
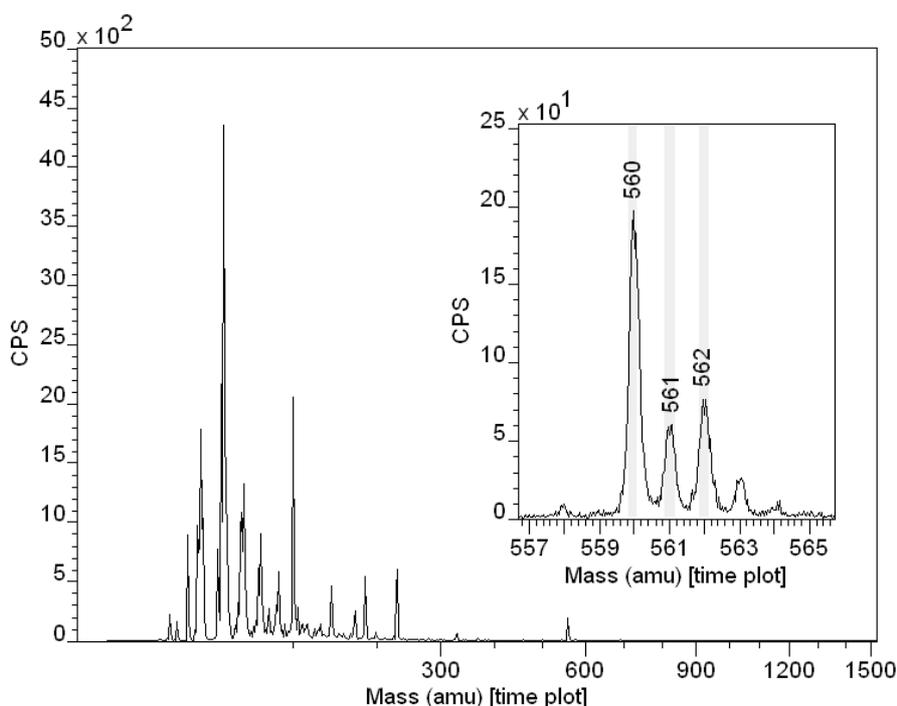


Figure 2: An example of a poor mass calibration based on extrapolation.

When calibrating the mass scale, the primary objective is to assign each visible peak to a nominal mass. For some spectra and instruments, there may be perfectly good reasons why this objective may fail, but in general each peak in the data should be associated with a nominal mass; any mass defect from the nominal mass provides information about the atomic or molecular ion responsible for the peak. It is not necessary nor is it always possible to attribute each peak to a known ion, however, when properly calibrated, if the observable peaks deviate from the sequence of nominal masses then the accuracy of the calibration may be in doubt. The problem of calibrating the mass scale reduces to identifying a set of peaks sufficiently well distributed over the mass scale to provide plausible mass assignments for each and every

peak in the spectrum. Figure 1 is an example of a mass calibration in which the set of peaks displayed matches well with the computed mass positions; however the calibration is performed using only those peaks within the window in Figure 1 and a similar agreement, when using the same calibration, for the molecules shown in Figure 2 is not achieved. The poor mass calibration is remedied by simply including at least one of the peaks in Figure 2 as part of the calibration set. The concept of progressively adding calibration points to the set used to mass calibrate a spectrum is developed in following sections.

### ***Calibration Based on Nominal Masses***

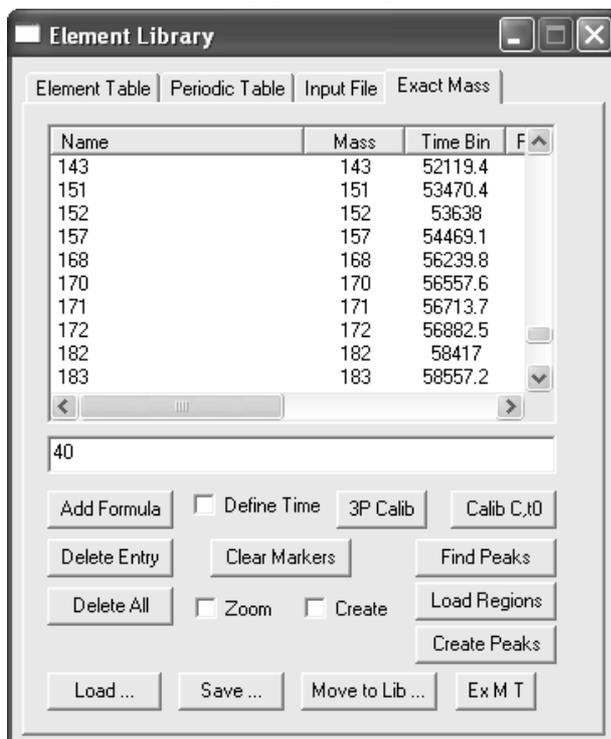


**Figure 3: Nominal mass calibration**

The procedure for calibrating a spectrum can be summarised as follows: following an initial assignment based on at least two peaks, new peaks are progressively added to the set of mass/time pairs until the observed peaks are sequentially associated with nominal masses. The spectrum in Figure 3 is calibrated based on nominal masses and an iterative improvement procedure. This process can be performed manually using the Exact Mass property page (Figure 4), where peaks are associated with formulae using the mouse, or alternatively nominal masses are used in a sequence of steps involving repeatedly:

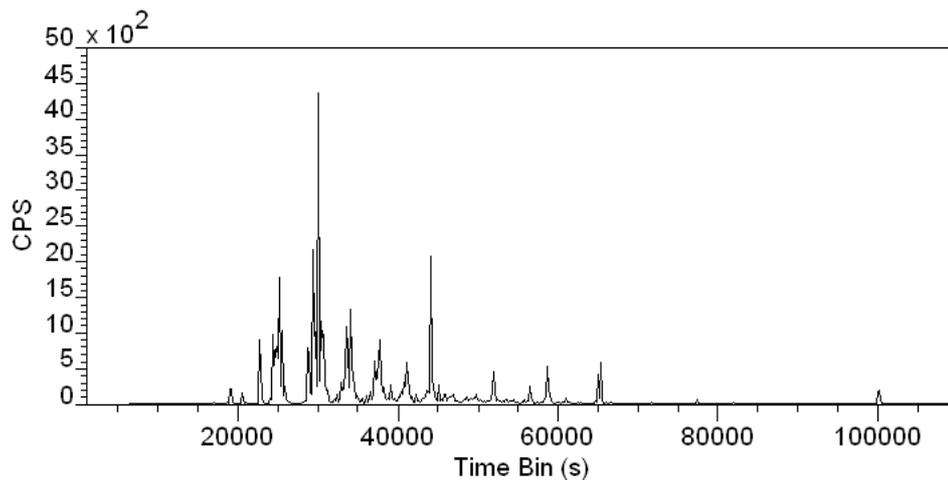
1. Finding the peaks using the Find Peaks button.

2. Replacing the current calibration list by nominal masses and times determined from the regions obtained from the Find Peak operation. The Load Regions button transfers the required information from the current set of regions to the calibration list on the Exact Mass property page.
3. Recalibrate the mass scale by pressing the Calib C,t0 button.



**Figure 4: Exact Mass Calculator Property Page.**

The Find Peaks button uses a threshold to identify peak structures in the data; then for each peak identified, a region is created on the spectrum using the name derived from the nominal mass determined from the region. The Load Regions button transfers those nominal mass names and computed positions to the calibration table on the Exact Mass property page for which the computed mass is within a tolerance of the nominal mass. The search for these acceptable mass/time pairs begins with the low masses, so the initial calibration should begin with small masses, but typically greater than 10 amu. With each repetition of these steps, the number of regions loaded into the calibration table should increase until, ideally, all the peaks found are included in the calibration table. At this point, the spectrum so calibrated should be surveyed to ensure the peaks, both minor and major, are associated with the nominal masses on the abscissa scale.

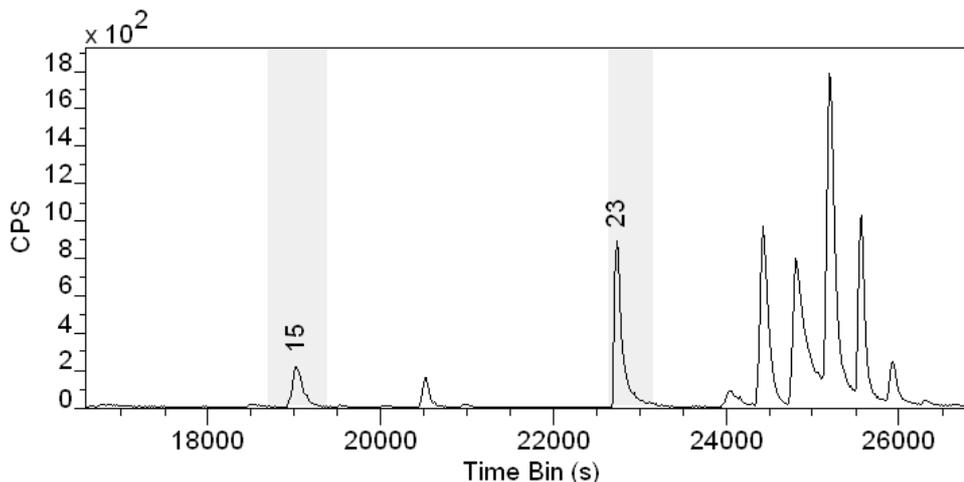


**Figure 5: Raw time-binned spectrum.**

Calibration using nominal mass values is not always appropriate, for example heavy molecular ions; however, for some spectra, calibration using exact masses is equally inappropriate. The data in Figure 1 is an example of a spectrum for which it is beneficial to use nominal masses rather than exact masses; the spectrum derives from a total ion list file containing image information and minor variations in acquisition conditions across the imaged surface cause small shifts in the underlying peaks summed to form the total ion spectrum. Peaks are neither high enough in mass resolution nor well enough defined in terms of position to use an exact mass position. The latter can be demonstrated using false colour images to extract spectra from different zones on the image.

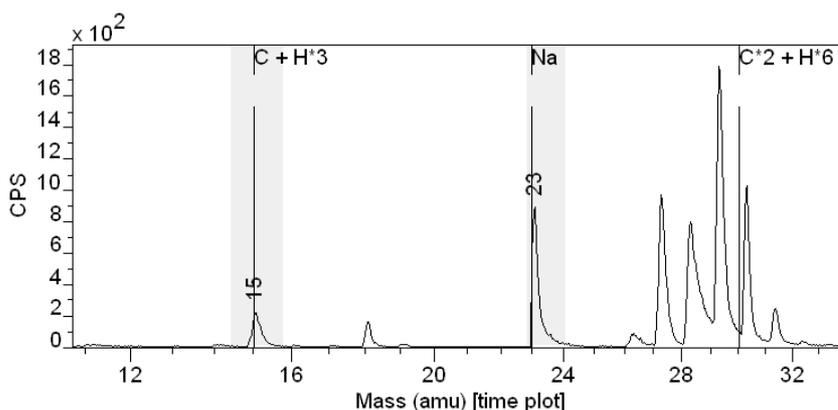
### **An Example of Mass Calibration using Nominal Masses**

Initially the spectrum is without a mass calibration as seen in Figure 5. The first step is to identify two peaks.



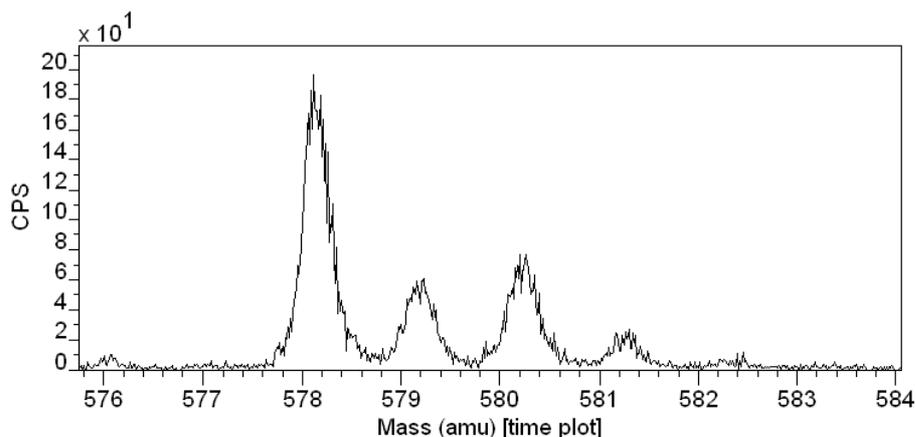
**Figure 6: Two peaks are identified by creating quantification regions.**

The regions defined on the spectrum in Figure 6 represent the initial pair of mass/time coordinates used to produce a rough calibration for the mass scale. The regions are created using the Regions property page on the Quantification Parameters dialog window. Each region calculates the time-bin representative of the peak, while the mass corresponding to the computed time-bin is entered into the name field of the quantification region. In this case, the name fields are entered with the nominal masses 15 and 23, although these values could equally well have been entered using the formulae  $C+H*3$  and  $Na$ , respectively. Calibration based on these two regions is performed by pressing the  toolbar button. When the toolbar button is pressed, any spectra appearing in the Active Tile will be calibrated based on regions so defined on the displayed spectra.



**Figure 7: Spectrum after initial mass calibration.**

While the calibration in Figure 7 looks reasonable for masses close to the calibration points, the high mass peaks are poorly calibrated. The largest peak in Figure 8 differs by about 18 amu from the mass calibration shown in Figure 3.



**Figure 8: Poor mass calibration for high mass peaks. Same peaks as those displayed using the inset tile in Figure 3.**

While the initial mass calibration based to only two low mass peaks is clearly a problem at higher masses, the accuracy is sufficient to begin the iterative process of build a fuller set of mass calibration points.

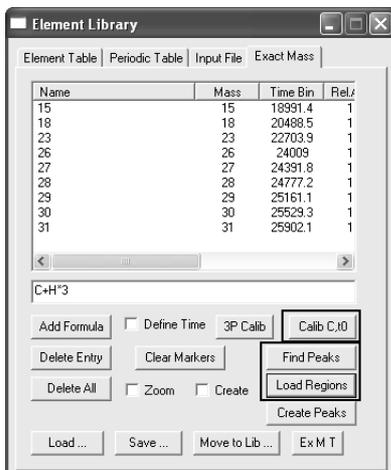


Figure 9: Exact Mass property page.

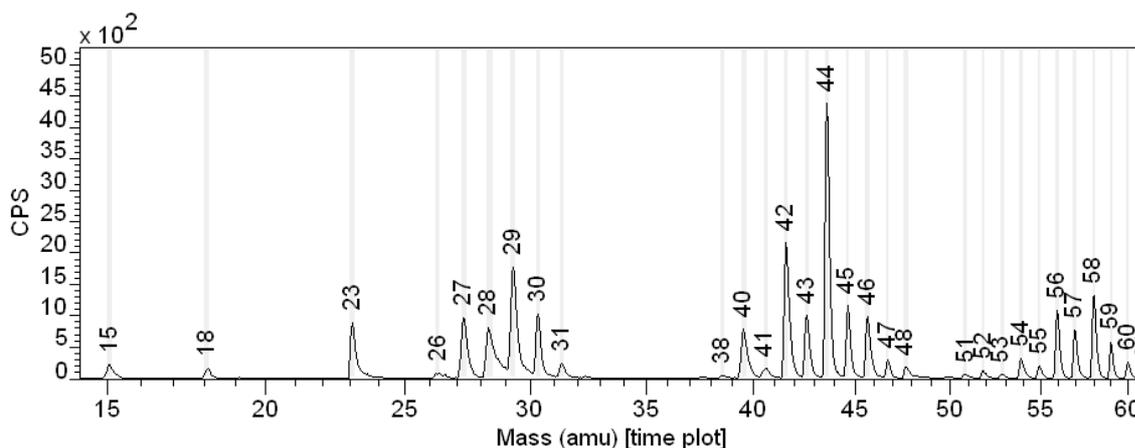
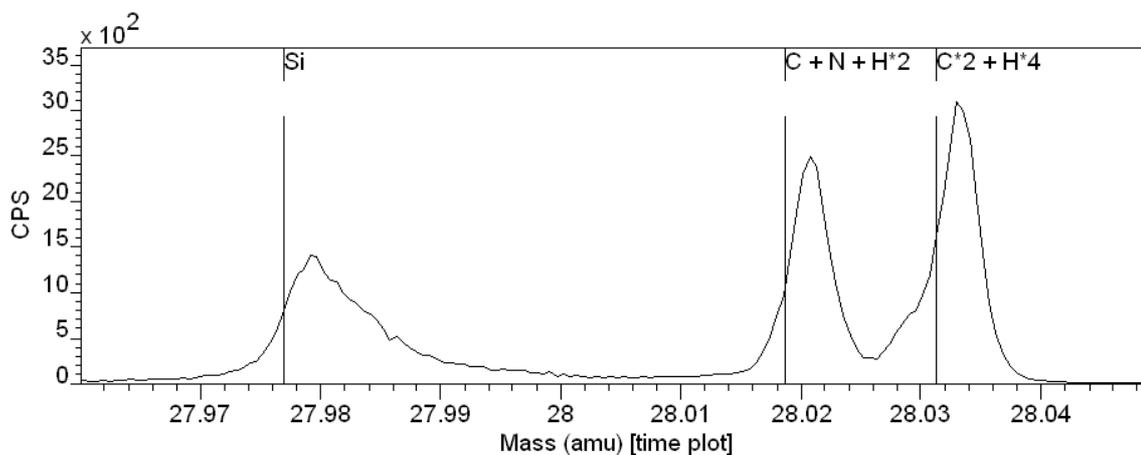


Figure 10: Result of Find Peaks with a threshold of 20.

Given the initial mass calibration based on the peaks labelled 15 and 23, the Find Peaks button on the Exact Mass property page shown in Figure 9 can be used to assign nominal masses to all peaks characterized by a threshold value. On pressing the Find Peaks button, a dialog window appears in which a threshold value can be entered. In the case of the results shown in Figure 10 the threshold value was set to 20. Once a new set of regions are created using the Find Peaks button, the Load Regions button is pressed, the consequence of which is the mass calibration table on the Exact Mass property page is loaded with the set of calibration points determined from the regions currently defined on the spectrum, subject to the condition that the mass determined from the time bin for each region is within a tolerance of the nominal mass entered into the name field of the region. Following the

initial mass calibration and application of the Find Peaks button, the set of regions generated by the Find Peaks button in Figure 10 are limited by the Load Regions button to those displayed in Figure 9. That is, all regions above nominal mass 31 were sufficiently different from the nominal mass to be rejected. The deviation of the computed mass for peaks above 31 amu from the nominal mass is a measure of the error in the original mass calibration. Given the new set of calibration points, the Calib button on the Exact Mass property page can be pressed resulting in an improved mass calibration. Repeating the Find Peaks operation followed by reloading the regions into the calibration table reveals that peaks up to 53 amu are now included in the calibration table. A third iteration of these steps produced a calibration table including peaks up to 228 amu, while a fourth iteration extends the calibration table up to 561 amu, exhausting the set of peaks found using the Find Peaks button. The mass calibration based on nominal masses is now complete. All that remains is to verify the mass calibration by stepping through the spectral peaks to confirm the presence of peaks at each amu and that known peaks are correctly assigned.



**Figure 11: High resolution ToF peaks clearly distinct from the nominal mass of 28 amu.**

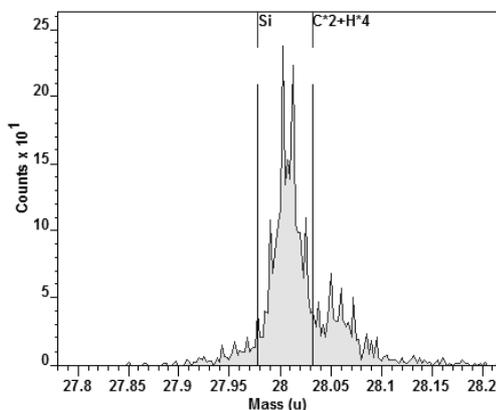
The procedure is not without flaw, so verification is necessary, but can provide a means of improving an initial calibration with minimal effort. For high resolution ToF spectra, the use of nominal masses will lead to a rough mass scale which requires refinement using resolved peaks and exact mass formulae (Figure 11).

NB: The peak marker in Figure 11 for elemental Si is positioned to the left-hand side of the peak. When a ToF spectrum is calibrated using the option on the toolbar, the position of peaks with respect to time are determined from the regions. While the peak maximum may appear to be a good choice for

the peak position, the asymmetry typically observed in ToF peaks and the variety of peak shapes over a spectrum suggest, in general, the peak maximum is less well defined than the leading edge of a peak. For this reason, the position of the peak used for the calibration procedure is taken to be the lower full width half maximum. Hence the peak markers will align with the leading edge of the peaks rather than the peak maxima. Note that the calibration option on the Exact Mass property page offers the choice of peak position to the user without limitation.

## Recalibration of Mass Scale for ToF Spectra

Occasionally ToF Spectra are supplied as mass binned data. While data in mass bins is convenient for those without the ability to handle the relatively large time binned spectra, the possibility exists that the mass calibration used to mass-bin the spectra may not be accurate enough for the application in question. For high resolution mass spectra, a small error in the original time-to-mass calibration may lead to the type of uncertainty illustrated in Figure 12, where the peak maximum falls between the two most likely assignments for the measured data. A recalibration of the mass bins is therefore required.

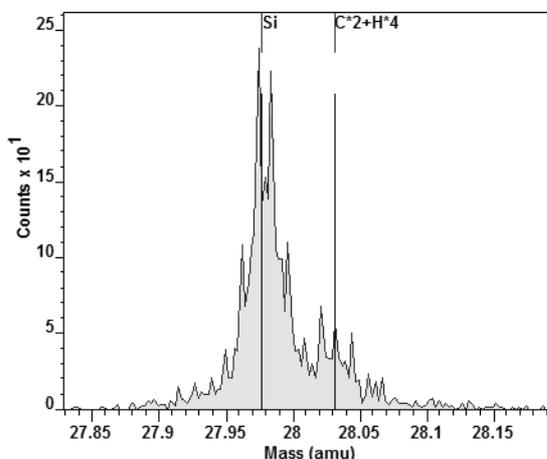


**Figure 12: An example of a mass-binned spectrum where the original mass calibration is not sufficiently accurate for the resolution of the peak shown.**

The recalibration of mass-binned data differs from a time-to-mass calibration of time-binned data in that the act of reallocating the counts to mass-bins from the original time-binned data (performed during the creation of the mass spectrum), results in the loss of information. Namely, two or more time-bins may map into the same mass-bin, therefore it is impossible to take a mass-bin and repopulate the time-bins with the same distribution found in the original data set. The consequence of there being a fundamental

difference between these two operations is that, when recalibrating a mass-binned spectrum, the functional form used to assign the data bins to mass values must involve a general three parameter quadratic function rather than the stiffer model used to calibrate time-bins to mass-bins. The two parameter calibration function recommended for time-to-mass calibration is too specific to the counting mechanism used to acquire the ToF MS data. The extra flexibility offered by the three parameter quadratic is needed to model the errors in the original time-to-mass calibration; the stiffer two-parameter quadratic model used for time-to-mass calibration is dictated by and appropriate to the physics of the ToF instrument.

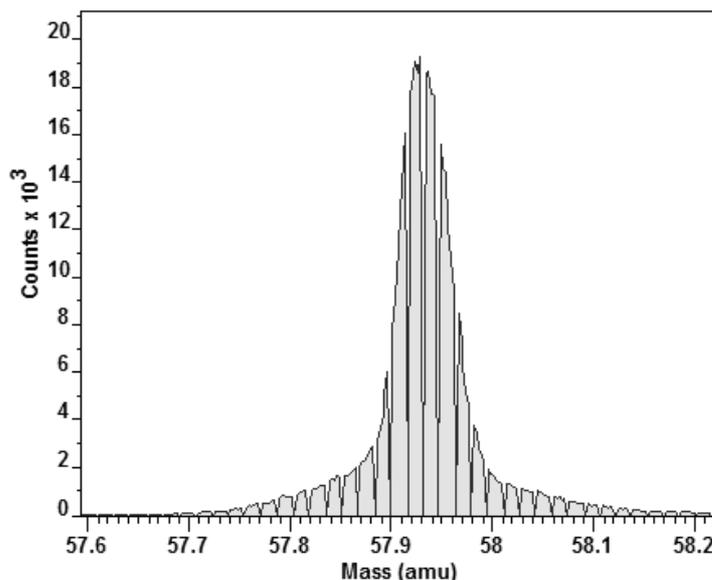
While CasaXPS allows time-to-mass calibration using both the recommended two-parameter quadratic model and the general three-parameter quadratic function, the same warning about the three-parameter functional form is equally applicable to both situations. That is, the flexibility offered by the general quadratic function allows non-physical solutions for the mass assignment of peaks. It is possible to create a mass calibration when using the three-parameter quadratic for which known peaks are apparently correctly assigned to masses, yet other peaks in the spectrum are incorrectly assigned. Extrapolation based on the three parameter model should be viewed with suspicion. Ideally, ToF MS data should be provided in the time domain, nevertheless situations do occur where mass-binned data must be managed and therefore CasaXPS provides a mean of recalibrating the mass-binned data. Figure 13 shows the same data seen in Figure 12 following the recalibration procedure described below.



**Figure 13: The same mass spectrum after recalibration.**

## Recalibration Steps

1. Cancel the Mass calibrated status of the spectra: overlay the mass-binned spectra in the Active Tile and press the  toolbar button on the SIMS toolbar. The label for the abscissa will return to “Time Bin”, which indicates the data is in a state where a new calibration can be created. Note, the abscissa values will be bin indices, not true time-bins, but nevertheless it is necessary to the calibration procedure that the abscissa label is assigned the string “Time Bin”.
2. Using the Exact Mass Calculator, a new calibration set defining the relationship between the peaks and the mass assignment must be established. The procedure is identical to creating a time-to-mass calibration described elsewhere.
3. Perform the recalibration using the  button on the Exact Mass Calculator property page of the Element Library dialog window.



**Figure 14: A mass-binned peak illustrating the peak deformations due to the re-binning algorithm used to create the mass spectrum.**

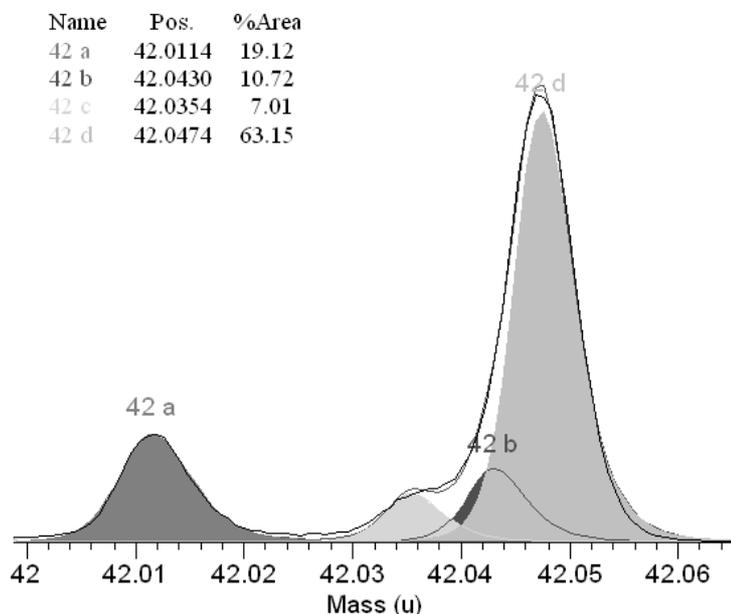
An alternative procedure is to create quantification regions and apply the recalibration using the  toolbar button. While possible, this approach suffers from the information lost during the time-to-mass conversion procedure, that is, the mass-bins for higher mass values tend to be poorly defined compared to the original time data (Figure 14). The algorithms for identifying a peak position and therefore determining the calibration points

assumes the data obeys Poisson statistics, but otherwise varies smoothly; it is clear from Figure 14 that the mass-binned data contains anomalous values.

## Peak Fitting ToF SIMS Data

The features in CasaXPS typically used to model XPS data envelopes can also be used to analyse overlapping peaks in high resolution ToF SIMS spectra. The principal difference between ToF SIMS and XPS is that asymmetry in ToF SIMS peaks is, in general, in the opposite direction to that found for XPS peaks. As a result, not all line-shapes in CasaXPS are appropriate for ToF SIMS peaks, however the more recently introduced asymmetric line-shapes of **LA** and **LF** provide a means of creating line-shapes appropriate for the range of ToF SIMS peaks observed in practice.

The data in Figure 15 illustrates the similarities between XPS and ToF SIMS, where the mass peaks associated with a nominal mass of 42 are very typical of polymer XPS spectra such as PMMA or PET. The problems of understanding the data are also similar in that both the position and the intensity of the underlying peaks are of importance when identifying the molecular ions responsible for the measured data.



**Figure 15: Example of ToF SIMS peak structure.**

The procedure for adding synthetic components to the data involves first adding a quantification region to the data with background type set of “Zero” before adding synthetic line-shapes. Creating and adjusting regions and components is performed on the Quantification Parameters dialog window

available from the Quantify option on the Options menu or the  toolbar button on the top toolbar of CasaXPS. Regions and components are managed using the tables found on the **Regions** and **Components** property pages of the Quantification Parameters dialog window shown in Figure 16.

The peaks shown in Figure 15 are defined using the parameters displayed in the table on the Components property page illustrated in Figure 16. The line-shape parameter in this example is defined using the **LA** functional form, where the parameters provide a degree of asymmetry to the right of the peak maximum. The meaning of these parameters is described below.

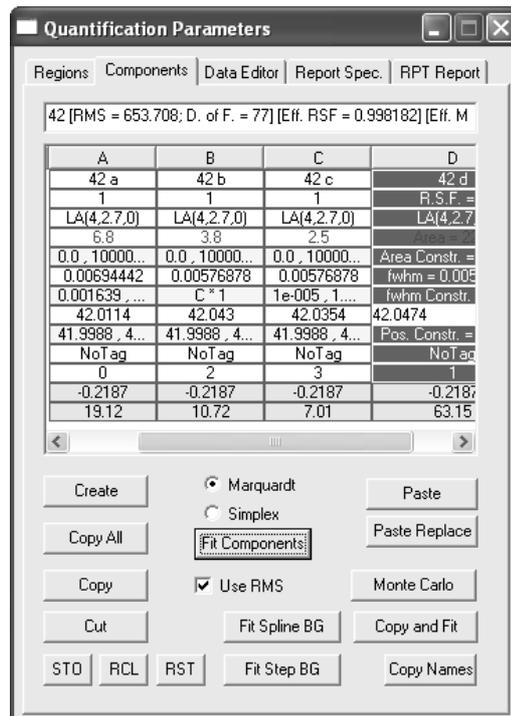


Figure 16: Quantification Dialog Window.

## Line-shapes Suitable for ToF SIMS Spectra

The success of a peak fit is dependent on an appropriate choice for the line-shape parameter. As stated above, the **LA** and **LF** line-shapes offer sufficient flexibility for most ToF SIMS peak shapes.

The Lorentzian line-shape with FWHM  $F$  and position  $M$  is given by

$$L(x; f, e) = \frac{1}{1 + 4 \left( \frac{x - e}{f} \right)^2} \quad (1)$$

The functional form is symmetrical about  $x = M$ . In order to retain the characteristics of the Lorentzian line-shape and yet also introduce asymmetry, the **LA** line-shape is defined in two halves as

$$LA(x: \alpha, \beta, f, e) = \begin{cases} [L(x: f, e)]^\alpha & x \leq e \\ [L(x: f, e)]^\beta & x > e \end{cases} \quad (2)$$

**LA( $\alpha, \beta, m$ )**: Equation (2) defines the first two parameters used in the line-shape **LA( $\alpha, \beta, m$ )** shown in Figure 16. The third parameter **m** is used to control the width of a Gaussian convolution applied to the functional form defined by Equation (2). As a consequence of the definition for the **LA** line-shape, an asymmetry line-shape is established by specifying  $\alpha$  not equal to  $\beta$ . Further, if  $\alpha$  is greater than  $\beta$  then the resulting peak will be asymmetric with an extended tail to the right of the peak maximum. Adjusting the Gaussian convolution parameter causes the extent of the asymmetric tail to reduce and also shifts the peak maximum towards the extended tail.

**LF( $\alpha, \beta, w, m$ )**: Identical to the LA line-shape with the exception that the specified values of  $\alpha$  and  $\beta$  are forced to increase to a constant value via a smooth function determined by the width parameter **w**. The **w** parameter is used to restrict the extent of the tail.

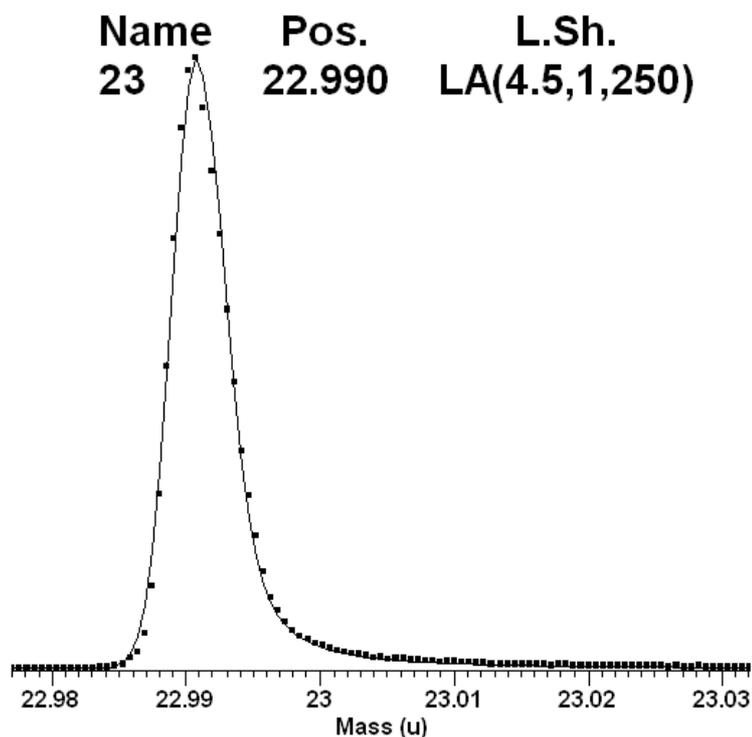
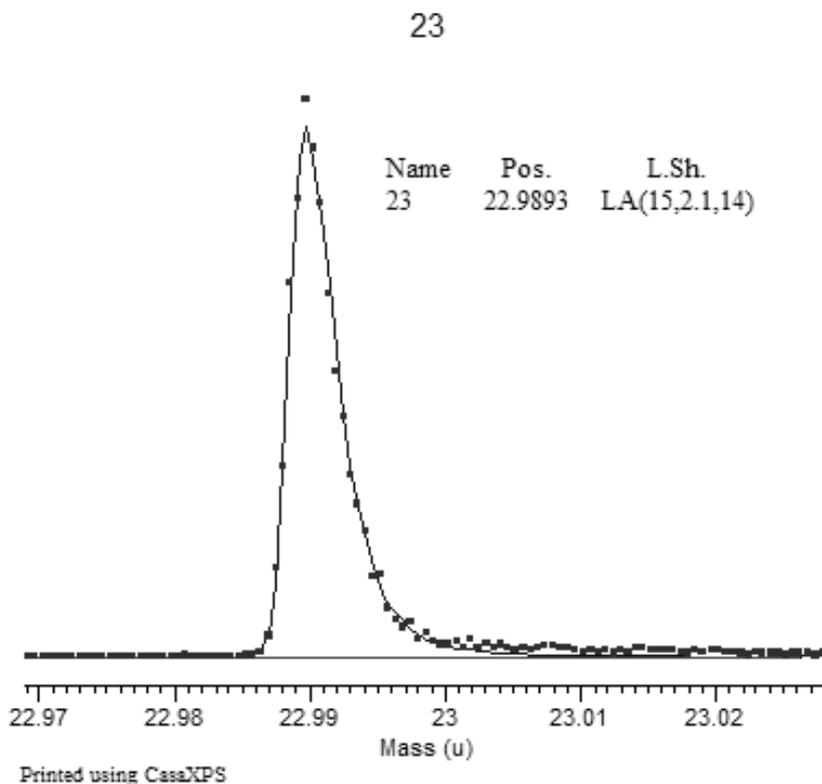


Figure 17: Asymmetric Mass Peak fitted using a single LA line-shape.

By way of example, the elemental sodium mass peak shown in Figure 17 exhibits significant asymmetry to the right of the peak maximum, which can be modelled using the LA line-shape. Note that the line-shape included in the annotation of the peak in Figure 17 is achieved by setting the first parameter to a value greater than unity, thus compressing the tail to the left compared

to the tail to the right. Further, the Lorentzian tail to the right of the peak maximum is adjusted by convoluting the functional shape with a Gaussian of characteristic width described by a value of 250 for the  $m$  parameter in the LA definition. The degree of asymmetry is determined by the relative size of the first parameter compared to the second, that is  $\alpha > \beta$ .



**Figure 18**

The line-shape used in Figure 17 should be compared with the line-shape in Figure 18 corresponding to a similar sodium peak measured using the same IonToF instrument but using a different ion gun. The peak in Figure 18 rises more quickly than the peak in Figure 17, therefore the  $\alpha$ -parameter is now much larger than the  $\beta$ -parameter, which is also set to a value greater than unity. The larger the values for these two parameters the steeper the edge of the peak appears. Also note in Figure 18 that the Gaussian convolution is much narrower than that used in Figure 17. Possible values for the Gaussian parameter are between 0 and 499;  $m = 0$  corresponds to no convolution being performed.

## Peak Identification and Reduction

High resolution ToF spectra typically consist of numerous peaks, however for some analyses only a small number of correlated peaks are significant for

distinguishing between samples. That is, a peak at one mass is only characteristic of a particular compound when also accompanied by peaks at a set of very specific masses. Given the plethora of peaks typically present in ToF MS data, a means of grouping and displaying only significant peaks is required. To visualise the spectrum with respect to only significant peaks, a ToF spectrum can be organised in CasaXPS 2.3.15 such that the Element Library property page simplifies the mechanism by which these significant peaks can be displayed for visual inspection. In addition to the element marks, a spectrum can be broken into an array of VAMAS blocks representing the peak information associated with the nominal masses and the element library used to display appropriate subsets of these VAMAS blocks for interpretation.

The procedure for splitting a ToF spectrum into a set of mass calibrated VAMAS blocks can be performed using the toolbar button indicated in Figure 19. As an alternative approach, for data files for which a mass calibration is available to CasaXPS at the time of conversion the division of the data into mass calibrated VAMAS blocks can be performed at the time the data are converted. Either route to the mass calibrated VAMAS blocks requires a mass calibration for the data.

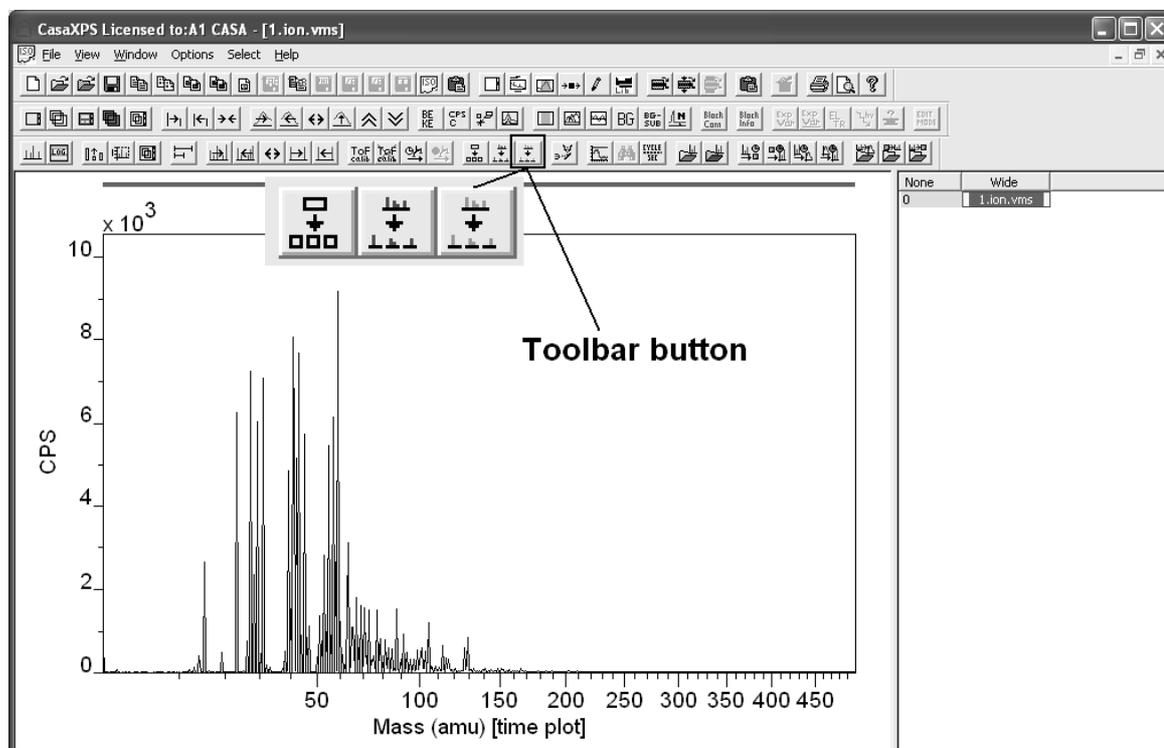
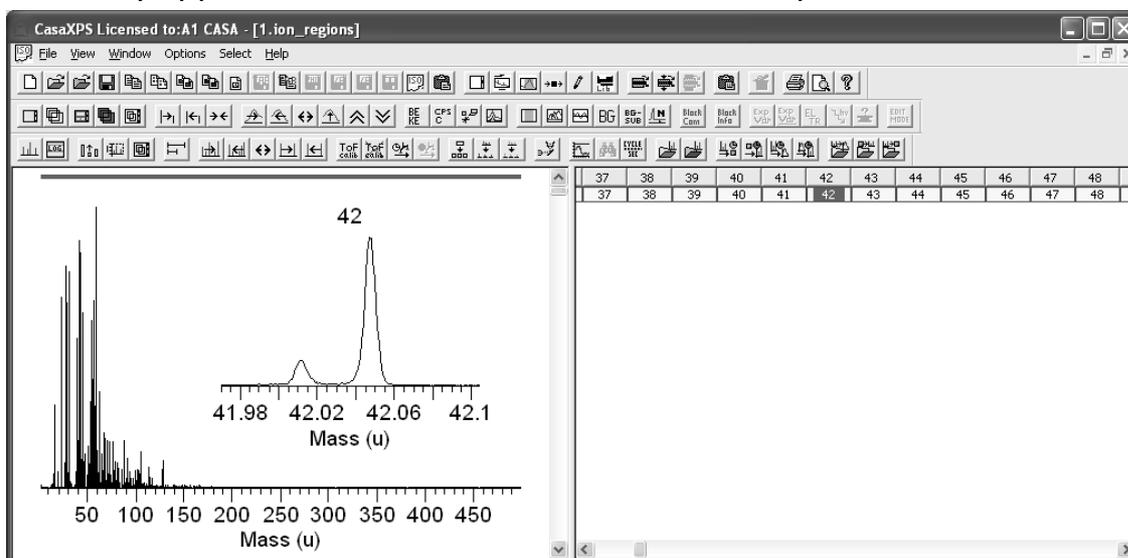


Figure 19: ToF Spectrum with data in time domain.

The data in Figure 19 are converted to a mass calibrated set of VAMAS blocks by pressing the  toolbar button with hint **Split into Unit Mass Spectra**. The result of converting the data in Figure 19 is shown in Figure 20, where the right-hand pane displays the set of VAMAS blocks derived from the single VAMAS block in Figure 19.

The display in Figure 20 is achieved by overlaying the full set of VAMAS blocks from the right-hand pane in the active tile. An inset tile is used to display a specific VAMAS block, namely the VAMAS block corresponding to a nominal mass of 42. Note that since the individual VAMAS blocks are mass calibrated, the overlay appears in the form of a mass calibrated spectrum.



**Figure 20: ToF Spectrum after conversion to mass calibrated VAMAS blocks.**

The discussion that follows relates to data prepared in the format shown in Figure 20. Presenting the spectrum as a set of VAMAS block provides the basis for the tools within CasaXPS. Before describing these tools, the method for converting data files directly to mass calibrated sets of VAMAS blocks will be addressed. Version 2.3.15 of CasaXPS only offers data conversion to the multiple VAMAS block format for ASCII files formatted using the convention adopted by the IonToF data system.

## IonToF Peak Identification

IonToF spectra are exported in ASCII files in the format shown in Figure 21. The follow describes the options in CasaXPS for importing these data in formats suitable for compiling peak lists.

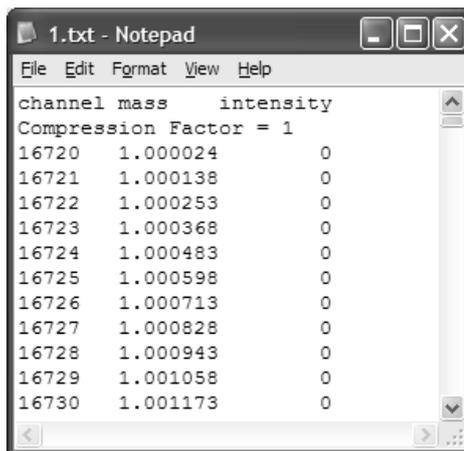


Figure 21: IonToF ASCII format.

The SIMS toolbar in CasaXPS offers two toolbar buttons for controlling the import of data in the format shown in Figure 21. These toolbar buttons are indicated in Figure 22.



Figure 22: SIMS Toolbar buttons

The traditional method for working with ToF data is based on a single data block approach, however the tools for peak identification now added to CasaXPS are organized on a partitioning of the data into numerous data blocks based on the nominal mass for each group of peaks. The objective is to analyze a directory of spectra and determine a set of mass peaks and intensities for each spectrum in the directory.

### Converting IonToF Spectra

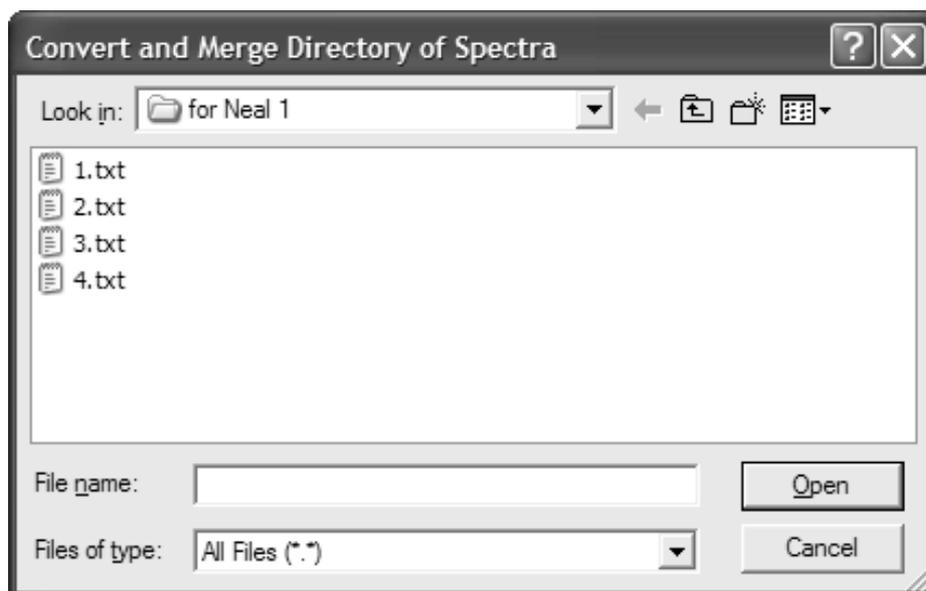


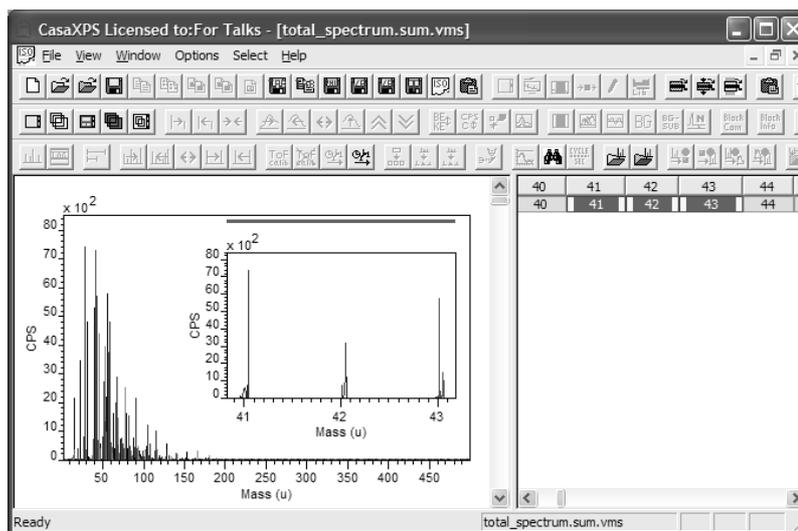
Figure 23: ASCII txt files exported from the IonToF software.

A data directory initially contains a set of spectra exported from the IonToF software as ASCII txt files. Figure 23 illustrates such a directory which is displayed using the File Dialog window offered by the  toolbar button. The conversion of these data may be performed using several filter strings as follows:

1. “.ion”
2. “.amu”
3. “.sum”.

To initiate a conversion sequence, a name followed by one of the above strings must be entered into the File name text-field on the File Dialog in Figure 23. For example, to convert and merge the set of txt files in a format suitable for peak identification, the File name text-field should be entered with the string “datafile.amu”. The base-name is arbitrary, however the extension “.amu” instructs the set of txt files to be converted to VAMAS format (a new VAMAS file will appear in the directory for each txt file processed) then these converted files are merged into a single experiment frame in CasaXPS. Note that these data are large; therefore the process is both time consuming and requires plenty of PC memory!

The different filter strings determine the nature of the data files generated from the IonToF ASCII files. The individual VAMAS files generated from the ASCII files are identical for both the “.amu” and “.sum” filters; the final outcome differs however, where the “.amu” filter causes the merger of the spectra into a single experiment frame as separate spectra equivalent to the original ASCII data, while the “.sum” filter results in the total counts from the set of spectra in the ASCII files forming the equivalent of a single mass spectrum. In both cases, the mass spectrum from each of the IonToF files is partitioned into VAMAS blocks corresponding to data in the vicinity of the nominal mass values. Figure 24 shows the result of using the “.sum” filter on the data directory depicted in Figure 23. Both display tiles in Figure 24 display an overlay of *all* the data blocks in the right-hand pane of the experiment frame and the inset tile shows the data from the three highlight blocks containing intensities for nominal masses 41, 42 and 43 amu.



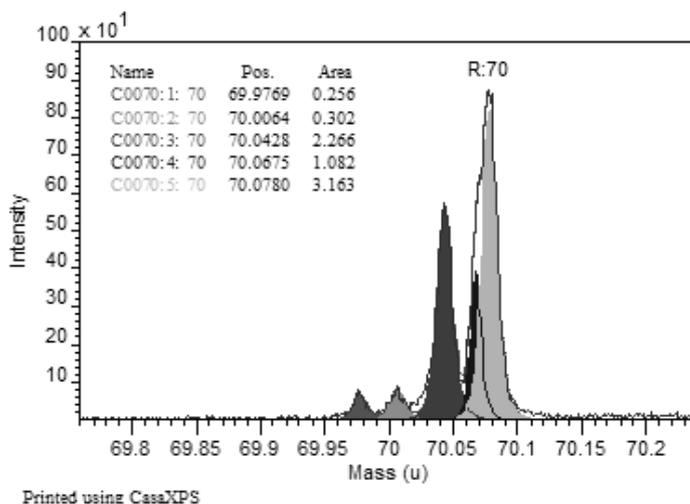
**Figure 24: Example of a total counts spectrum formed from the four ASCII files shown in Figure 23.**

The conversion filter ".ion" when applied to a directory merges the data into a single experiment frame containing one spectrum per original ASCII file, but maintains the data for each spectrum as a single block. While the format adopted is more traditional for mass spectra, the peak identification option uses peak-fitting and therefore the format shown in Figure 24 is more suited to the algorithms involved. The single block of data provided by the ".ion" is for visual inspection of the full data set and should not be used when peak identification is employed.

### ***Directory Profiling***

The objective addressed by the features described here, is to identify and quantify in terms of mass assignments and intensities the set of peaks characteristic of a sample. The peak structures within a ToF spectrum are illustrated in Figure 25, where it can be seen that at least five overlapping peaks to varying degrees are responsible for the data envelope. Peak intensity and peak position are determined for these types of peak structures using optimized peak modelling. The very fact that peak modelling is required highlights the difficulty of automatically identifying all the peaks for a given data envelope. For a directory of similar spectra, automatically identifying mass peaks from data such as that in Figure 25 is fraught with dangers and therefore the strategy in CasaXPS for processing directories of similar spectra is one of aiding the construction of a template spectrum, for which peak models are prepared to be exhaustive with respect to the data under analysis, then the automatic application of the template models to a

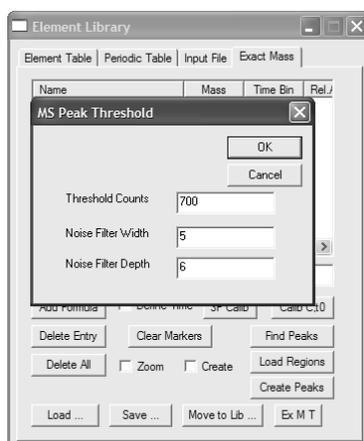
directory of spectra forms the basis for extracting the quantitative information for each spectrum in the directory.



**Figure 25: Mass peak structure from a ToF spectrum.**

The creation of peak models for each significant mass peak in a file such as the one shown in Figure 24 is central to the profiling options in CasaXPS. About 500 data blocks corresponding to the nominal masses potentially require the construction of regions and synthetic peaks. The success of the template approach relies on the peak models adequately describing the peaks with appropriate constraints in terms of relative positions and FWHM to permit the peak intensities to be calculated from the fitted model. To assist this initial step, an option on the Exact Mass Calculator property page of the Element Library dialog window offers a means of creating peak models based on a threshold limit.

The **Create Peaks** button on the Exact Mass Calculator property page (Figure 26) uses the threshold value to limit the number of peaks created for a given data block.



**Figure 26: Exact Mass Calculator Property page.**

The peak creation mechanism uses the threshold value entered on the **MS Peak Threshold** dialog window to create a region and synthetic peaks for each data block overlaid in the active tile. The smaller the threshold values, the smaller the peaks will be that are included in the peak search. Since the significance of mass peaks may not depend entirely on peak intensity, it is worth noting that different threshold values may be appropriate for different ranges in the mass scale. It is therefore unlikely that a single application of the **Create Peaks** button will generate all the appropriate peaks, however, by the user selectively overlaying data blocks and choosing different thresholds, peaks can be created on large numbers of data blocks while still retaining the discretion of the operator. Ultimately, the success or failure of the profiling step will depend on the way these peak models are constructed and time spent in getting these models right will be recovered by the accuracy and automatic application of these models to larger data directories.

### Profile Directory Toolbar Option

The options for profiling a directory of IonToF spectra are as follows:

1. “.amu”
2. “.fit”
3. “.vfc”

These conversion filters are used to control the nature of the directory profile. On providing a base name followed by one of these filter strings, the directory located by the File Dialog window invoked by the toolbar button  is scanned for the appropriate file types and, on accepting the Continue prompt via the resulting message dialog, the set of files are one-by-one processed to produce several text file reports and a VAMAS file containing the profile information from the directory.

The two profile filters “.amu” and “.fit” both require a template spectrum to be loaded and displayed in the active tile. In the case of the “.amu” profile filter, the ASCII .txt IonToF files are converted to VAMAS files before applying the template information to these newly converted data, which are also saved in the processed state as .vms files. On completion, several text files provide the results of the profile, one offering the context information for the numerical tabulations located in the other files. In addition, the profile information is presented in VAMAS format within the current CasaXPS session.

The second profile filter “.fit” performs the same sequence of steps as the “.amu” with the exception that the files processed from the directory are the “.vms” files. This removes the conversion step from the operation and is appropriate if, for example, the data directory has been previously processed using the “.sum” conversion filter described above. The “.sum” conversion filter generates a single spectrum from a set of files in a directory and also, as part of the process, converts the ASCII files to VAMAS format. The total counts spectrum created from the “.sum” operation may appear in the same directory as the converted files, but provided the filename retains the “.sum” sub-string, the total spectrum will not appear in the final profile results generated from applying the template file to the set of .vms files in the current directory.

An alternative way to profile a directory of .vms files is to apply the “.vfc” profile filter. In this case, no fitting is performed, but rather the existing peak fits within the set of VAMAS files is used to construct the profile information. The “.vfc” profile filter allows the individual files to be inspected and any anomalies rectified on a file-by-file basis before creating the profile information. It is important that the same set of VAMAS blocks and number of synthetic peaks are used on each of the data blocks, however profiling the directory without automatic peak fitting allows user-intervention to override poor fitting scenarios.

## **Working with ToF Spectra in CasaXPS**

### ***Time to Mass Calibration Procedures***

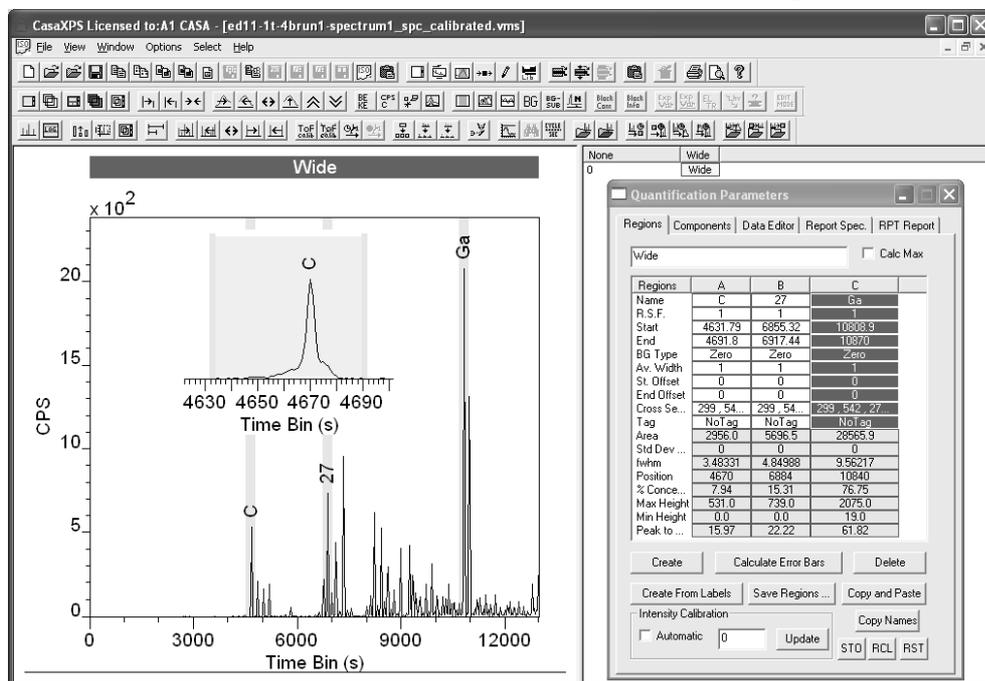
A raw ToF spectrum is recorded in the time domain. Mass calibration of a ToF spectrum is performed in CasaXPS by identifying a set of peaks in the data with specific masses; then, by using these pairs of mass/time values a quadratic relationship between the time and mass scales is created. A linear least squares procedure determines the two constants within the quadratic expression and therefore two or more mass/time pairs must be supplied to perform the calibration procedure. The accuracy of the mass-to-time calibration is dependent of the precision of the mass/time pairs used in the least squares calculation; the more pairs used to compute the least squares solution, the more tolerant the calibration will be to errors in the mass/time specification.

CasaXPS offers two methods for calibrating ToF MS data:

1. Peaks and corresponding masses specified using quantification regions.
2. Mouse identification of the peaks coupled with an exact mass calculator located on the Element Library dialog window.

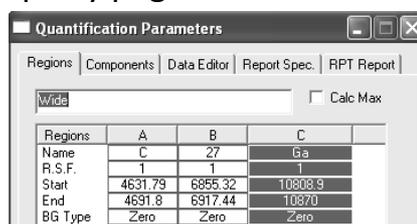
## Mass Calibration using Regions and Propagation of Regions between Spectra

The Quantification Parameters Dialog window  provides a means of defining time intervals, within which systematic positions are defined (computed from a peak bounded by an interval) and linked to masses via an exact mass formula entered into the Name field for the regions.



**Figure 27: Quantification Parameters Dialog Window shown three regions defined for the purpose of calibrating the time scale to mass.**

The spectrum in Figure 27 is an example of ToF SIMS data where three quantification regions are defined suitable for calibrating the time scale to mass. The mass associated with each region is entered into the Name field and may be a numerical value exemplified by the region headed column **B** or a string corresponding to any exact mass formula equivalent to expressions use on the Exact Mass property page of the Element Library dialog window.



Regions	A	B	C
Name	C	27	Ga
R.S.F.	1	1	1
Start	4631.79	6895.32	10808.9
End	4631.8	6917.44	10870
BG Type	Zero	Zero	Zero

For example, the mass of a peak might be defined using the expression  $C+H*3$ , which when evaluated would result in a mass of 15.0235 Daltons.

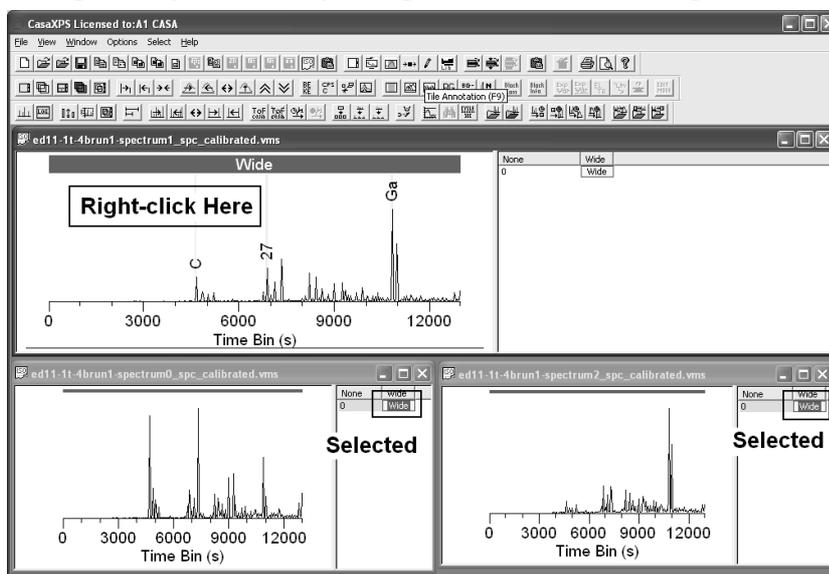
## Mass Calibration

One or more time domain spectra can be prepared with calibration regions as described above and overlaid in the active tile in the left-hand pane of the experiment frame. On pressing the  toolbar button, each spectrum in the active tile is calibrated using the peaks within the regions. Since multiple spectra can be mass calibrated using a single invocation of the toolbar button, the use of this procedure is supported by the propagation of the calibration regions to similar spectra, thus avoiding the need to manually create regions for each spectrum requiring a mass calibration.

## Propagation of Calibration Regions

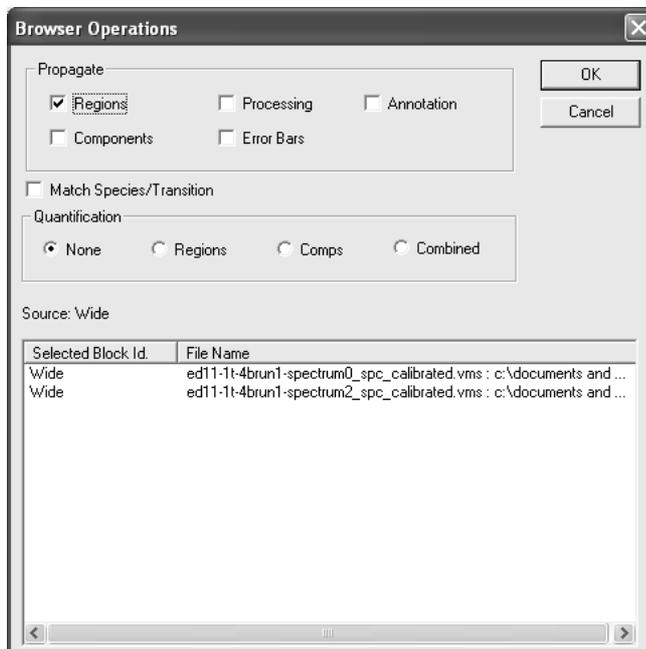
The procedure to propagate the calibration regions from the spectrum as defined in Figure 27 to two other similar spectra is as follows:

1. Select the VAMAS blocks in each of the two experiment frames containing the spectra requiring the calibration regions.

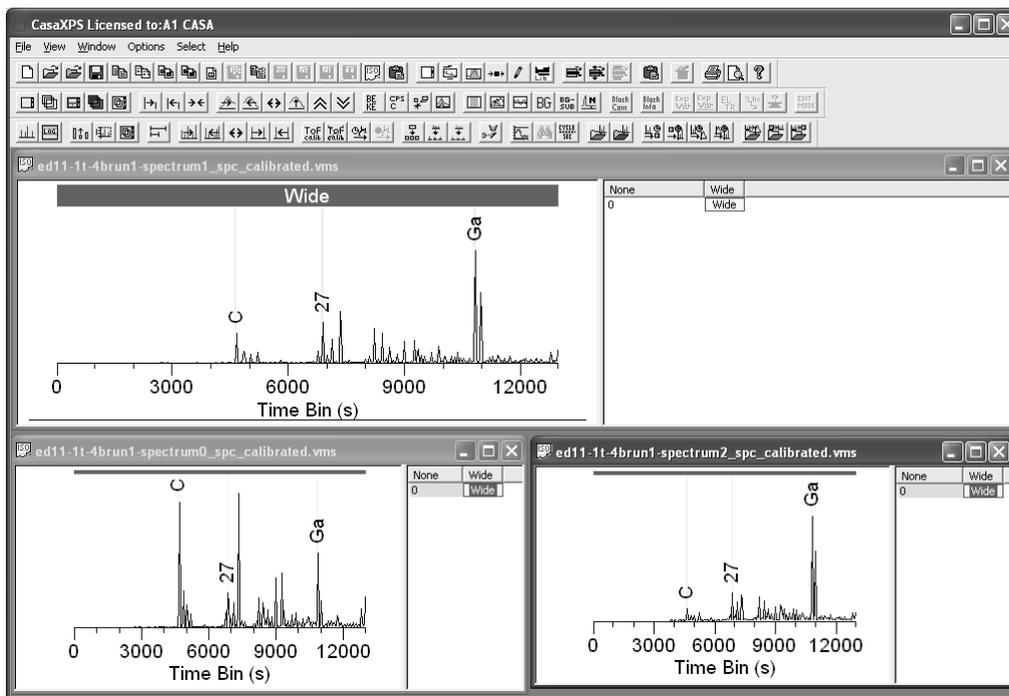


The CasaXPS window is arranged in a tiled format using the Tile option from the Window menu at the top of the CasaXPS main window. The arrangement of the experiment frames allows the selection to be made by left-clicking the first VAMAS block in the experiment frame to the bottom-left and then holding the Control-Key down and left-clicking the VAMAS block in the bottom-right experiment frame

- The Browser Operations dialog window is invoked by right-clicking the mouse with the cursor over the left-hand pane of the top-most experiment frame. The objective is to right-click over the display tile in which the spectrum containing the calibration regions is displayed.

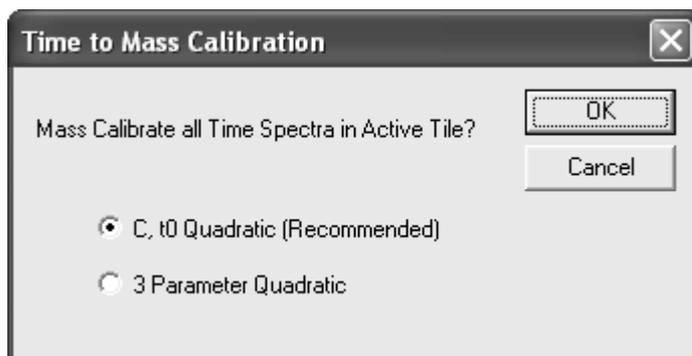


- To propagate regions to the two selected VAMAS blocks, which are listed on the Browser Operations dialog window, tick the radio button in the Propagate section of the dialog window and press the OK button. Region labels are now visible on the spectra.

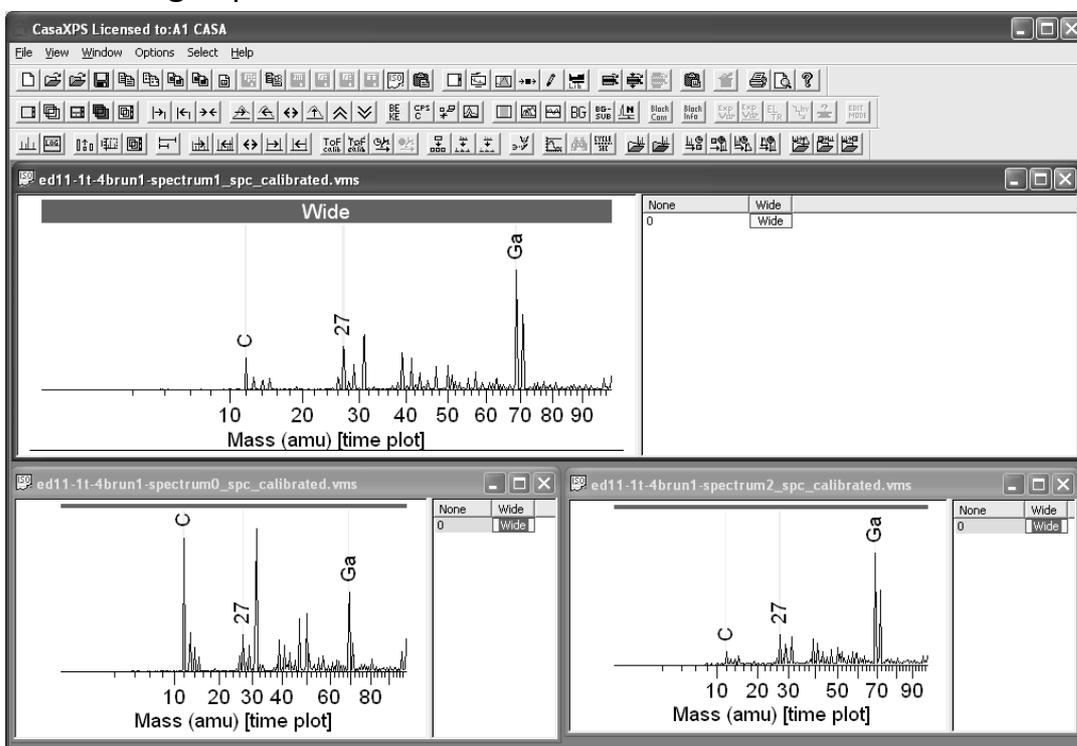


The data in each of the three experiment frames are calibrated by switching focus between the experiment frames and each time pressing the  toolbar

button. Control-TAB moves the focus between the experiment frames within CasaXPS.



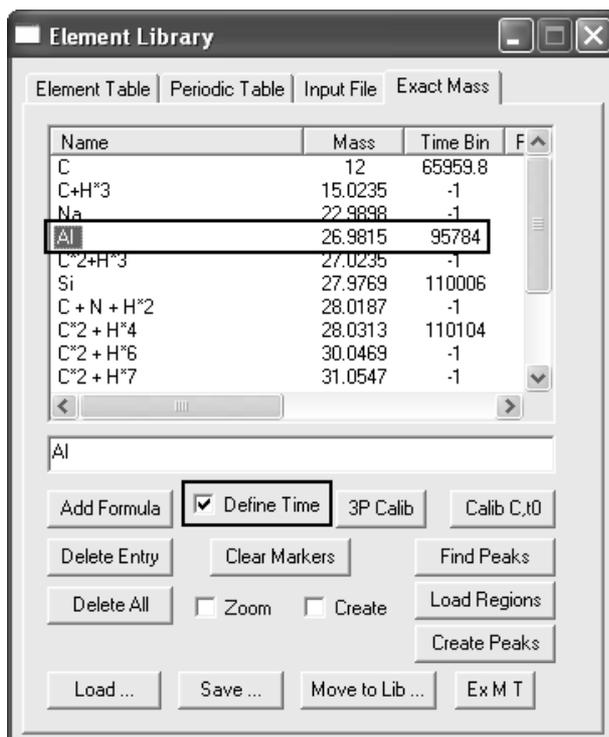
The time to mass calibration for the time domain data may be seen labelling the x-axis using a quadratic mass scale.



### Mass Calibration using the Exact Mass Calculator Property Page:

The procedure for calibrating a spectrum involves creating a set of mass/time-bin pairs within the scrolled-list on the Exact Mass property page on the Element Library dialog window.

The example below illustrates how the columns in the scrolled-list headed Mass and Time store the information relating these two parameters. Before an assignment for a given entry has been made, the value in the Time column is set to -1. The mass for an entry in the table is computed from the chemical formula entered into the name column.

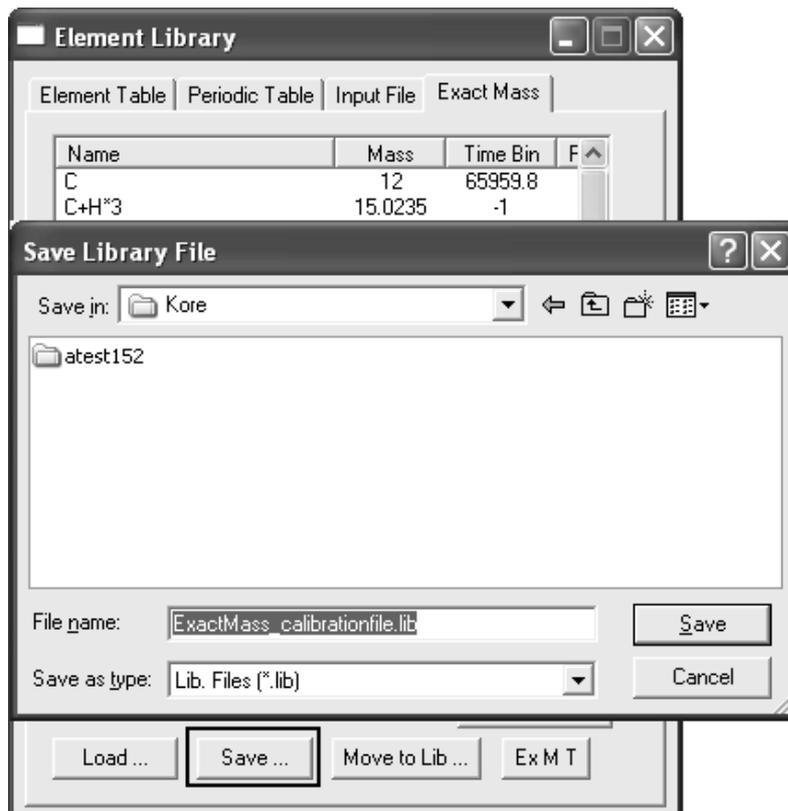


To add an entry to the calibration table:

1. Type a chemical formula into the text-field below the scrolled list and press the Add Formula button or press the return key on the keyboard. The formula for an ion may be entered using the chemical symbols used to on the Periodic Table property page of the Element Library dialog window.
2. Select the name in the scrolled-list. To select a name field, place the cursor over the text within the Name column and left-click the mouse. The name entry will appear highlighted when successfully selected.
3. Zoom into the known peak in the spectrum displayed in the active tile. It is important to perform the zoom operation before step 4 is taken.
4. Tick the tick-box labelled "Define Time".
5. Using the mouse cursor, click on the known peak at a location representative of the mass already defined by the selected entry in the scrolled list. The value in the Time column is updated and the Define Time tick-box is cleared.

At least two entries must be specified in the scrolled-list before pressing the Calib C,t0 button on the Exact Mass property page. The more entries assigned mass/time pairs, the better the mass to time calibration will be computed in the least squares sense.

Once a calibration table has been prepared, a file containing the calibration points can be saved to a separate text file from the data.



These files can be reloaded at a later time to provide an initial calibration for other data or for making adjustments to the calibration of the original spectrum used to create the calibration file. Note, while the Save button on the Exact Mass property page saves the current calibration table, the Load button will merge a saved file with the current set of entries on the scrolled-list. To return the table to the entries within a file, it is first necessary to press the Delete All button. The Delete All button removes the current entries in the scrolled-list, while the Delete Entry button removes the currently selected entry.

If an assignment is incorrect, the individual entry must be deleted from the table. The name field for the deleted entry is entered into the text field below the scrolled list; therefore a selected entry can be deleted then reinstated by immediately pressing the Add Formula button. The Time field will return to a value of -1 and therefore be ignored during any subsequent calibration operation.

### ***The Element Library from a ToF Perspective***

The element library in CasaXPS is an ASCII file. On startup, CasaXPS loads the default element library from within the same directory as the one in which the CasaXPS.exe executable file is located. The name of the default element

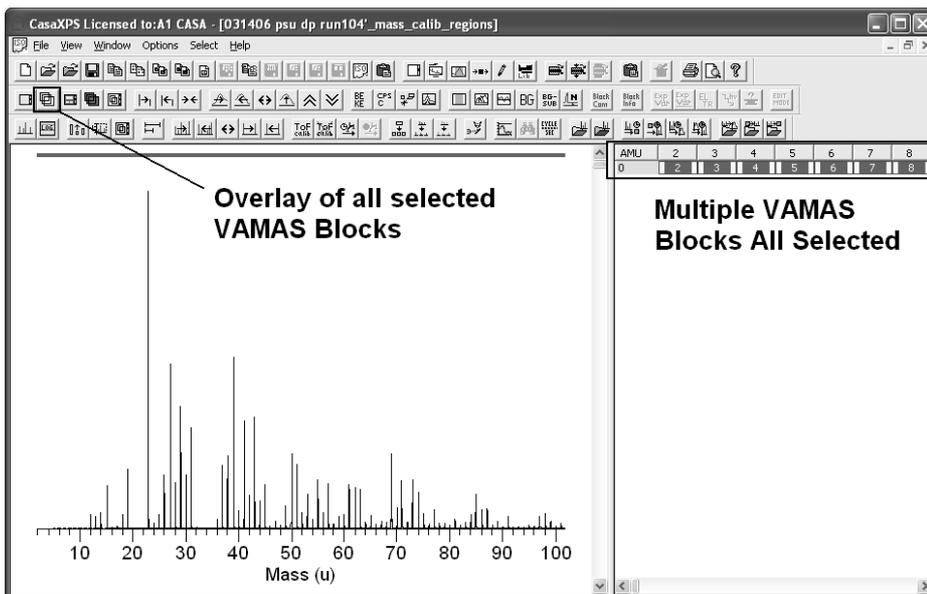
library file is CasaXPS.lib and is designed with the view that the element library can be constructed for specific applications. For example, in the case of quadrupole MS, a library consisting of elemental isotopes is appropriate to the resolution of quadrupole mass spectra, while for high resolution ToF MS a library consisting of entries for molecular fragments is required when assigning mass peaks.

Preparing an element library file for mass spectra may be performed using a spreadsheet program such as Excel or tools on the Exact Mass Calculator property page allowing correctly formatted library files to be constructed from lists of chemical formulae. Methods for displaying the significant peaks based on selections from an element library constructed from one or more library files are described below.

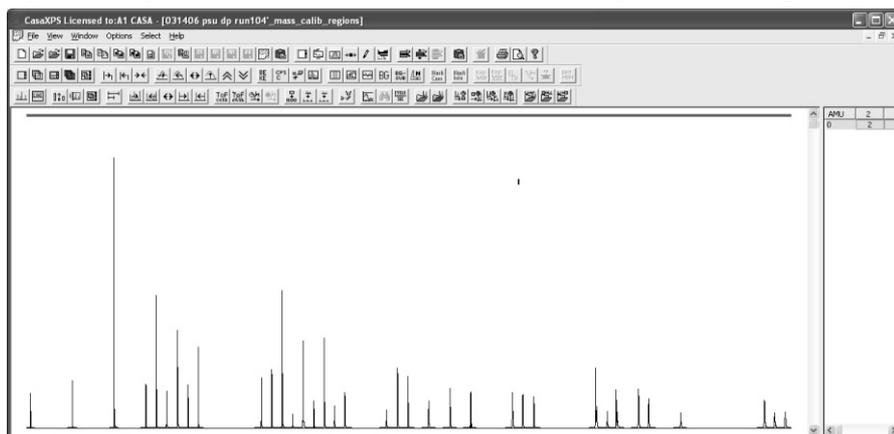
### **The Element Library and Linking ToF Peaks for Display**

High resolution ToF spectra typically consist of numerous peaks; however for some analyses only a small number of correlated peaks are significant for distinguishing between samples; a peak at one mass is only characteristic of a particular compound when also accompanied by other peaks in the spectrum. A strong link between the element library and displaying data for inspection is therefore introduced in CasaXPS 2.3.15. The objective is to use the element library to specify a set of mass peaks grouped with respect to correlated peaks which are used to make selections of VAMAS blocks. These selections of VAMAS blocks containing narrow interval mass spectra combine with the display tools in CasaXPS to provide a perspective in which overall spectral distribution and localised peak structure can be assessed with relative ease.

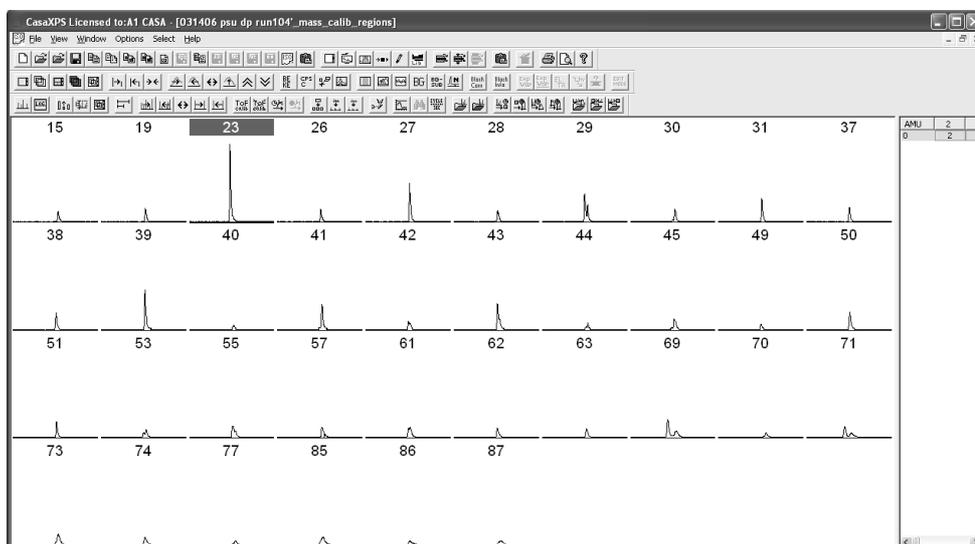
A ToF data set presented as a set of unit mass VAMAS blocks can be viewed in the more traditional form of a single plot. The traditional perspective of a ToF spectrum is achieved by selecting all the VAMAS blocks in the right-hand pane, then pressing the overlay toolbar button. When viewed as a single continuous display, all the features for manipulating the display are still open for use.



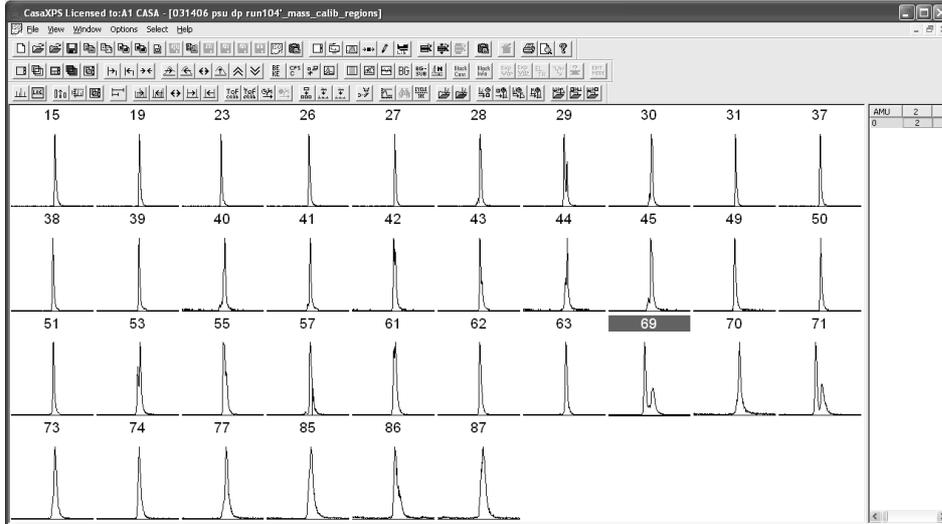
The advantage of creating a set of mass calibrated VAMAS files is that the spectrum can be dissected and displayed with a variety of options: Display only those peaks more than 5% in intensity of the largest peak.



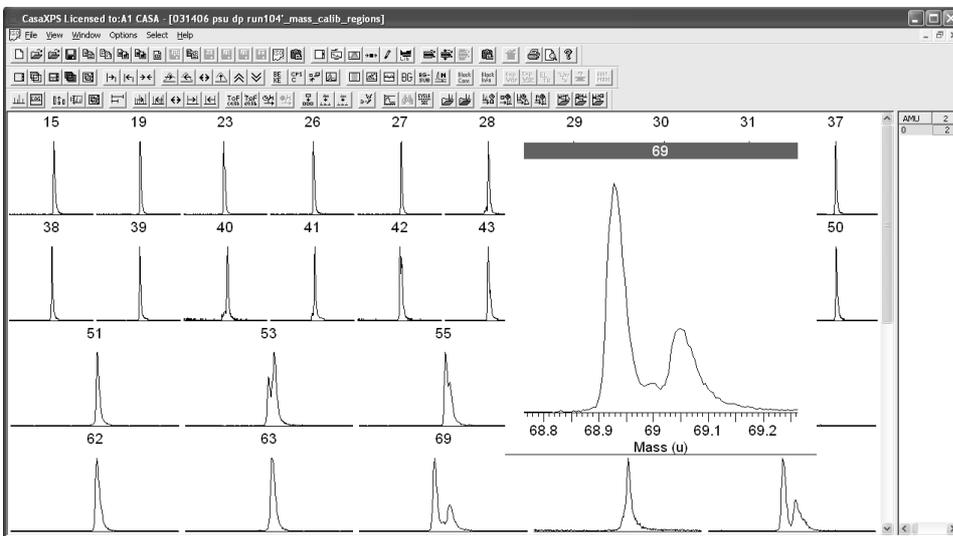
Display one VAMAS block per tile for those peaks greater than 5% of the maximum peak. All peaks scaled with respect to a specific peak; mass 23 in this case.



Scale the peaks on an individual basis.



Take a closer look at specific peaks.



Enhancements for manipulating the selection and display for ToF MS data are available on the Element Table property page of the Element Library dialog window.

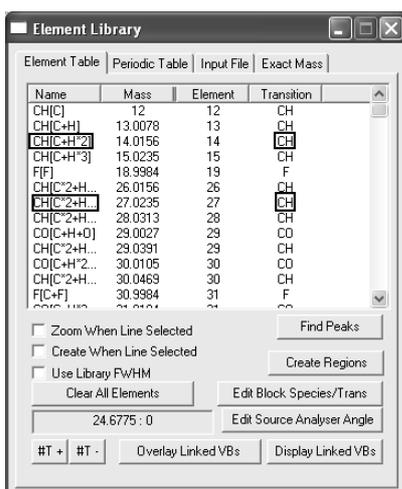
Name	Mass	Time Bin	Rel.Abund.	Line Sh:
H1	1.00782	1	99.985	GLQ
H2	2.0141	1	0.01	GLQ
He3	3.01603	1	0.00013	GLQ
He4	4.0026	1	99.9999	GLQ
Li6	6.01512	1	7.4	GLQ
Li7	7.016	1	92.6	GLQ
Be9	9.01218	1	100	GLQ
B10	10.0129	1	18.7	GLQ
Be10	10.0135	1	0	GLQ
B11	11.0093	1	81.3	GLQ
C12	12	1	98.9	GLQ
C13	13.0034	1	1.1	GLQ

Zoom When Line Selected    Find Peaks  
 Create When Line Selected    Create Regions  
 Use Library FWHM  
 Clear All Elements    Edit Block Species/Trans  
    Edit Source Analyser Angle  
 #T +   #T -   Overlay Linked VBs   Display Linked VBs

The mechanisms offered on the Element Table property page are described in the following sections.

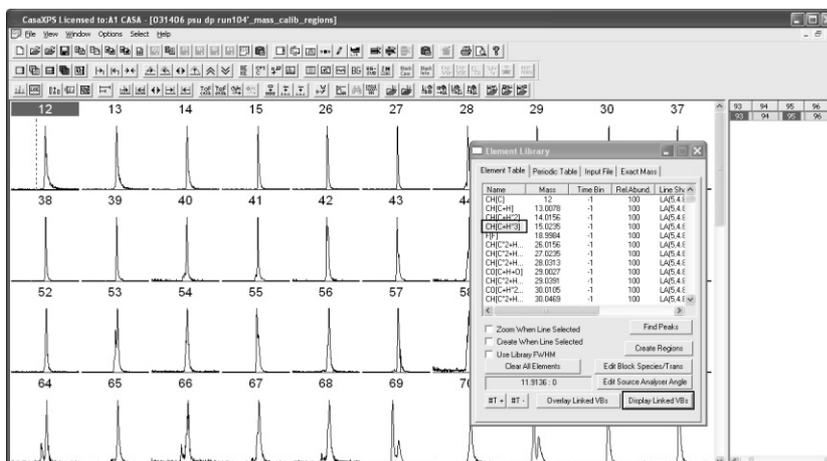
### Linking Element Library Entries

A CasaXPS library file may be prepared with a set of entries corresponding to particular sample chemistry. Such a library file can be loaded or merged with the existing library file whenever appropriate. The essential feature of the entries in the given library file is that a set of mass formulae are all assigned the same unique string for the Transition column.

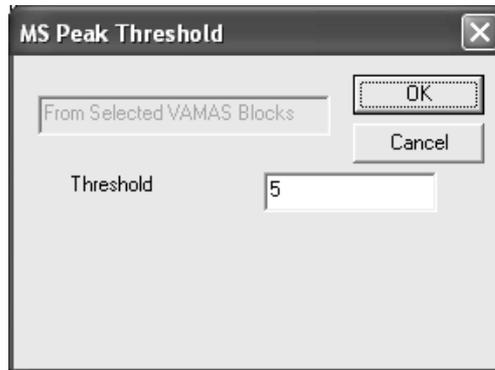


### Using the Selection Mechanism

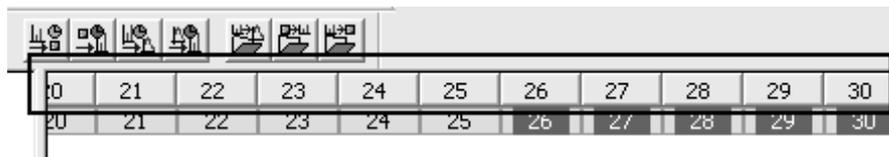
By way of example, a set of formulae only involving carbon and hydrogen are assigned the Transition string **CH**. On selecting one of the entries using the Name column of the table on the Element Table property page bearing the **CH** Transition string before pressing the **Display Linked VBs** button on the Element Table property page causes all those VAMAS blocks (in the experiment frame with focus) to be displayed in the left-hand pane, one VAMAS block per tile. Thus, a set of related mass peaks can be easily displayed for inspection.



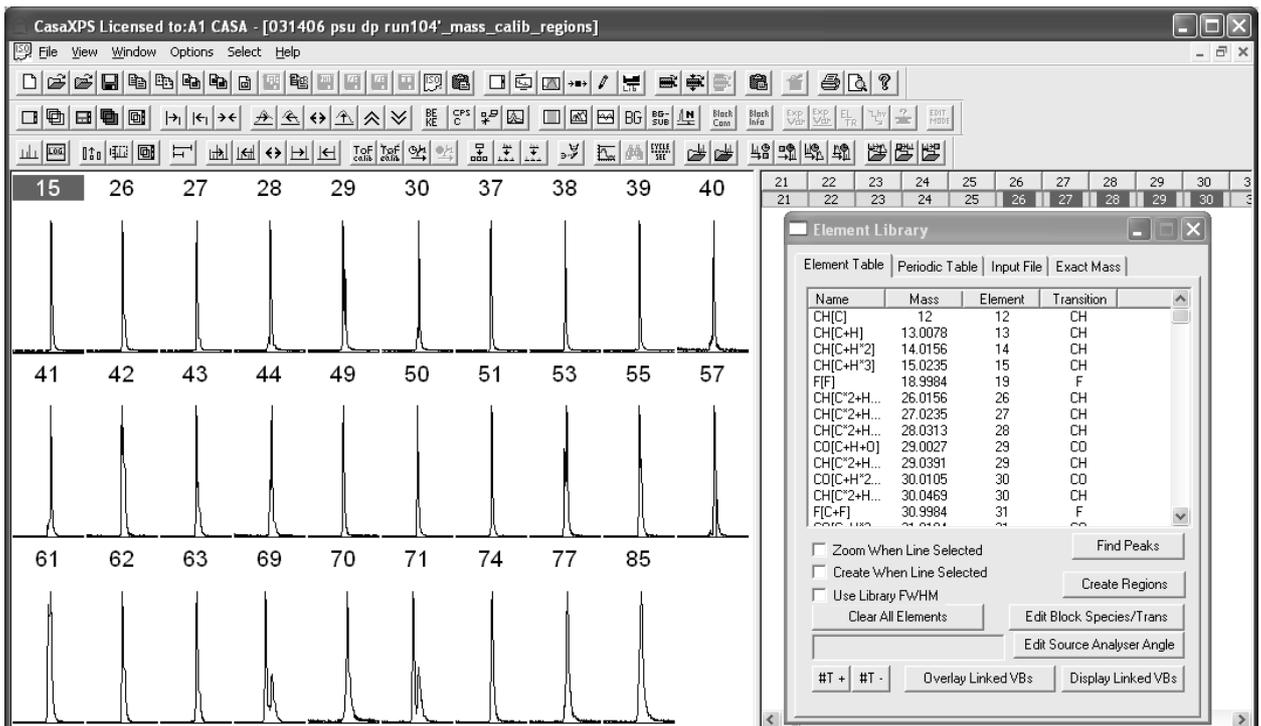
A dialog window provides a means of only selecting those VAMAS blocks for which the peak intensity is greater than the specified percentage of the maximum peak in the data.



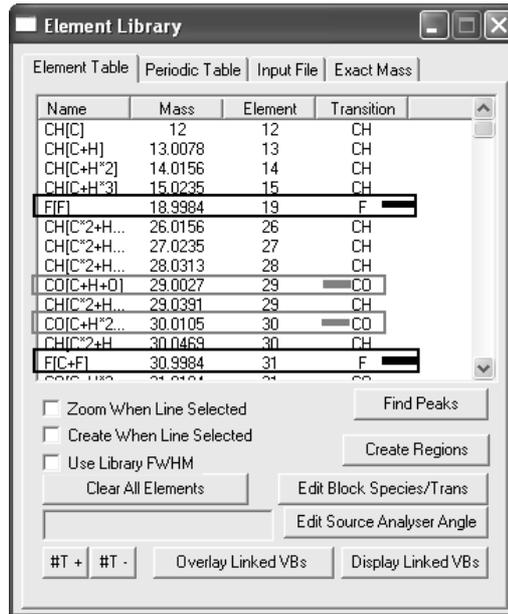
The key used to match the VAMAS blocks in the experiment frame is the string corresponding to the Species VAMAS field within each VAMAS block. The Species VAMAS field is used in the header string for each column of blocks in the right-hand pane of the experiment frame.



The ToF spectral files, when split into sets of VAMAS blocks, are created using the appropriate nominal masses to create these Species fields and the library entries with the common Transition library field are used to compute the corresponding nominal mass for each library entry, which when matched to the Species VAMAS fields causes the data to be displayed in the tile list.



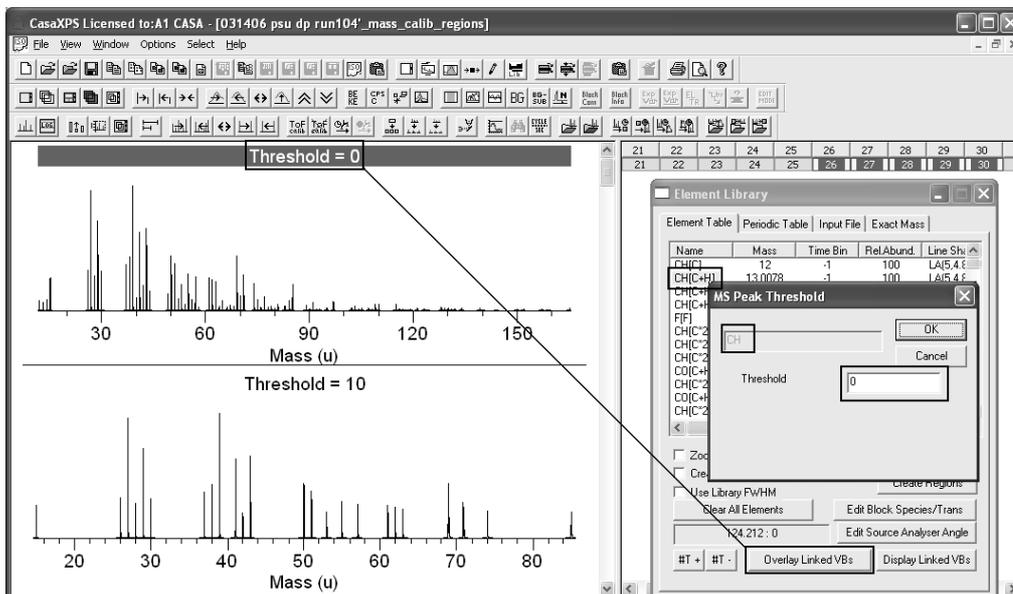
The element library file also includes Transition strings **CO** and **F**.



The different assignments for the Transition strings are simply a partition of the file between three possible sets of mass peaks; however a more realistic example might involve significant peaks from any combination of mass peaks, all of which would be collectively assigned a common Transition string. Should the same mass peak correspond to more than one compound, the element library file can include repeated entries differing only by the Transition string.

**Overlaying Related VAMAS Blocks**

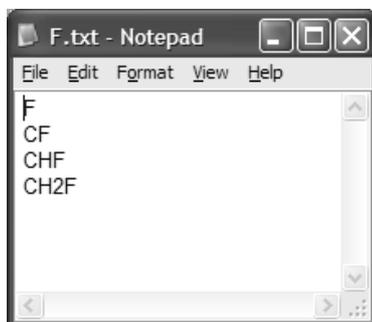
The Element Table property page also includes a button for overlaying VAMAS blocks selected from the current file using the same mechanism as the **Display Linked VBs** button described above.



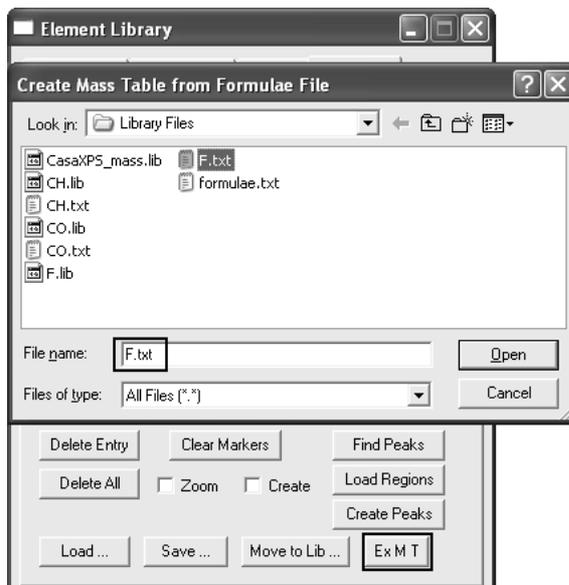
To overlay a set of VAMAS blocks corresponding to a predefined compound, one of the entries in the element-table list for the compound is selected before pressing the **Overlay Linked VBs** button. A dialog window appears offering a threshold value, which represents the percentage of the maximum height intensity of the peaks in the experiment frame. Only peaks of intensity greater than the percentage specified on the dialog window will be included in the set of VAMAS blocks overlaid in the active tile.

### ***Constructing an Element Library File***

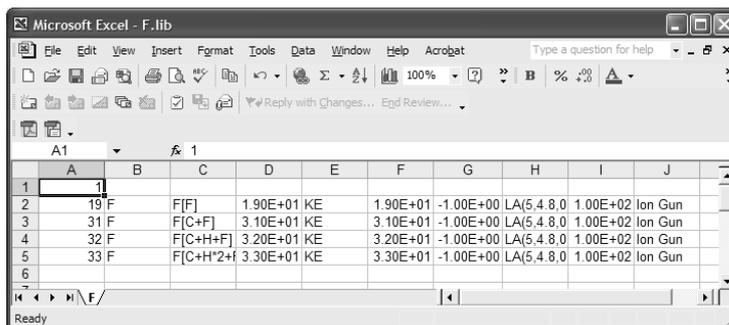
The element library file was constructed using the **Ex M T** button on the Exact Mass property page and three text files containing lists of chemical formulae. An example file containing formulae used to compute exact masses for library entries is as follows.



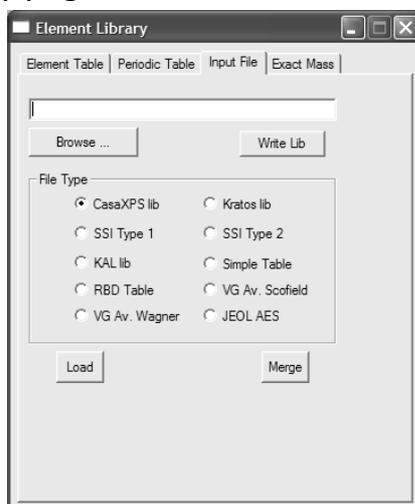
To create a corresponding library file, select the text file via the File Dialog invoked by the **Ex M T** button.



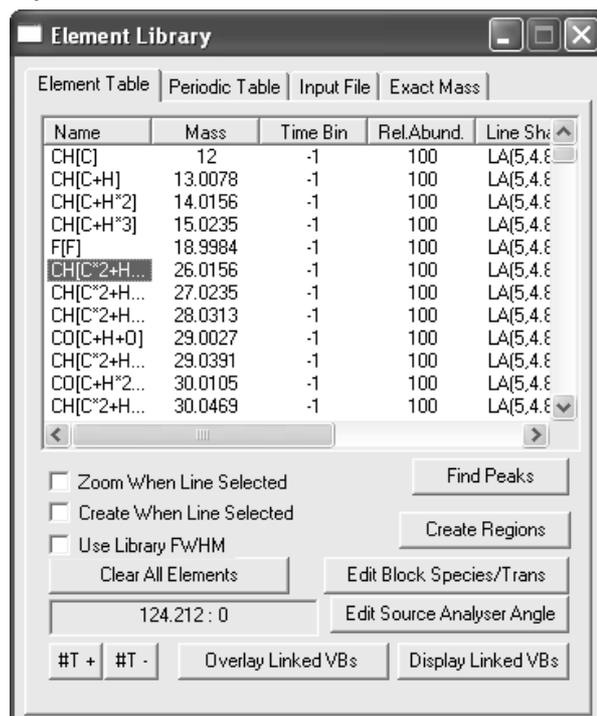
The base-name for the text file is used to assign a string to the Transition field in the resulting library file created when the Open button is pressed on the File Dialog window. The new library file appears in the directory where the original text file is located.



The intension is that a text file is prepared for those mass fragments characteristic of a particular compound, from which a library file is then created. When it is desired to visually inspect a ToF spectrum for evidence of the given compound, the library file for the compound is loaded into CasaXPS via the Input File property page.



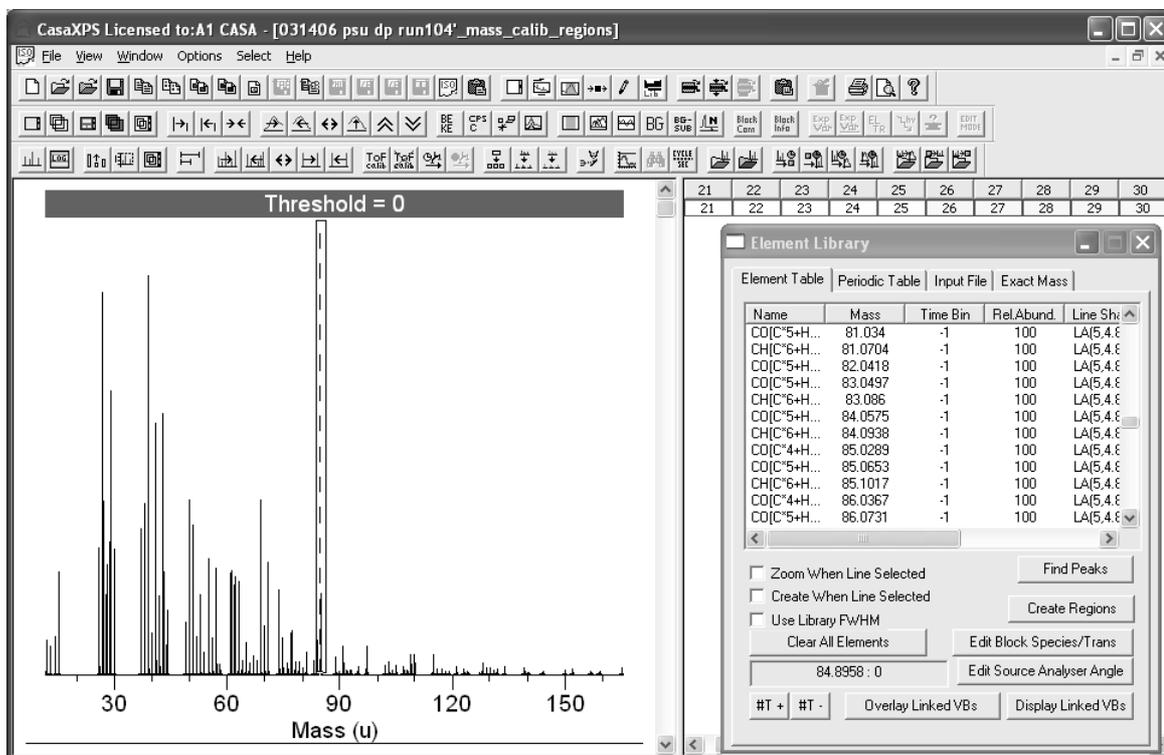
The library file displayed via the Element Table scrolled list



is a combination of loading three different library files using the Input File property sheet. The first file was selected using the **Browse** button, and then pressing the **Load** button caused the selected library file to replace the existing library entries. The two remaining files were merged with the first file by again using the **Browse** button to select the files followed by pressing the **Merge** button.

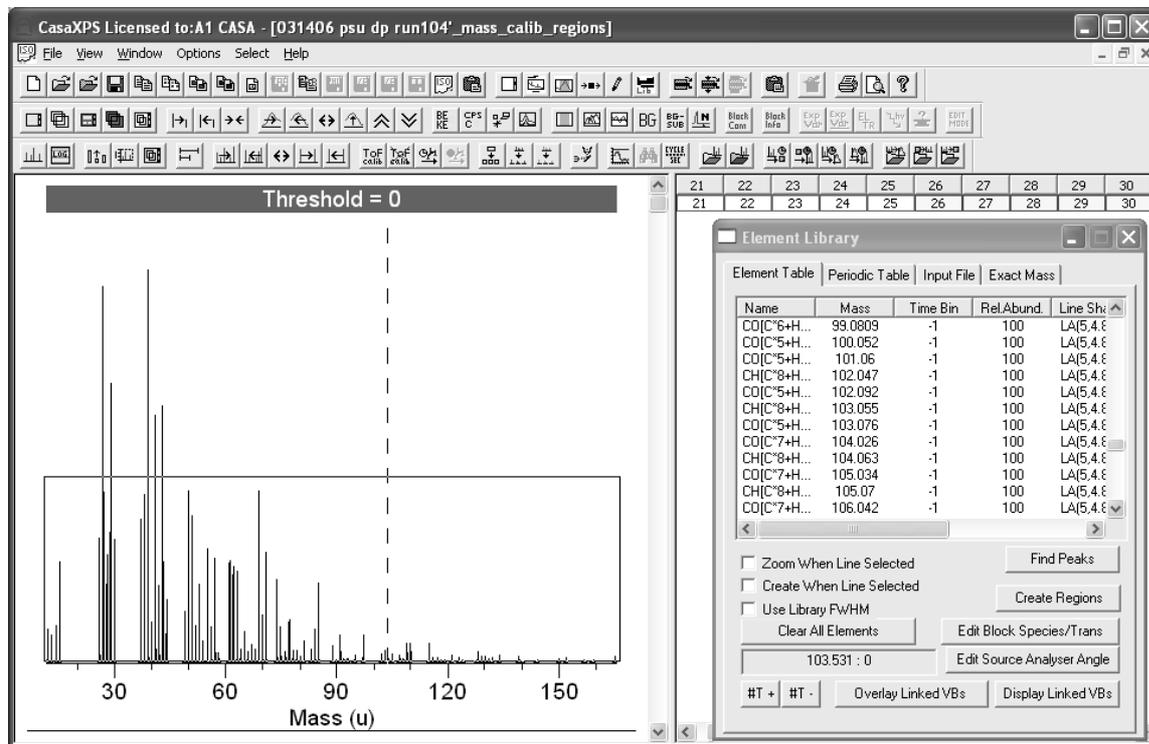
### ***Examining the Peak Structure using Zoom Actions***

The standard method for defining a range of intensities in CasaXPS is to use the left-mouse button to drag a box over the peaks of interest before left-clicking inside the box on the display tile. The mechanism used in the definition of the zoom-box is enhanced when the Element Table property page is top-most on the Element Library dialog window. These enhancements are enabled by holding down the Control Key or the Control Key at the same time as the Shift Key on the key board. The result of combining the Control Key with the Element Table top-most on the Element Library dialog window is to create a narrow and tall zoom box at the location of the cursor whenever the left-mouse button is clicked.



The second modification to the zoom mechanism is designed to provide a means of creating a limited intensity applicable to the mass range currently in effect. Holding down the Control Key at the same time as the Shift Key alters

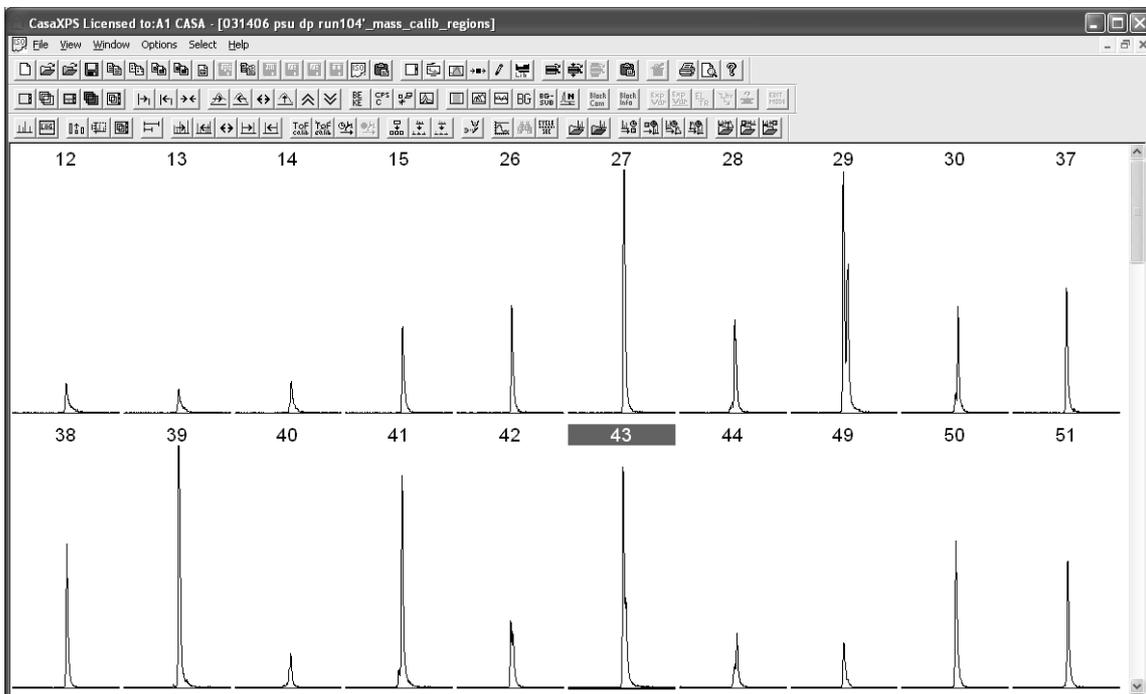
the behaviour of the mouse drag action such that the zoom box always extends over the current mass range, but permits the height of the box to be determined from the cursor's final position.



To perform the zoom action, click inside the zoom box.

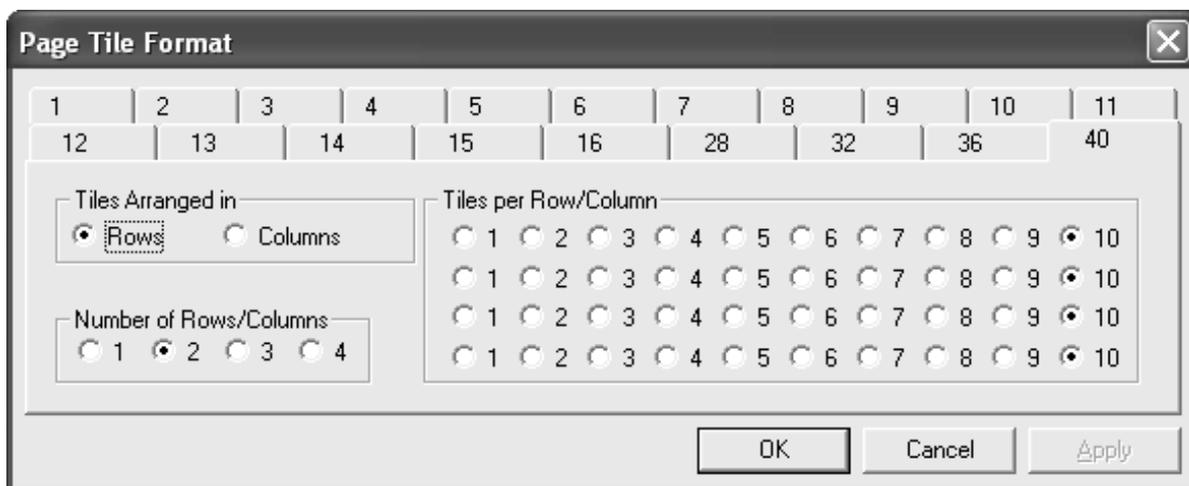
While zoom-actions permit a global perspective of a spectrum to be transformed into the display of a specific peak, there is always a cost associated with mouse actions required when transforming the display to see the peaks located at a nominal mass. The problem lies in the sparse nature of the mass peaks compared to the number of data bins comprising a spectrum. It is for this reason that the nominal masses can be broken down into individual VAMAS blocks using the **Display Linked VBs** button on the Element Table property page described above, thus offering a means of individually displaying a user defined set of VAMAS blocks. When these blocks are displayed, each spectrum appears such that the intensity scale is appropriate for each and every VAMAS block. However, while ensuring the peak structures are visible, the relative scale of these data, when viewed as individually scaled tiles, is lost. For this reason new SIMS toolbar buttons  are introduced to permit the intensity scale for the entire set of data displayed in the left-hand pane of an experiment frame to be determined from the active tile. These toolbar buttons when coupled with the extension to the number of tiles per row, from four to ten, allows the peak structures

within each VAMAS block to be visualized with a similar perspective of intensity as that seen in an overlaid plot of the data. The following display shows two rows of VAMAS blocks after scaling with respect to the tile with heading 43.

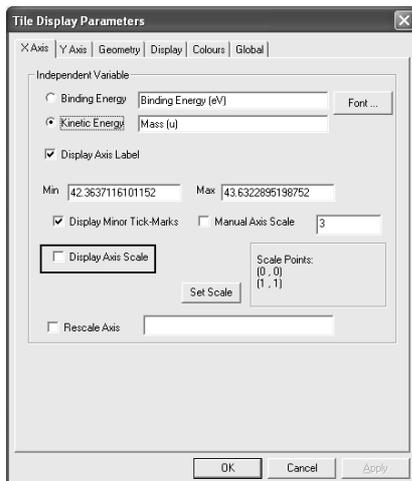


The Page Tile Format dialog window provides the means of adjusting the number of tiles per row and the Tile Display Parameter dialog window offers display settings for switching the tile display to those seen. The organization of the VAMAS blocks in the scrolled list means that paging down the scroll list effectively scrolls through the mass range in the spectrum being displayed.

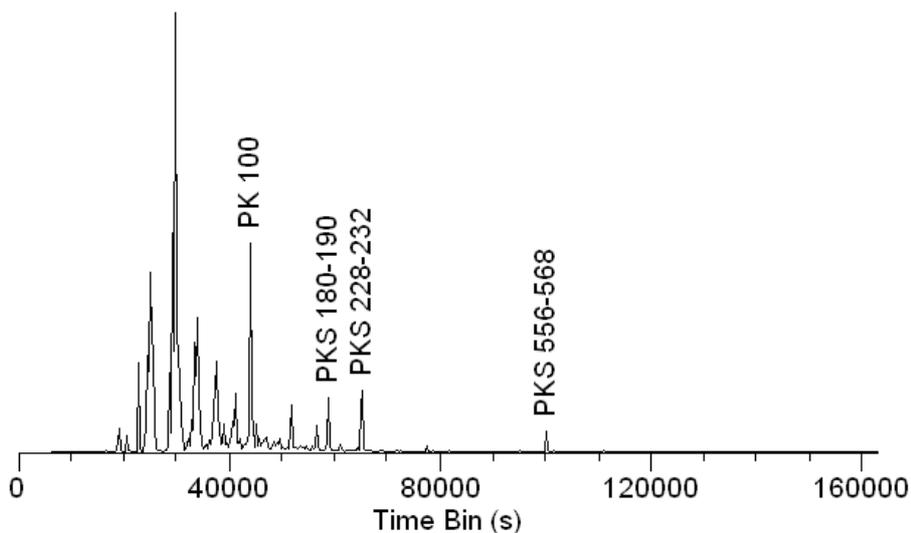
The enhanced Page Tile Format window  provides the means of changing the number of tiles per scroll position in the left-hand pane of the experiment frame.



To display the VAMAS blocks without an x-axis, the Tile Display Parameters dialog window is used.



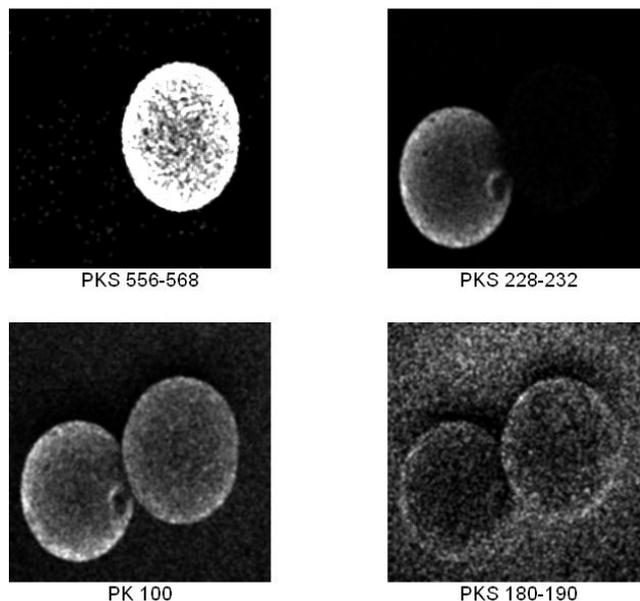
## Profiling Features for ToF data



**Figure 28 ToF Mass Spectrum displayed using Time Bins. Data provided by Prof. Winograd, Pennsylvania State University, USA.**

ToF MS is often categorized according to the method for generating the ions from the sample. The data in Figure 28 is an example of Secondary Ion Mass Spectrometry SIMS, where the ToF technique is used to separate ions with different mass-to-charge ratio following exposing the sample to a focused beam of ions from an ion gun. Since the beam from the ion-gun can be scanned across the sample surface, ToF data may be collected over a set of points on the sample. Knowledge of where on the sample a time event was recorded allows the spectral data in Figure 28 to be assigned to pixels in mass resolved images as seen in Figure 29. These images in Figure 29 correspond

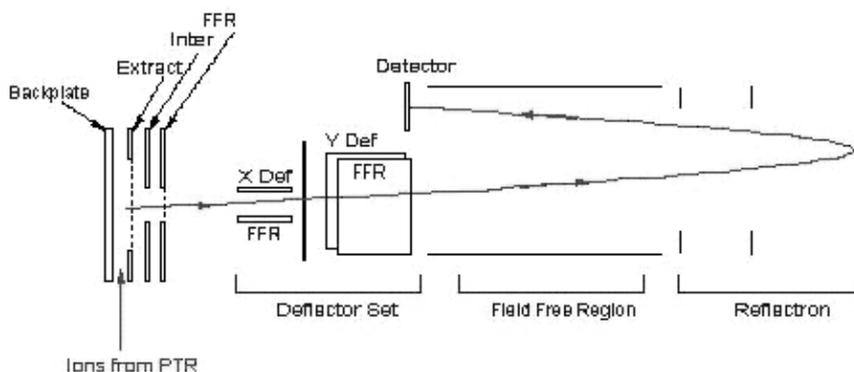
to the peaks identified in Figure 28, that is, each image is obtained by only counting time-events contributing to the peaks labelled on the spectrum.



**Figure 29: Mass resolved images extracted from the ToF SIMS data file corresponding to the histogram Figure 28.**

Similarly, identifying pixels in an image and only counting time-events corresponding to the selected pixels permits multiple spectra to be extracted from a single ToF data file. Given the complex nature of ToF spectra, the ability to retrospectively examine the data from an experiment is a powerful tool in understanding the information in the spectra.

ToF MS is used to obtain spectra through ionization mechanisms other than SIMS. Proton Transfer Reactor (PTR) ToF MS (Figure 30) provides a soft ionization mechanism of an analyte by the transfer of a proton from  $H_3O^+$  to the analyte. While spatial information is not appropriate for PTR ToF MS, the technique provides temporal separation of spectra, where variation of mass-peaks with time provides a profile (Figure 31) of changes in a sample.



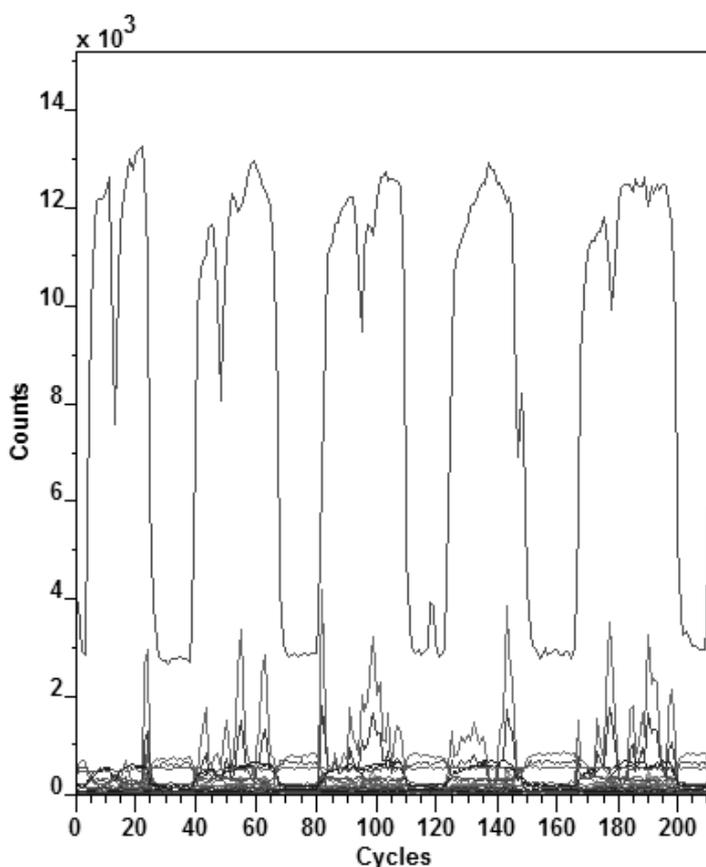
**Figure 30: Schematic of a PTR ToF MS (Kore Technology Limited, UK)**

The tools for the purpose of visualizing the data from a ToF MS experiment are described in following sections.

## ***ToF Data File Options***



The options on the SIMS toolbar for manipulating ToF MS data fall into two categories: those for which a new VAMAS file is created without reference to other data and those for which an existing spectrum or image is used to create spectra or images representing a subset of the data within a file.



**Figure 31: A profile of PTR ToF MS peaks.**

Currently, two types of file formats may be processed using these options: Kore Technology Limited list files and Prof Winograd's (Pennsylvania State University) Bio ToF XYT files. Both types of files contain time information as well as associating the time information with image pixels.

The first step to viewing a data file is to create a spectrum from the entire file of time values regardless of whether the file is a set of images or a profile of some description. From the total spectrum, peaks are identified from which

images or profiles are created. In turn, the images or profiles can be used to define the pixels or layers of interest, which once specified are used to extract pixel or layer filtered spectra from the original data file.

## Create a Total Ion Spectrum

A total ion spectrum is created from a data file specified using the resulting File Dialog window shown in Figure 32.

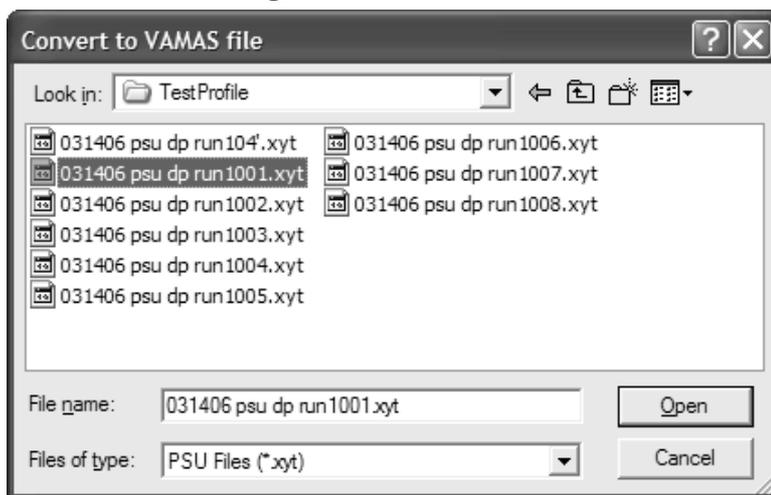


Figure 32: Convert to VAMAS File Dialog window used to specify the ToF MS files.

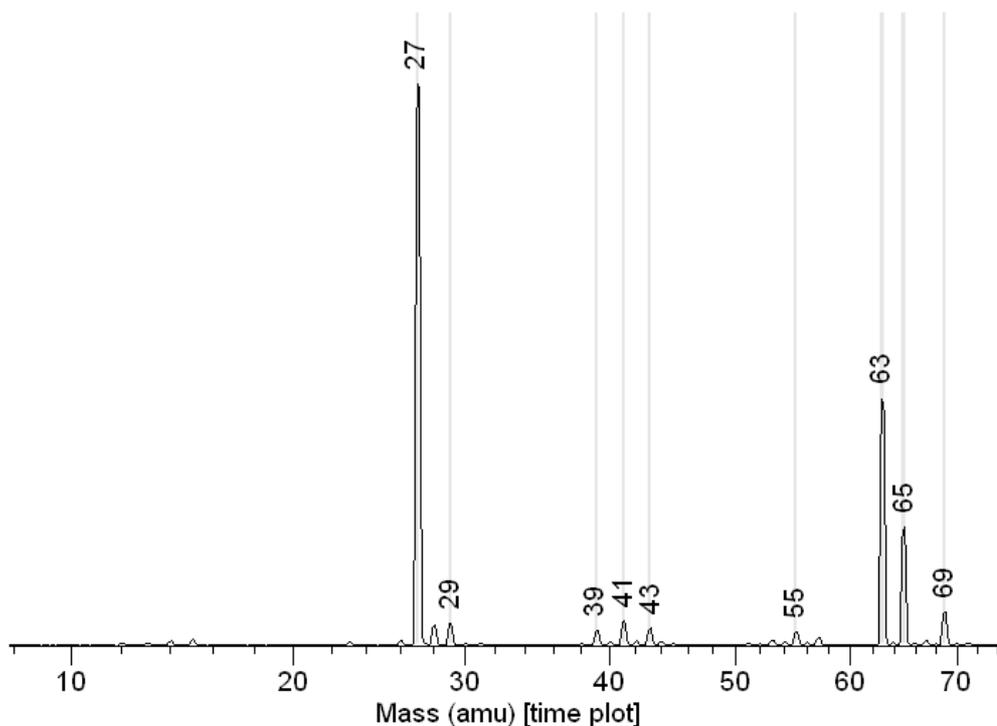
The file types supported are:

- 1) Files with the extension “lst” created using by the Kore Technology Ltd ToF MS instruments. The lst files contain a list of binary data in which each analysis ToF cycle appears as a sequence of start events followed by a list of stop events representing ions arriving at the detector. While these analysis cycles may be associated with a pixel in an image or a layer of a profile, the spectrum created from the lst file ignores these distinctions and generates a single time histogram from the timing information. Images or profiles are subsequently generating from the list file using the total spectrum as a reference.
- 2) Files with the extension “xyt” created from the Penn State University Bio ToF instrument. The xyt files are binary files containing a two dimensional array of lists, where each pixel in an image is associated with a list of stop events specifying the arrival times of ions at the detector. The total ion spectrum is created by ignoring the spatial information and generating a histogram from the entire set of time lists.
- 3) Files with the extension “spc” generated from the Kore Technology Ltd instruments. These spc files are already in the form of a time binned

histogram. No image or profile information is present in these files. Sets of spc files within a directory can be profiles using the options below.

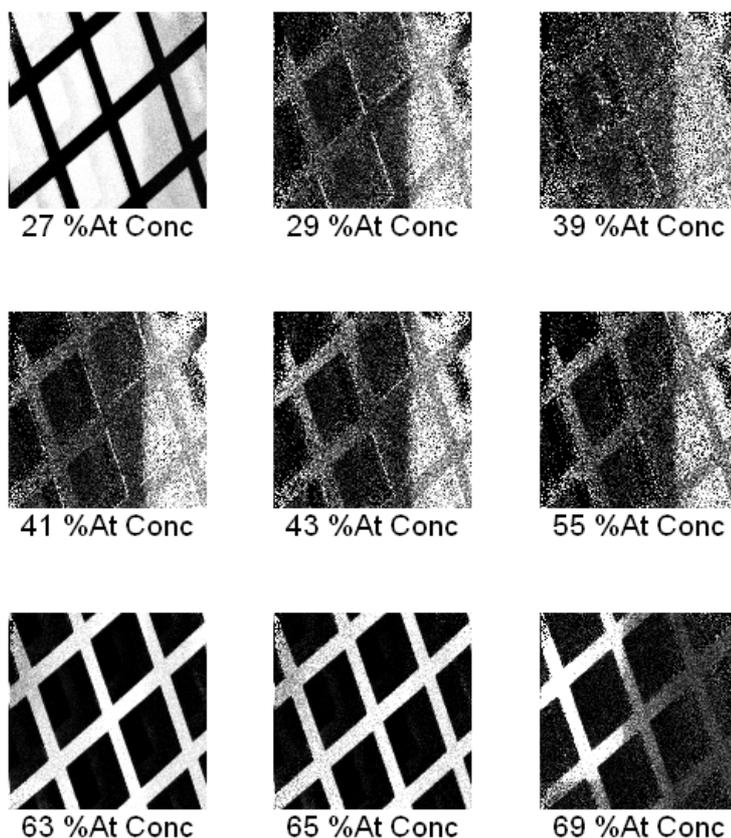
4) Files with the extension “dat” generated from the Penn State University Bio ToF instrument. The dat files are already in the format of a time binned histogram. No image or profile information is present in these files. Sets of dat files within a directory can be profiles using the options below.

Creating a time spectrum from a raw data file  involves selecting the file with the appropriate file extension using the File Dialog window shown in Figure 32. Once a file is converted and displayed in an experiment frame, the data can be selectively processed using information defined on the total ion spectrum.



**Figure 33: Total Ion Spectrum from an Image File.**

The spectrum in Figure 33 is a total ion histogram which is mass calibrated and prepared with quantification regions in anticipation of processing a set of images from the raw list file. The quantification regions define the time intervals over which ions are allocated to pixels in images as the list file is processed a second time. Figure 34 represents the outcome to the second pass through the list file; the images are obtained from the second pass by only collecting and allocating counts to images in accordance with the quantification regions define on the spectrum in Figure 33.



**Figure 34: Images processed from the list file corresponding to Figure 33.**

The steps taken to create these images will now be described.

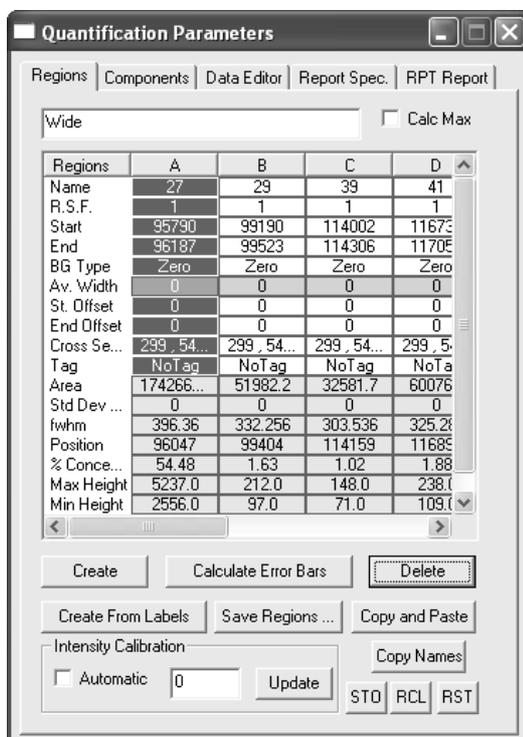
### **Create Images from Spectra using Quantification Regions**

Once a total ion spectrum is available, the data can be mass calibrated using one of two procedures: 1) define a set of calibration points in the form of (time, mass) pairs via the Exact Mass Calculator on the Element Library dialog window or 2) define a set of calibration regions using the Quantification Parameters dialog window and calibrate the spectrum using a button from the SIMS toolbar. While it is not necessary to calibrate the time bin spectrum before generating images, given a time-to-mass calibration the automatic region creation option on the Element Library dialog window will assign the nominal mass to the region names and therefore aids the interpretation of the data.

#### ***Defining Quantification Regions using the Find Peak buttons***

Regions defined on the total ion spectrum provide the time intervals over which counts are accumulated into images. The Quantification parameters dialog window permits regions to be created one at a time, however ToF MS is typically blessed with numerous peaks and creating a region for each of these peaks manually would be too time-consuming. As a result, the Element

Table and Periodic Table property pages offer Find Peak buttons, which for ToF data will create a region for each peak subject to a threshold criterion. While the regions are created by simply pressing the Find Peaks button on the Element Table property page, it is worth reviewing the limits of the regions using the Reset  and Zoom Out  toolbar buttons. When the Reset button is pressed, any regions created on a spectrum are loaded onto the zoom-list. Thus pressing Reset followed by repeatedly pressing the Zoom Out button will step through the regions created by the Find Peaks button. The limits for the regions can be adjusted under mouse control provided the Region property page is visible on the Quantification Parameters dialog window.



### Creating the Images

The total ion spectrum retains a record on the file from which it originated, therefore pressing the toolbar button  with toolbar hint *List File to Images* will cause the original list-file to be scanned a further time. During the second scan of the list file, counts are accumulated into images defined by the current set of regions on the spectrum displayed in the active tile. Note, regions created automatically may be numerous and therefore the resulting image data file is potentially large. The operation is similarly potentially time consuming and may take several tens of seconds, depending on: the number

of regions as well as the processor power, memory and disk speed of the PC performing the operation.

The spectrum in Figure 33 was used to create the images displayed in Figure 34 via the  toolbar button.

### Spectra Generated from Image Zones

Given an image of the sample, a false colour scale defined over intensity ranges offer a means of specifying which pixels from the image should be included in the procedure for creating time-bin histograms from the list file. As a result, one or more spectra can be extracted from the list file which will be referred to as LUT spectra (Look-Up Table); the colour used to display a pixel in a false colour image is defined using a “look-up table” of colour values.

The image in Figure 35 is an example of a mass resolved image displayed using a false-colour-scale consisting of four colours. The intensity scale is partitioned into the false colours defined using intensity ranges characteristic of the implanted gallium lettering PSU and the complementary pixels to the gallium lettering. Four spectra are generated from the list file based on the four false colours defined on the image by only collecting time events corresponding to the pixels displayed using the false colours. A comparison of these LUT spectra for the gallium mass range is made in Figure 36.

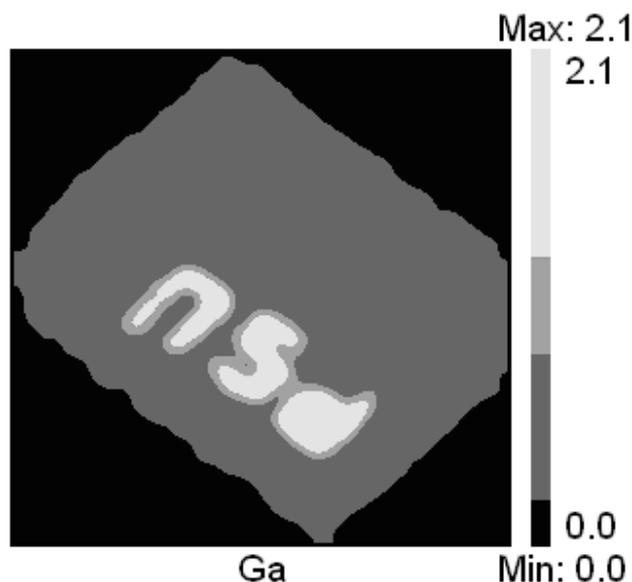


Figure 35

The procedure for generating LUT spectra is as follows:

1. Select an image generated from the original total ion spectrum for a list file.
2. On the Image Processing dialog window, available from the Options menu, select the Colour Scales property page.

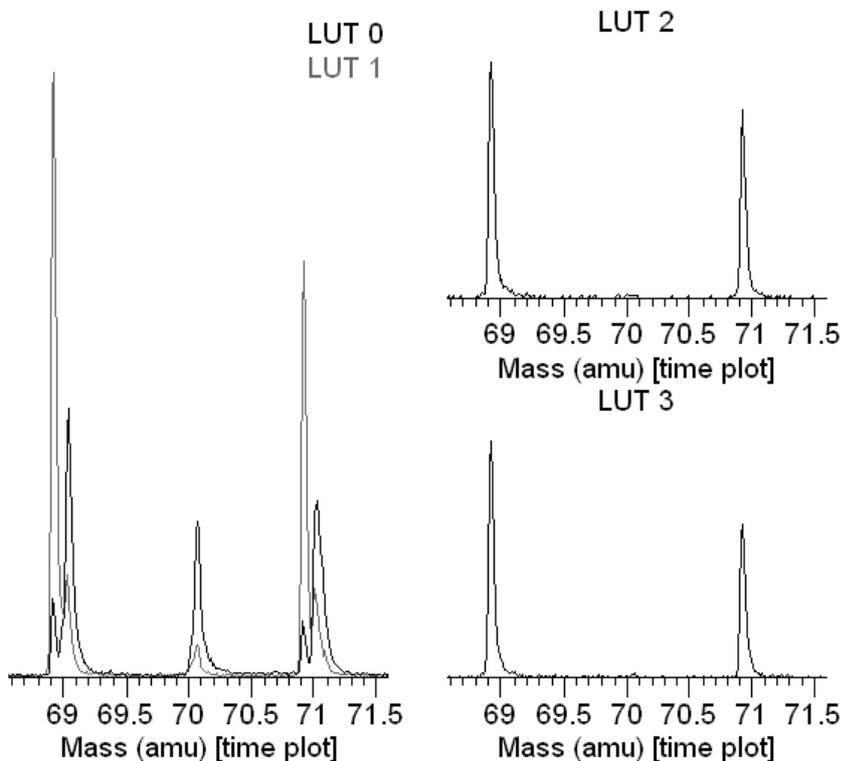
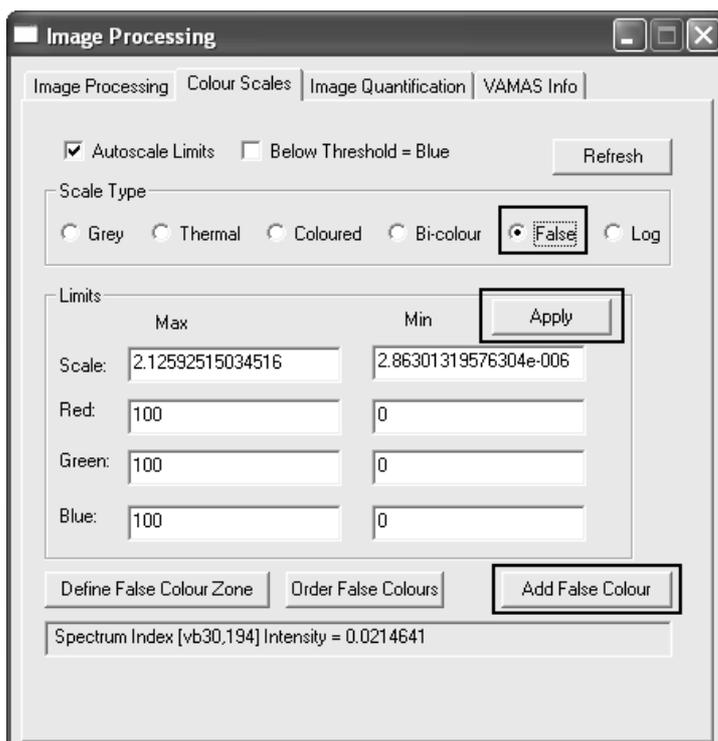


Figure 36

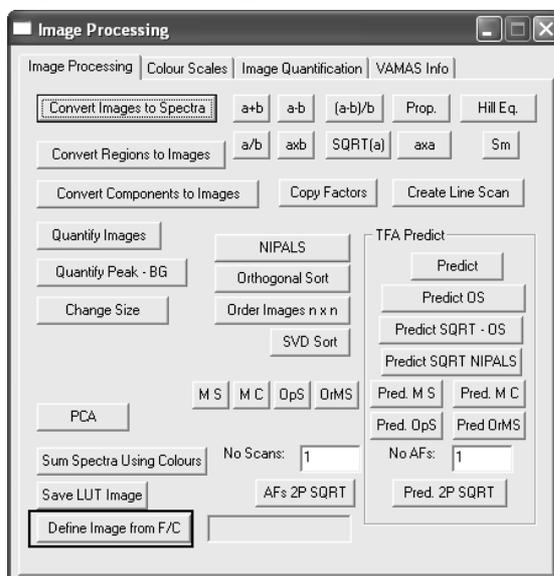
3. Select the False radio button from the Scale Type list and press the Apply button.



4. Mark a range on the image colour scale displayed next to the image in the left-hand-side of the experiment frame using the cursor whilst holding down the left-mouse-button.
5. Press the button labelled **Add False Colour**. The colours, as specified by the dialog window which appears when the button is pressed, are displayed in the colour scale in the active tile and the image itself is updated using the newly define false colour.

The default false colours are ordered to agree with the colours used to display spectra when overlaid in a tile.

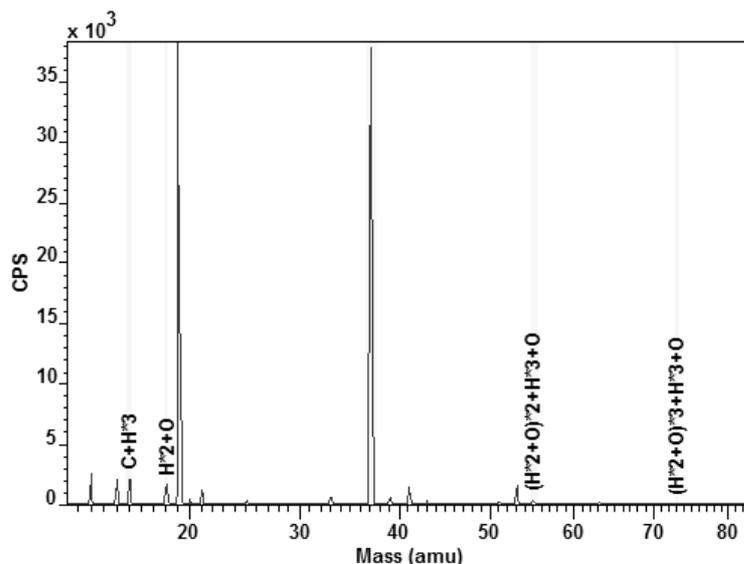
6. Once the desired zones of pixels are assigned false colours, the image can be made the current template using the **Define Image** on the Image Processing property page.



7. To generate the LUT spectra press the  toolbar button. The list file corresponding to the image is scanned and, for each false colour in the image defined by the previous step, a spectrum is added to a new experiment frame.

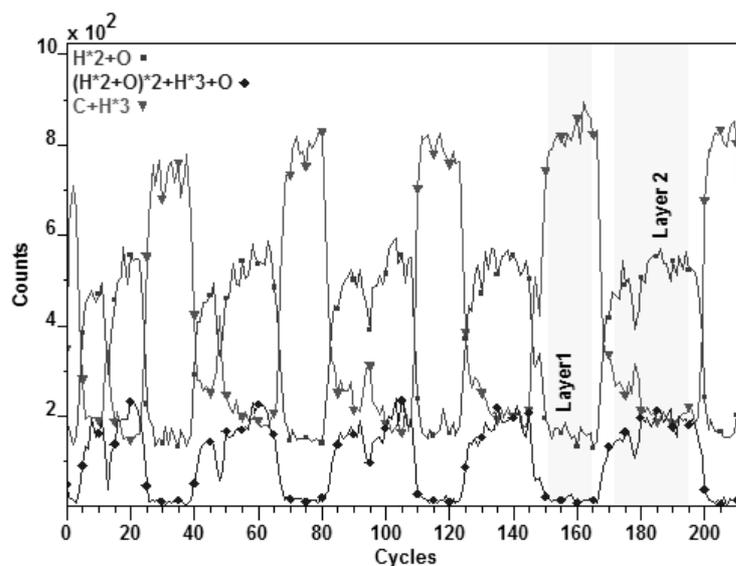
### Creating a Profile from a Total Ion Spectrum

The concept of a ToF list-file is applicable to time dependent measurements where spectra evolve during the course of an experiment. The data from such an experiment can be treated as a total ion spectrum. Just as the data from an image can be interpreted as a large area analysis to produce a single spectrum from all the data, so too can all the ToF timing information be interpreted as a single spectrum; the difference being that, in creating the total ion spectrum the for a profile, all the changes over time are ignored.



**Figure 37: PTR ToF MS total ion data showing quantification regions prepared for the purpose of creating time-dependent intensity profiles.**

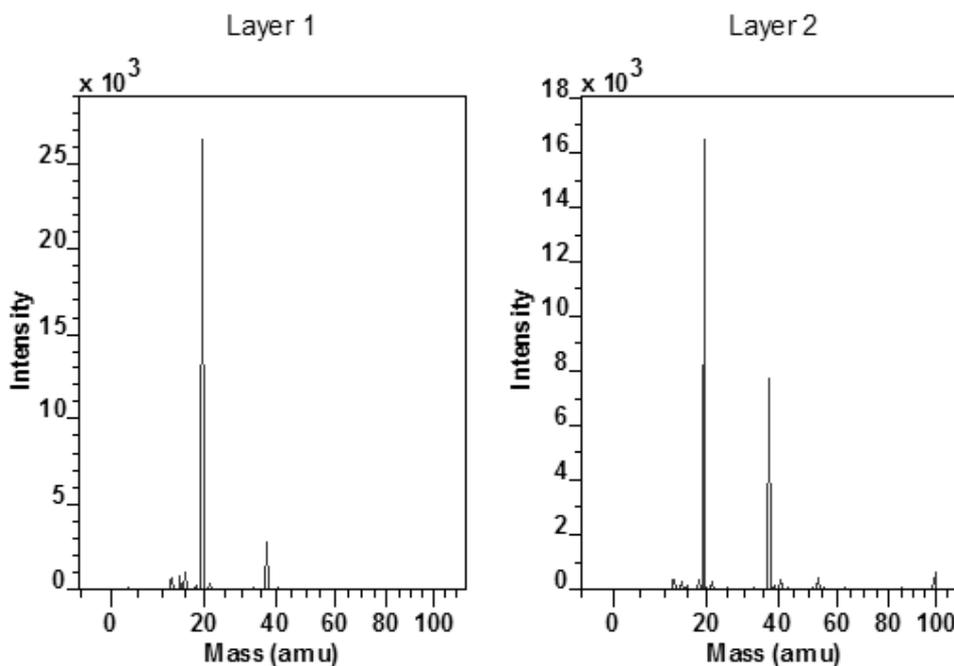
The total ion spectrum in Figure 37 provides a coarse description of the experiment, from which the time dependent information can be extracted. The procedure used to plot the variation of the spectra with time is similar to that of extracting images from an image list file, that is, quantification regions are assigned to the mass-peaks on the total ion spectrum followed by pressing the  toolbar button. The total ion spectrum maintains a reference to the original list-file, therefore on pressing the toolbar button, the list-file is scanned a second time producing a trace for each quantification region defined on the total ion spectrum.



**Figure 38: A plot of three traces from the regions defined on the total ion spectrum in Figure 37.**

The data in Figure 38 represents three quantification regions from the regions defined on the total ion spectrum in Figure 37. The oscillations in the profiles are due to changes in the air sampled from a subject whilst the mastication of food is performed.

## Spectra Generated from Profile Layers



**Figure 39: Spectra generated from the regions defined on the profile in Figure 38.**

Given a profile such as the one on Figure 38, spectra corresponding to a range of times or cycles can be generated as illustrated in Figure 39. For each quantification region defined on a profile, (Figure 38 includes two such regions) a spectrum is obtained by summing only those times falling into the ranges specified by the regions.

Quantification regions are added to a profile using the Quantification Parameter dialog window. Given the two regions in Figure 38, pressing the  toolbar button causes the list-file to be read a further time accumulating the spectra from the timing data. The spectra in Figure 39 are examples of data collected from layers within a profile experiment.

## Create a Profile from a Directory of Files

So far, ToF list files have been considered as the data structure managing images of spectra or profiles of spectra. The extension to the concept of a list

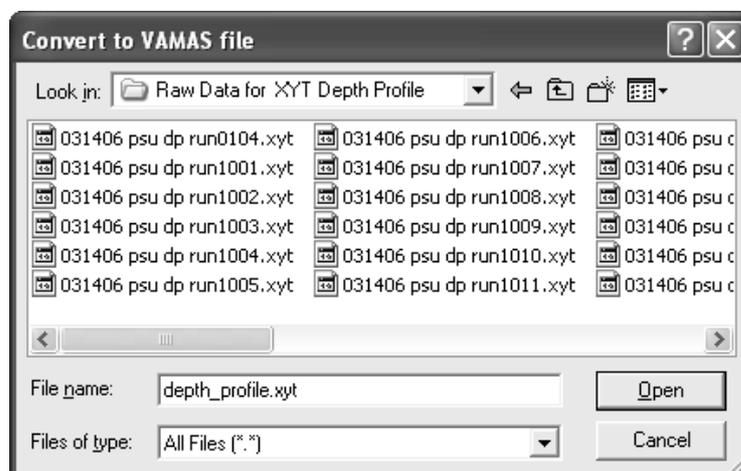
file is a directory of list files, where each list file represents a change in terms of the experiment performed. For example a depth profile of image list files offers the possibility of measuring an image of spectra for each layer within a sputter depth profile. The experimental conditions evolving during the course of the experiment are the depth beneath the surface at which an image of spectra is acquired. Such experiments are by nature time consuming and large in data size.

Creating a profile from a directory of list files involves selecting a representative spectrum from the directory of list files suitable for specifying the mass calibration and also the set of peaks to be profiled throughout the directory of files.

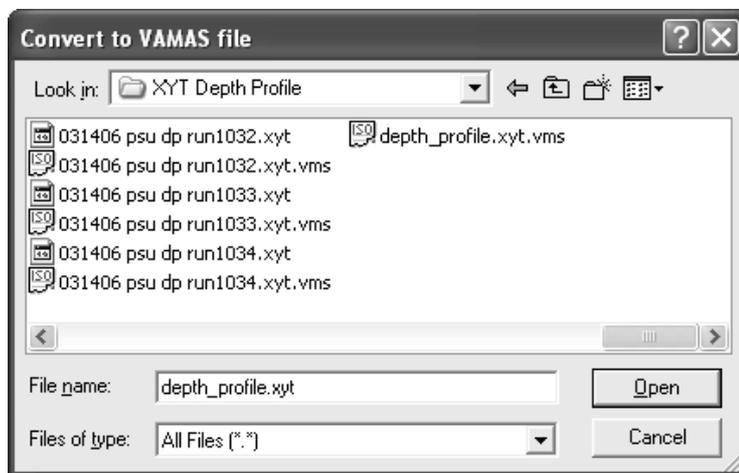
The active tile must display a spectrum for which regions are defined suitable for mass calibration. Once the spectrum is prepared the process is initiated via the  toolbar button. A File Dialog window allows the specification of a data directory containing the files for which the list files are processed as follows:

1. Converted to spectrum VAMAS files.
2. Each spectrum is mass calibrated using the regions defined on the spectrum in the active tile.
3. Peaks identified using an automatic threshold search and regions created for each of these peaks identified.
4. The region intensities are collected into profile traces for each region created in the peak identification step.
5. A new experiment frame created using the name specified on the File dialog window.

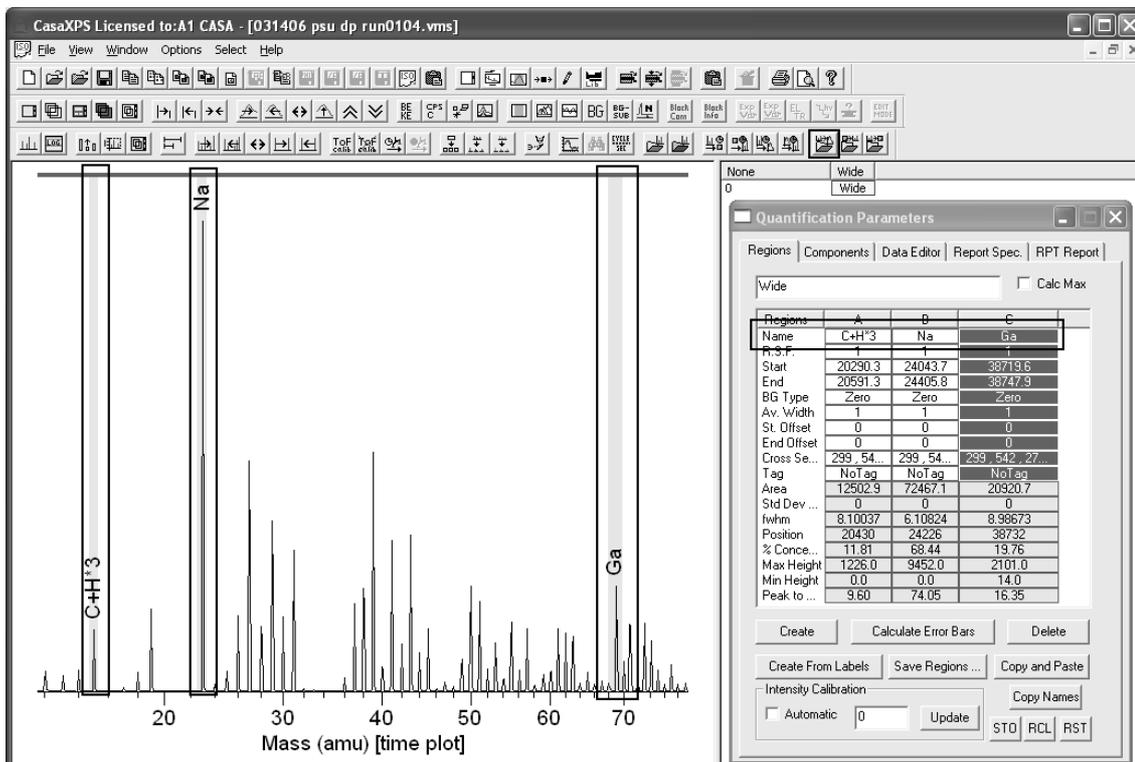
Initially the directory of list files appears as follows.



Each file with the directory is processed during the course of the profile procedure. On completion, the same directory appears with a VAMAS file corresponding to each original list file plus one further VAMAS file containing the profile traces for each peak identified as significant. After processing the directory appears as follows.



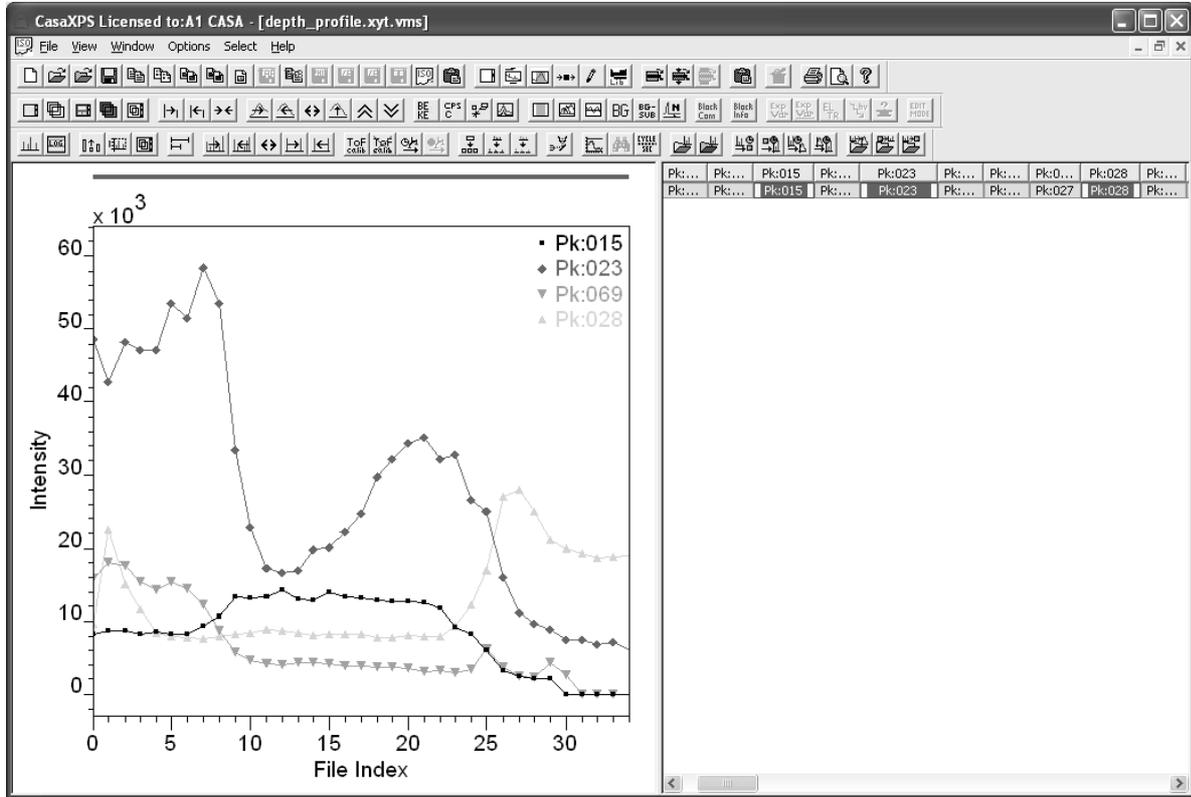
Before pressing the Profile from Files  toolbar button, a spectrum must be displayed in the active tile prepared with regions sufficient to provide an adequate mass calibration.



The file name for the profile with the appropriate list-file extension, entered in the Filename text-field on the File dialog window, specifies the type of list files in the current directory and on pressing the Open button, the profiling

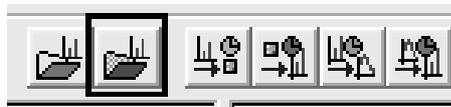
operation is initiated. These files tend to be large; therefore the time taken to complete the profiling task may be large too.

When the profile is complete, a new experiment frame opens in CasaXPS and the profile traces are displayed. A typical profile file will contain numerous profile traces.



### Convert and Merge a Directory of XYT File

An alternative to automatic profiling a directory of list files is to analyse the depth profile using the set of total-ion spectra converted from each XYT file in a directory.



A profile experiment, in which a sequence of images is acquired into separate XYT files, can be investigated in terms of the total ion spectra using the  toolbar button. A File Dialog window is used to specify both the directory containing the XYT files and the name of the file created by scanning the directory for XYT files; the XYT files are individually converted into VAMAS files containing the total ion spectra. After each XYT file in the directory is converted, the set of VAMAS files are merged into a new experiment frame.

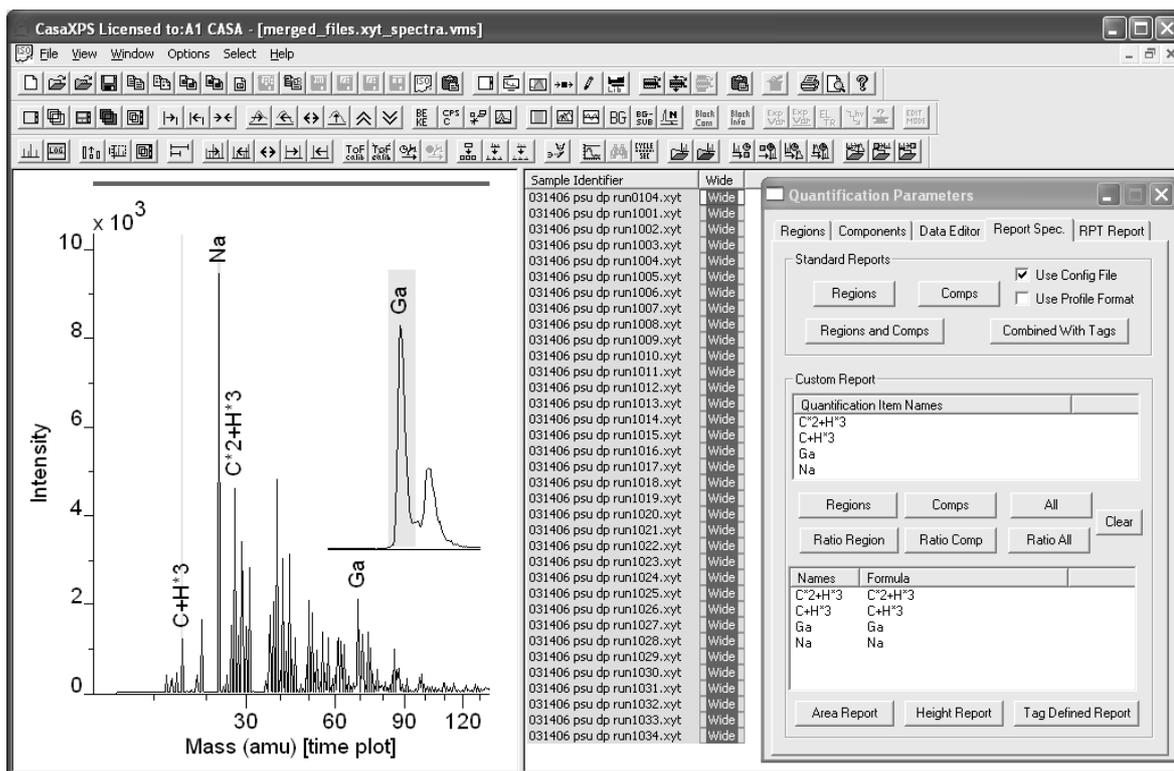


Figure 40: Merged XYT files

To load a directory of XYT files into a new experiment frame, select the  toolbar button to invoke a File Dialog window; move to the directory containing the XYT files then enter a name into the file name text-field with the file extension “.xyt”. ToF spectra tend to require large quantities of memory, therefore take care not to attempt to merge an excessive number of file as the operation may take considerable time to complete.

Once a set of spectra are loaded into an experiment frame, trends within the data can be assessed using the Custom Report mechanism on the Report Spec property page of the Quantification Parameters dialog window shown in Figure 40. A set of profiles determined from the data in Figure 40 are displayed in Figure 41. These profiles are obtained by defining a set of quantification regions using the Regions property page, generating an Area Report using the Custom Report on the Report Spec property page then creating a new VAMAS file from the tabulated report via the **Create Profile** menu option on the File menu.

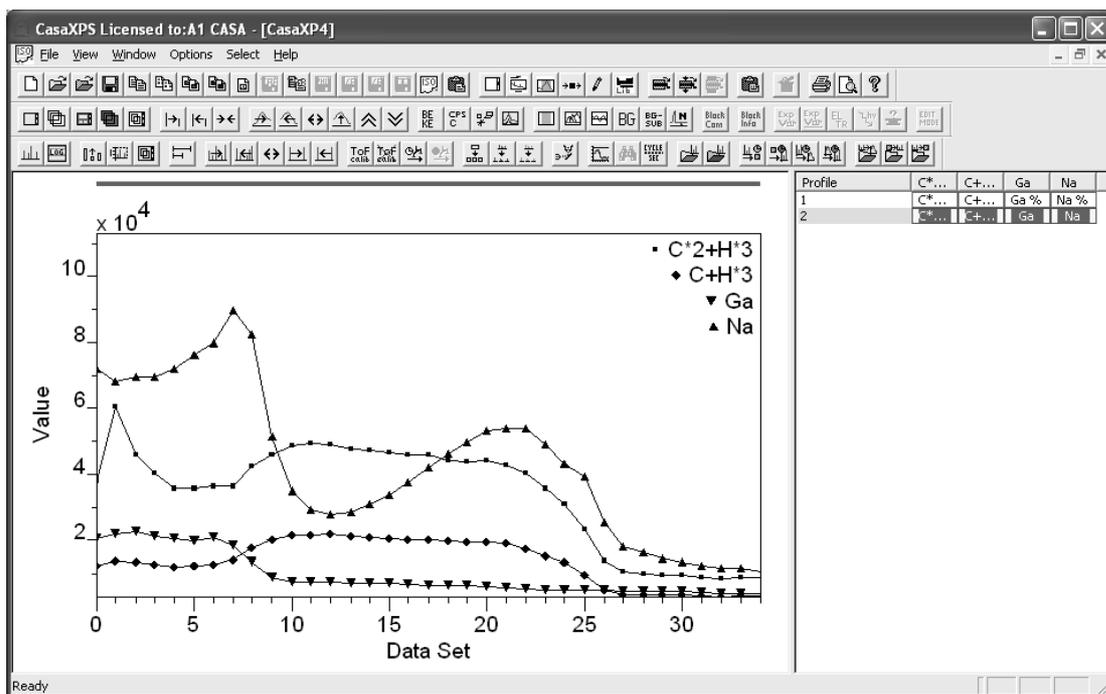


Figure 41: Profiles generated from the merged spectra shown in Figure 40.

### Image Depth Profile Data Analysis

Given a directory of xyt files:



Create an experiment frame containing a profile set of images corresponding to the set of regions defined on a spectrum in the active tile.

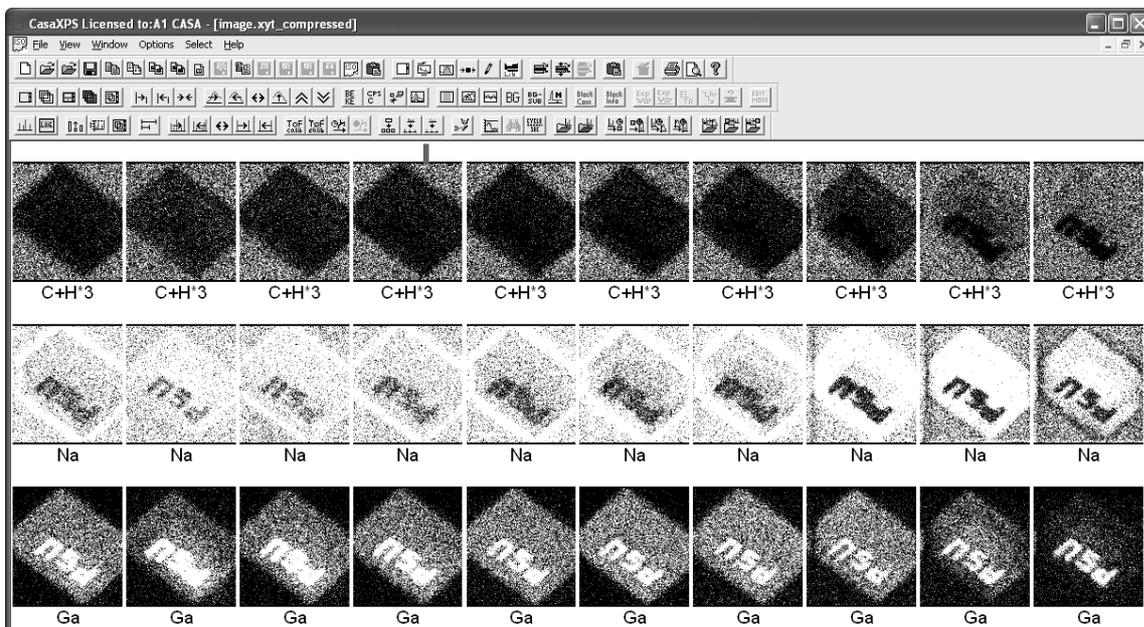


Figure 42: Set of images created by accumulating counts into pixels based on regions defined on a spectrum.

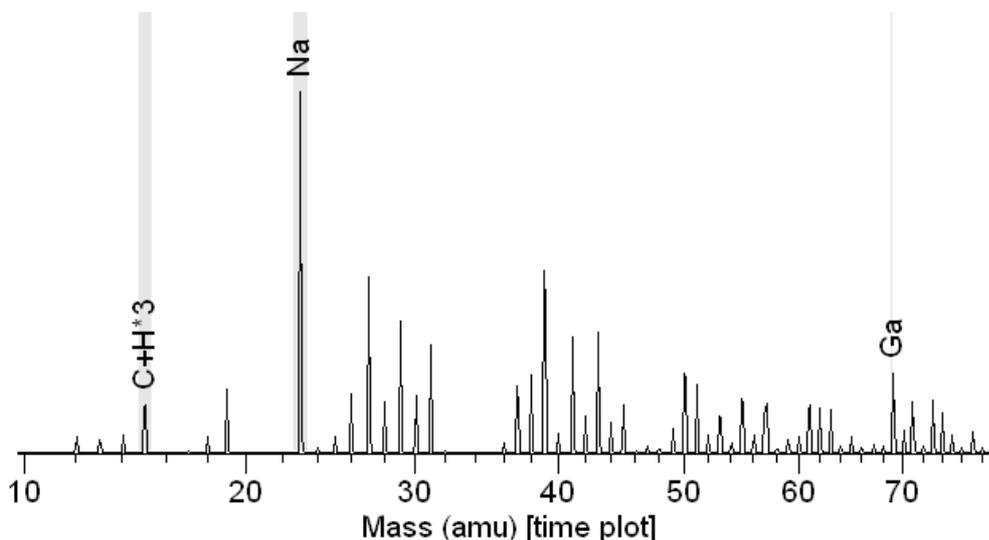


Figure 43: Spectrum used to create images in Figure 42.

The images displayed in Figure 42 were generated from a directory of XYT files, where data from the XYT files are processed only for those counts falling within the time windows specified by regions defined on the associated spectrum in Figure 43.

Three regions were defined using a total ion spectrum. The spectrum must be displayed in the active tile before pressing the  toolbar button. The operation involves reading the entire set of XYT files in the directory specified via the File Dialog window. The process is potentially time consuming. To process a directory of XYT files, a file name must be specified in the File name text-field on the File Dialog with extension .xyt. On completion, a new VAMAS file is created with the name specified concatenated with the .vms file extension.

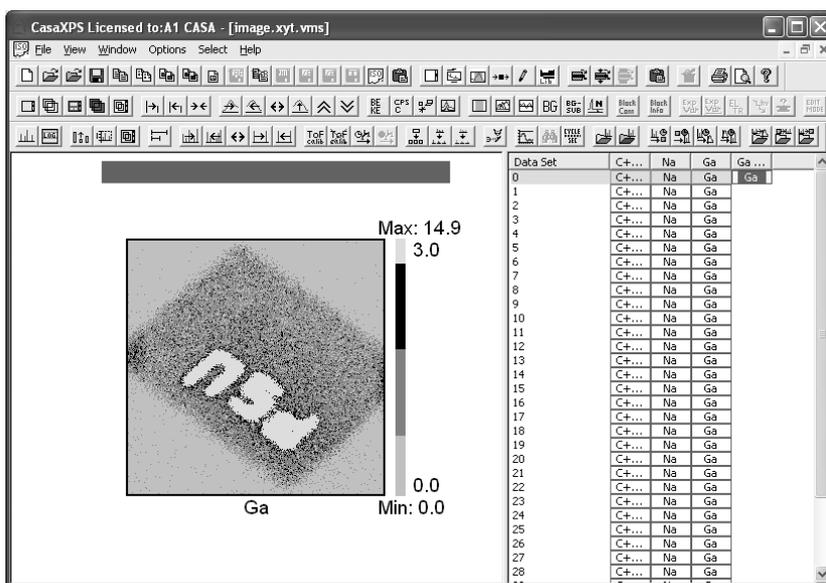
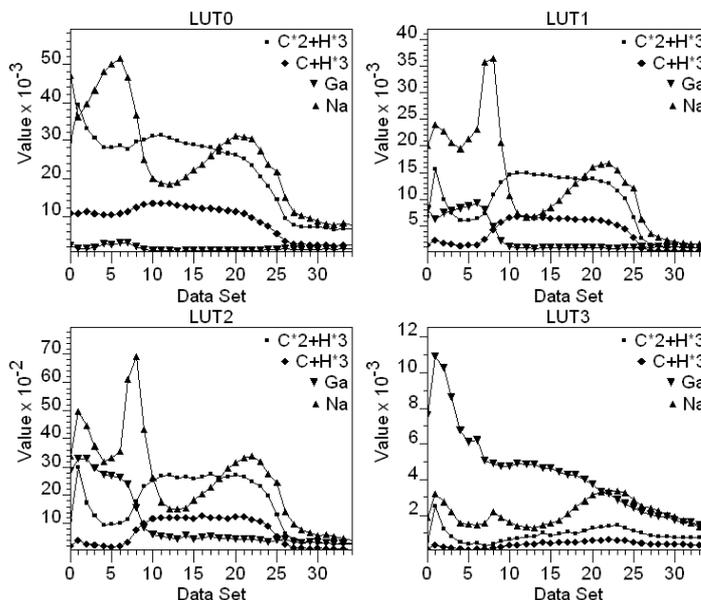


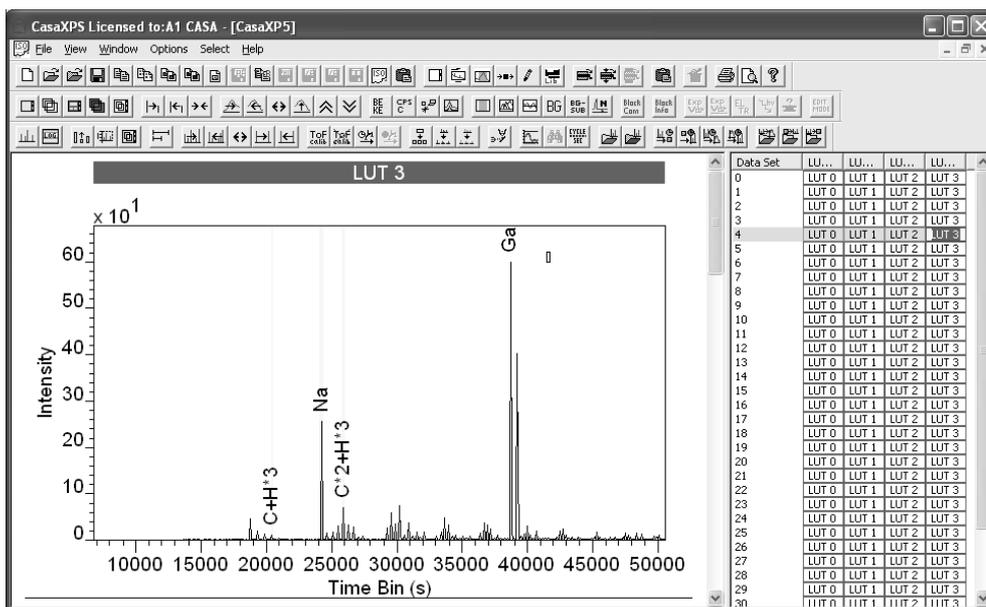
Figure 44: False colour image used to generate profiles in Figure 45.

The Image Processing dialog window on the Options menu offers tools for processing these sets of images. For example, the false colour image scale defined on the image displayed in Figure 44 may be used to generate depth profiles for the sum of pixel based on coloured zones.



**Figure 45: Profiles constructed from a directory of XYT files using the false colour image in Figure 44.**

Creating the profiles in Figure 45 requires the generation of LUT spectra from the directory of XYT files. Regions defined on the LUT spectra coupled with the Custom Report on the Report Spec property page of the Quantification Parameters dialog window provide to tools to create the profiles based on false colours.



**Figure 46: Spectra collected using the false colour image in Figure 44.**

## ***Generating LUT Spectra from a Directory of List Files***



### **Spectra from False Colour Zones**

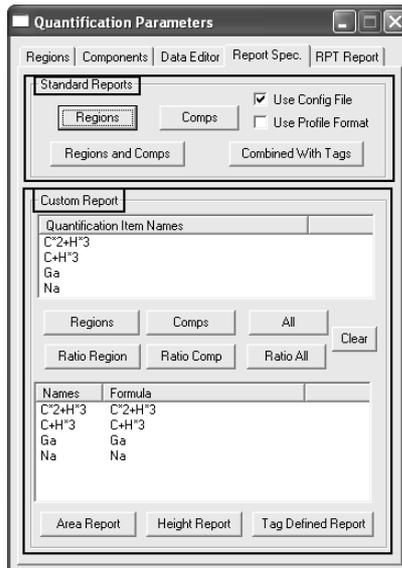
Given a directory of XYT files and a false colour image, the  toolbar button creates a new experiment frame containing a set of spectra from each XYT file, where the spectra are accumulated from the time information from only those pixels identified by the false colours in the image. For example, the false colour image in Figure 44 is the sum of all the gallium 69 isotope images and therefore the colour zones are determined by the gallium distributed throughout the volume sampled by the depth profile. Spectra from these four colour zones are collected into the new experiment frame shown in Figure 46, thus the depth profile can be examined from the perspective of gallium using these spectra.

## **Quantification Reports and ToF Data**

The intensity associated with a ToF mass spectrum represent ions counted at a detector. The time element of the measurement is less important than is the case for other techniques where a specific data channel is monitored for a specified time; data under these measurement conditions are typically quantified in terms of counts per second (CPS). For ToF Data, the pulsed extraction of ions and the delay required to allow ions to traverse the flight tube result in a departure from the need to consider counts per second, but rather to focus on the number of ions detected. CasaXPS generally assumes data are quantified in terms of CPS and peak areas are integrated with respect to the independent variable. Since the default quantification regime in CasaXPS is not appropriate for ToF data, there are ToF motivated configuration options to permit quantification of ToF intensities in terms of a summation of counts over time or mass bins.

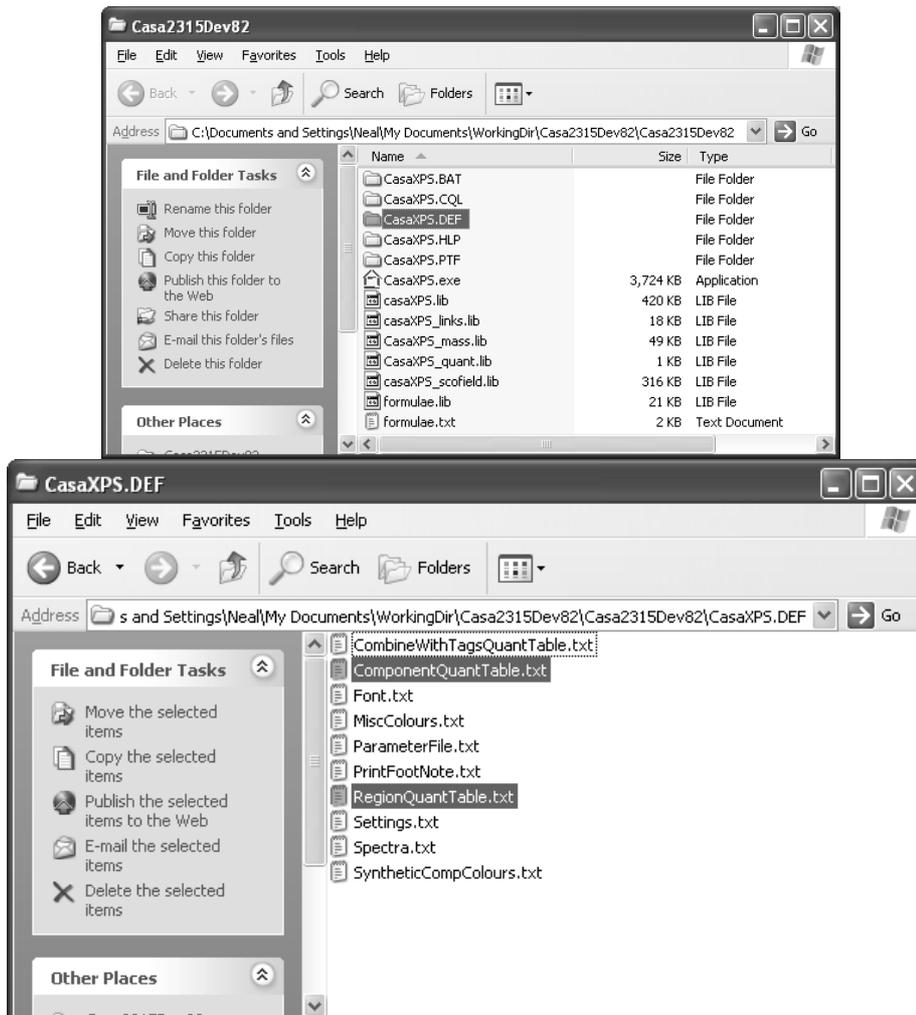
### ***Quantification via the Report Spec Property Page***

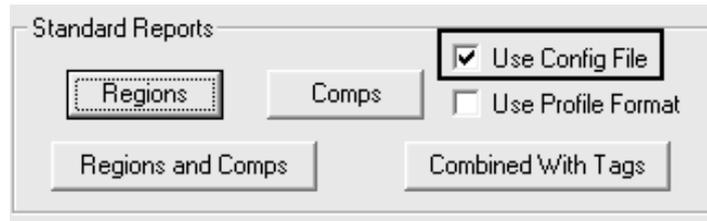
The Report Spec property page of the Quantification Parameters dialog window offers two methods for generating quantification reports. The Standard Report is predominantly aimed at tabulating results on a spectrum-by-spectrum basis; while the Custom Report is designed to support the profiling of data acquired sequentially, for example a depth profile.



## Standard Report

The Standard Report permits quantification in terms of quantification regions and/or synthetic components. For ToF data, quantification based on number of ions requires the specification of appropriate configuration files. These configuration files are located in the directory called CasaXPS.DEF.

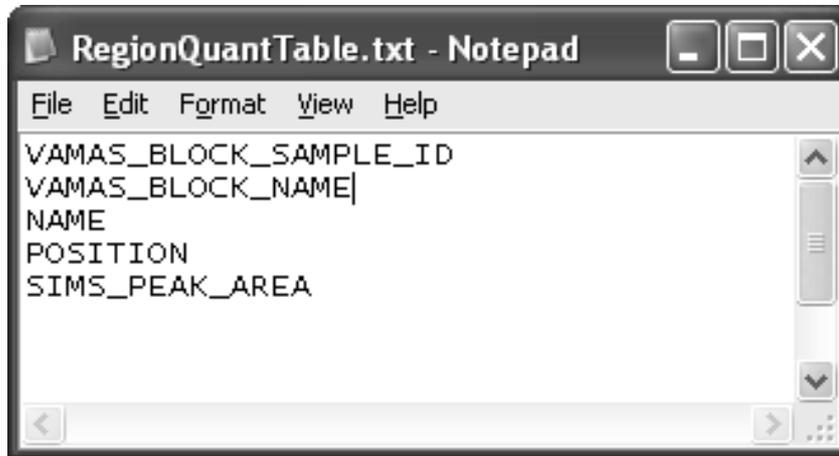




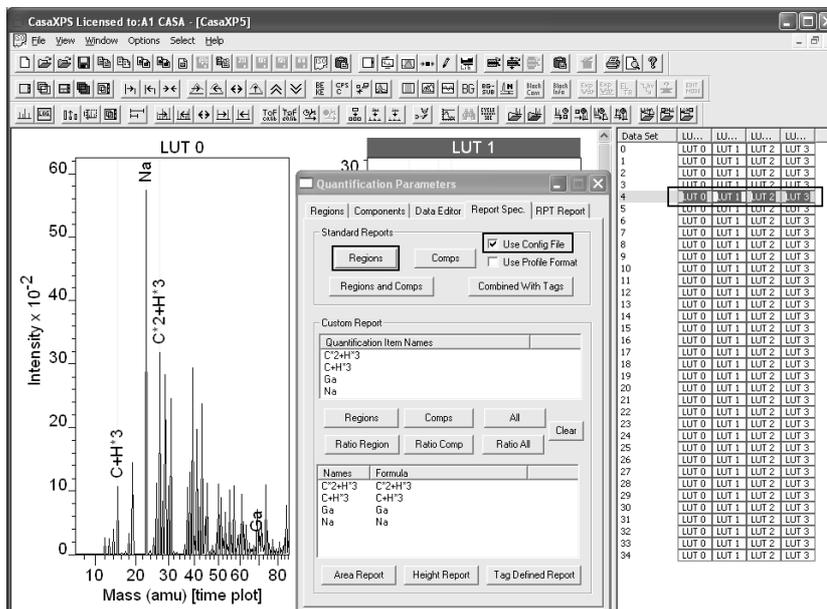
Generating a quantification report for ToF data requires the use of ASCII configuration files named:

Report Button Pressed	Configuration File Name
Quantification Regions	RegionQuantTable.txt
Synthetic Line shapes	ComponentQuantTable.txt
Regions and Comps	RegionComponentQuantTable.txt

The configuration files can be edited using Notepad or any other text based editor.



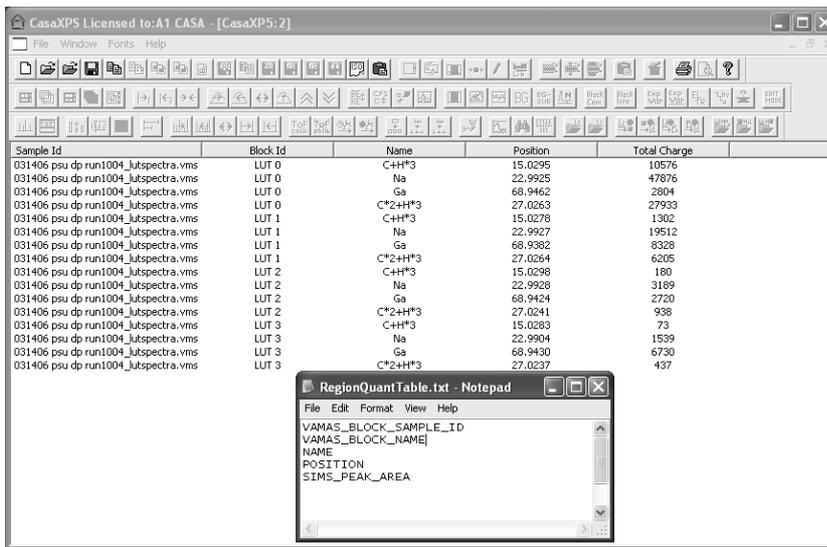
The format for the files is a list of keywords entered one per line, where each keyword specifies the type of information appearing in each column of the text quantification report generated when the corresponding button on the Standard Report is pressed.



A quantification report is created for those VAMAS blocks selected on the right-hand pane of the experiment frame with focus.

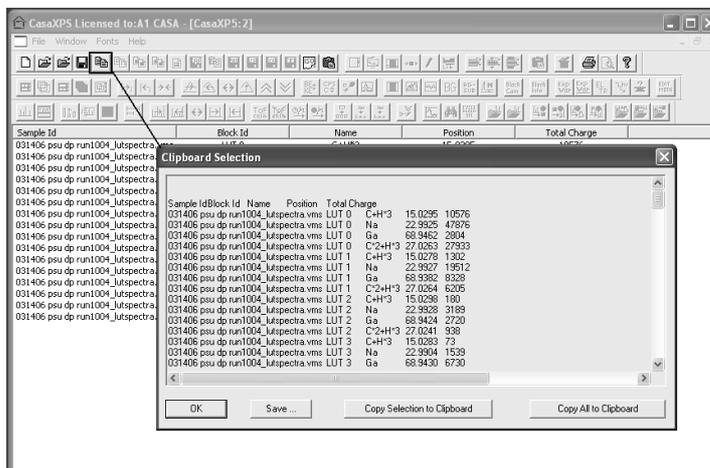
2	LUT 0	LUT 1	LUT 2	LUT 3
3	LUT 0	LUT 1	LUT 2	LUT 3
4	LUT 0	LUT 1	LUT 2	LUT 3
5	LUT 0	LUT 1	LUT 2	LUT 3
6	LUT 0	LUT 1	LUT 2	LUT 3

On pressing the Regions button from the Standard Report section with the Use Config File tick-box tricked, the following report is produced:

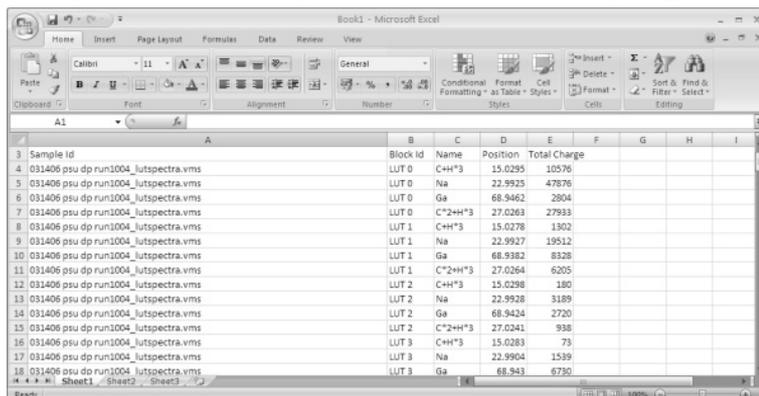


For ToF data, the important column is the one specified using the keyword **SIMS\_PEAK\_AREA** in the RegionQuantTable.txt configuration file. The columns in the quantification report have a one-to-one correspondence with the keywords entered in order one-per-line within the RegionQuantTable.txt file.

The quantification report is exported as a tab spaced ASCII data set through the clipboard. To move the quantification report to a spreadsheet, for example, press the Copy button on the top toolbar. A clipboard dialog window offers the option to save the data to file or copy the data onto the clipboard.

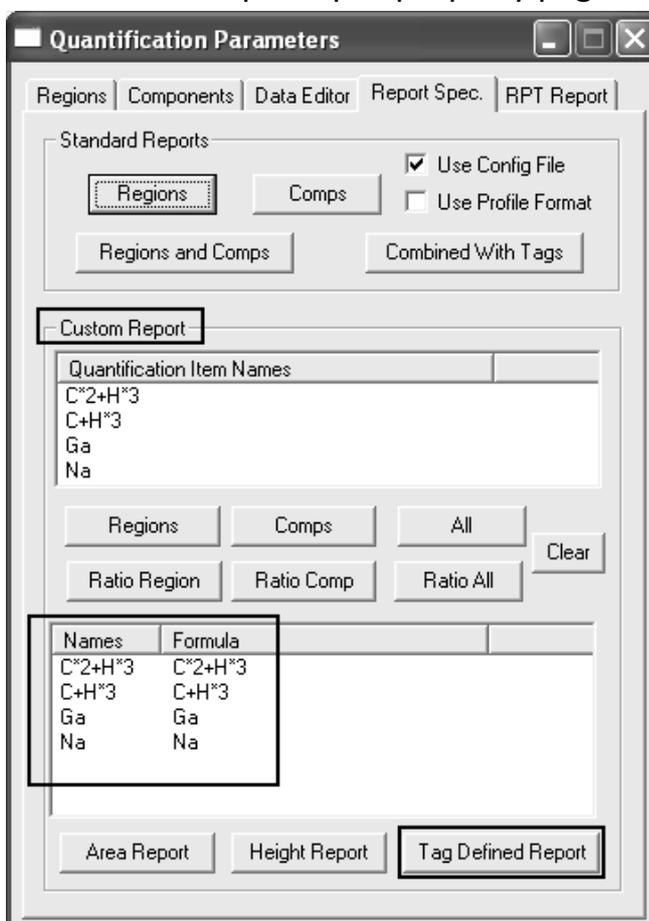


The data on the clipboard can be pasted into another program such as Excel.

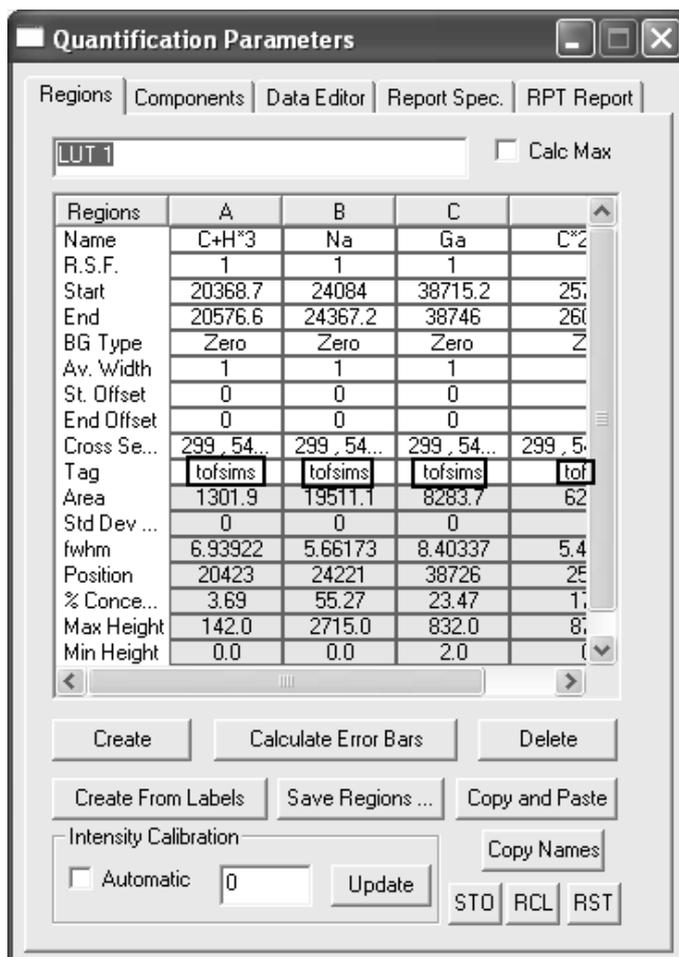


### Custom Report

The profiles in Figure 45 were created using quantification regions and the Custom Report section on the Report Spec property page.



Since ToF intensities are determined from the number of ions within a peak and not the peak area, quantification items defined on the spectra, either regions or components, must include a keyword in the Tag field and the report must be generated using the Tag Defined Report button. To indicate that a region or component derives from ToFSIMS data, the keyword **tofsims** must be entered in the Tag field for the quantification item.

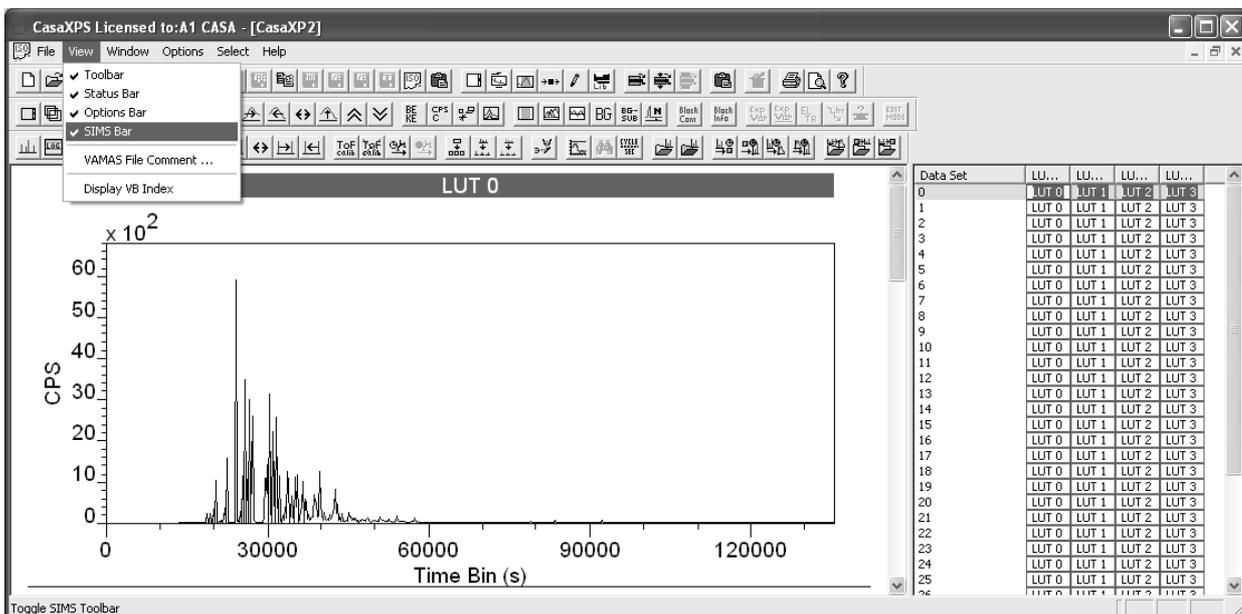


The Tag Defined Report button uses the keyword in the Tag field to determine the type of data to retrieve from the quantification item. The keyword **tofsims** causes the summation of the counts within the region or under the components on a bin-by-bin basis. Other keywords include **height**, which returns the maximum peak height as the measure for intensity. Note: for both keywords **tofsims** and **height**, the intensities are divided by the value entered in the RSF field; therefore the number of ions recorded for a given peak is only obtained for an RSF of unity.

A further word of warning: the Custom Report is defined in terms of a list of names and formulae. The formulae are constructed from the name fields used to specify the quantification items. There is no difference between how regions and components are treated within these formulae, both are considered to be quantification items and intensities from regions and/or components can be combined to create a quantification report. A key property of the Custom Report is that, intensities from either regions or components or both with the same name field are automatically summed together. To be sure that the profile is from exactly the intended items, ***always use different names for items included in the profile.***

# An Overview of Working with ToF Data in CasaXPS

The SIMS toolbar is displayed via the View menu on CasaXPS.



The SIMS toolbar offers a range of options for displaying and manipulating ToF MS data.

Display Options:



ToF Time to Mass Calibration Options:



Organization of Data:

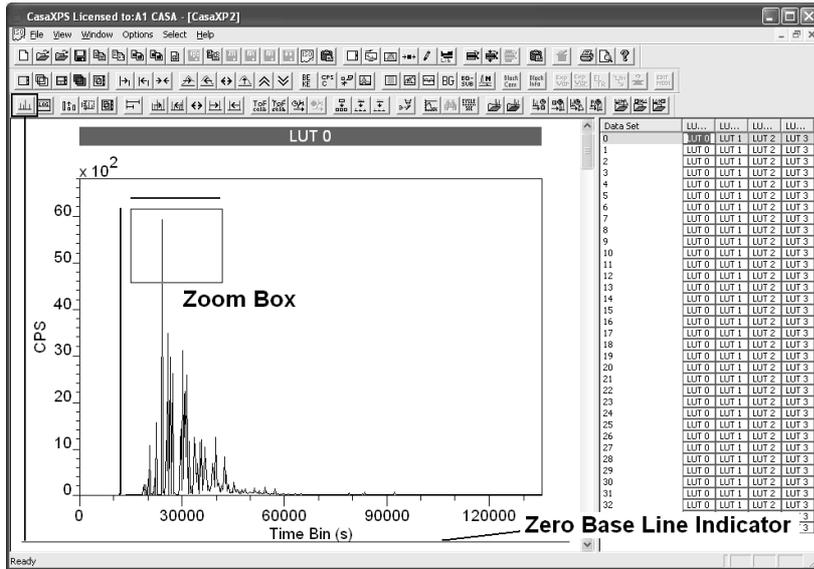


Data Conversion Options:

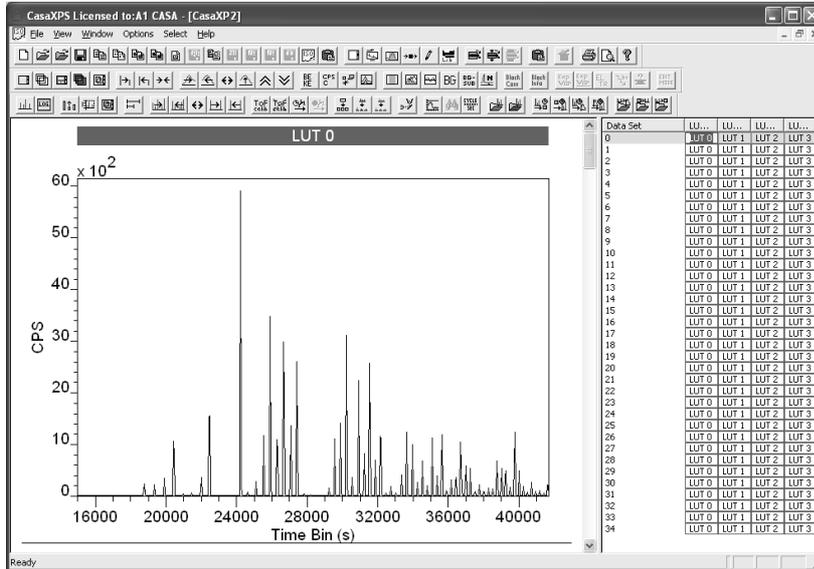


## ***SIMS Toolbar Buttons: Display Options***

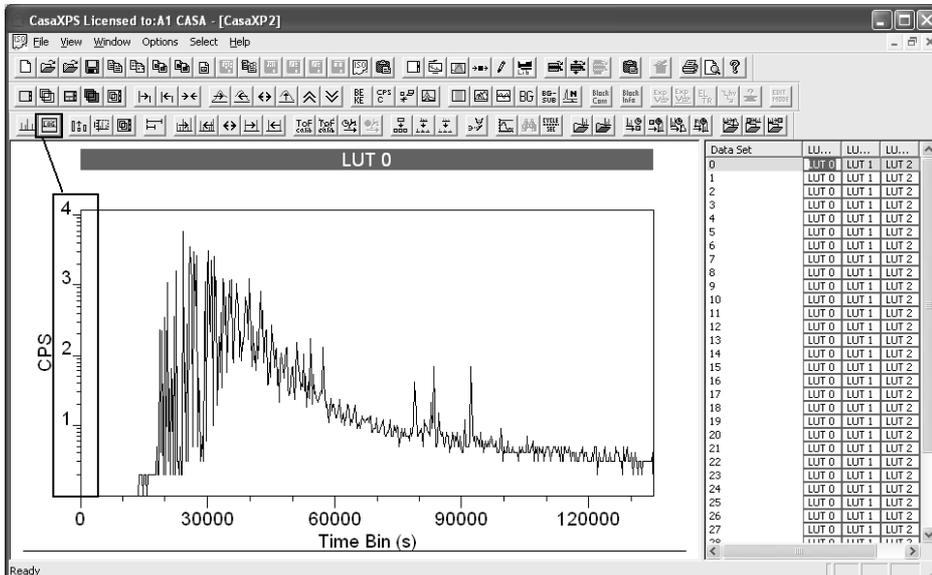
 The toolbar button switches the display setting between forcing data to be displayed with a lower intensity of zero and allowing a selectable lower limit. The default state for the display of ToF MS spectra is to force a lower limit of zero. A line is drawn at the bottom of the tile to indicate when the display is forced to plot intensities above zero intensity. When the line appears at the bottom of the tile displaying the ToF spectrum, a zoom box drawn over the display will only indicate the upper limit for the purposes of expanding the display.



On left-clicking inside the zoom box with the zero base line active the display becomes:

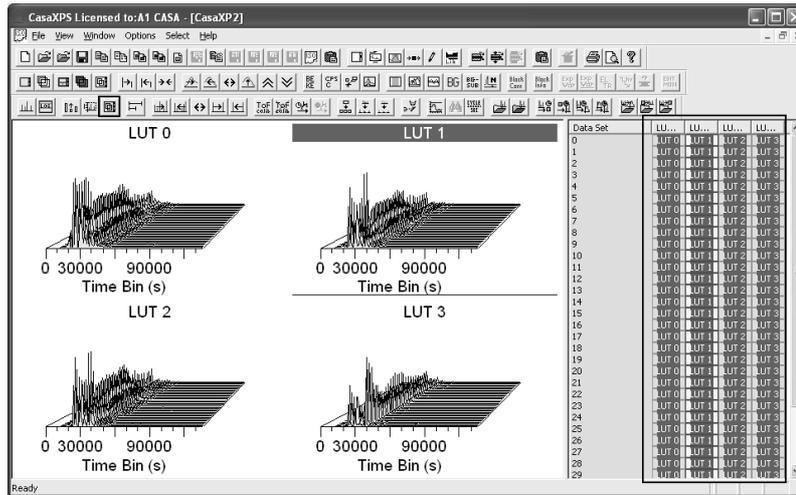


Toggles the display between log and linear display modes:





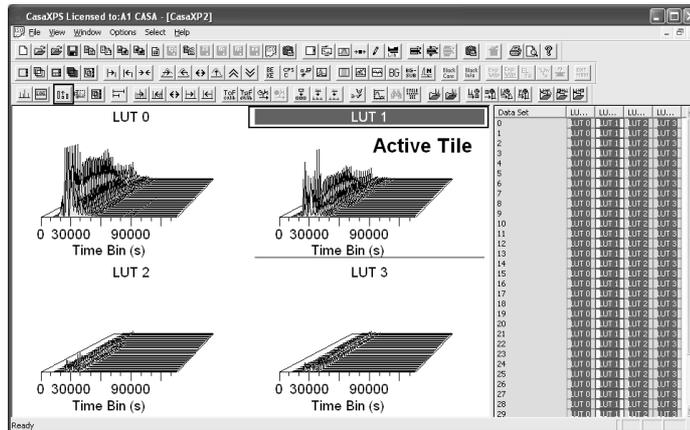
Overlay selected VAMAS blocks by column:



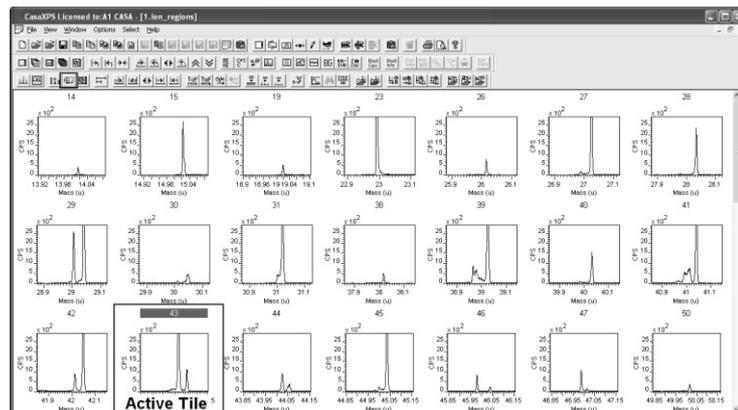
Given a selection of VAMAS blocks in the right-hand pane, display each column of VAMAS blocks in separate tiles in the left-hand pane. Each tile is scaled with respect to the spectra displayed within the tile.



Adjust the scale for the tiles displayed in the left-hand pane with respect to the intensity range determined from the active tile.

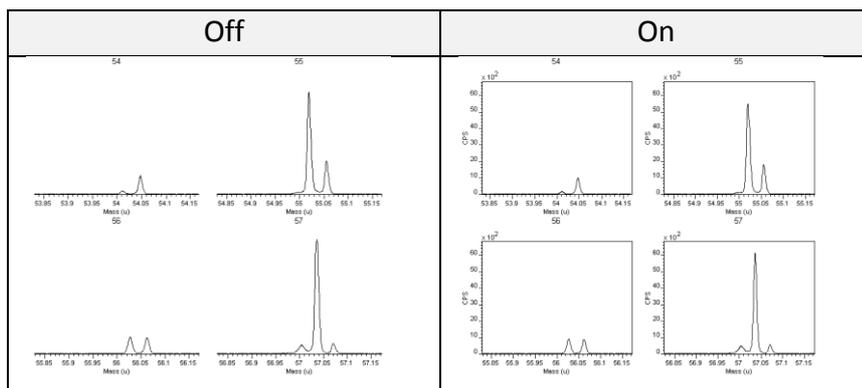


Adjust the scale for the tiles displayed in the left-hand pane with respect to the intensity range currently used in the active tile and toggle the mode for the y-axis display.

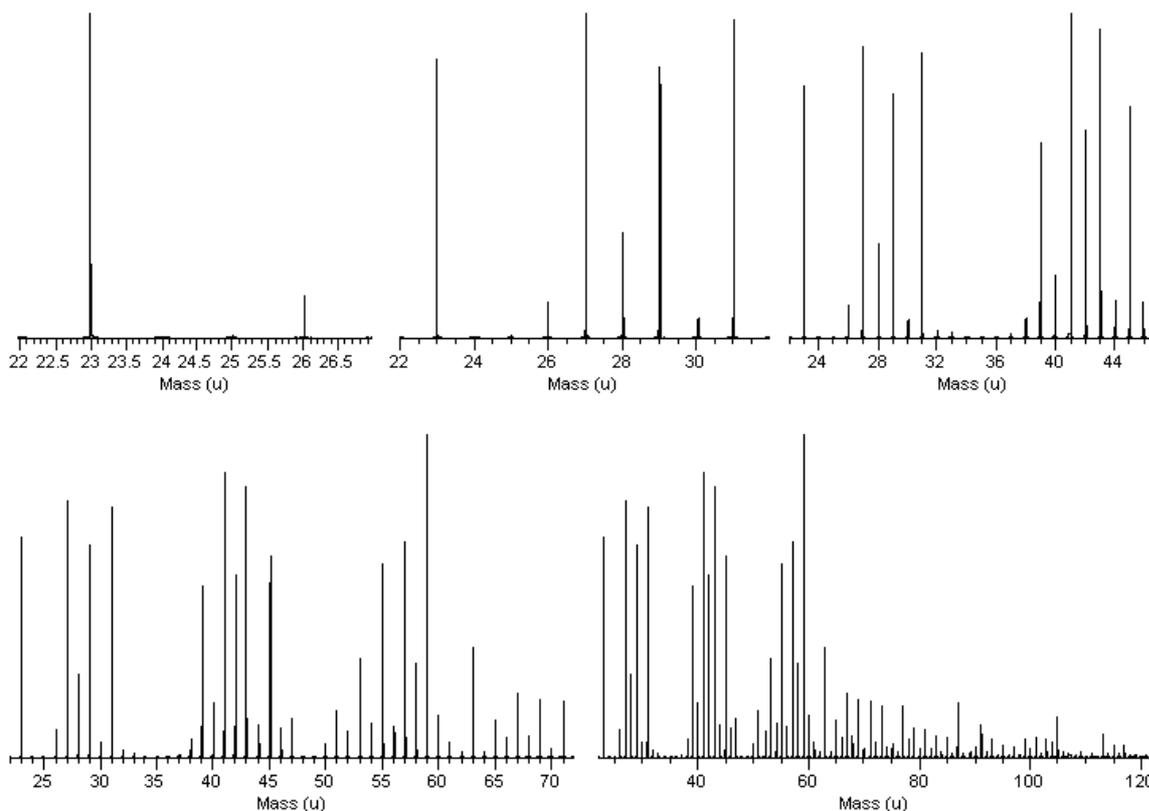




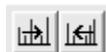
Display state modified by the toolbar button are as follows:



Cycle the display through a set of predefined mass ranges.

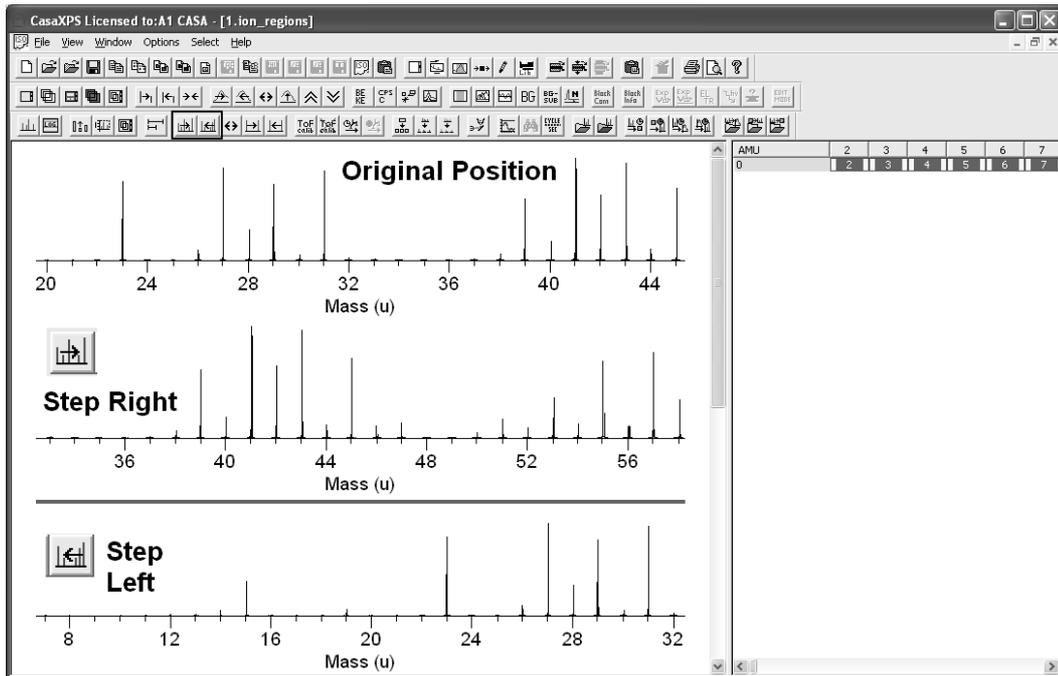


A spectrum displayed in the active tile changes the mass range used to view the data each time the  toolbar button is pressed. The mass range is always anchored by the smaller mass limit and with each press of the button the size of the display range cycles between 5 amu, 10 amu, 25 amu, 50 amu and 100 amu.

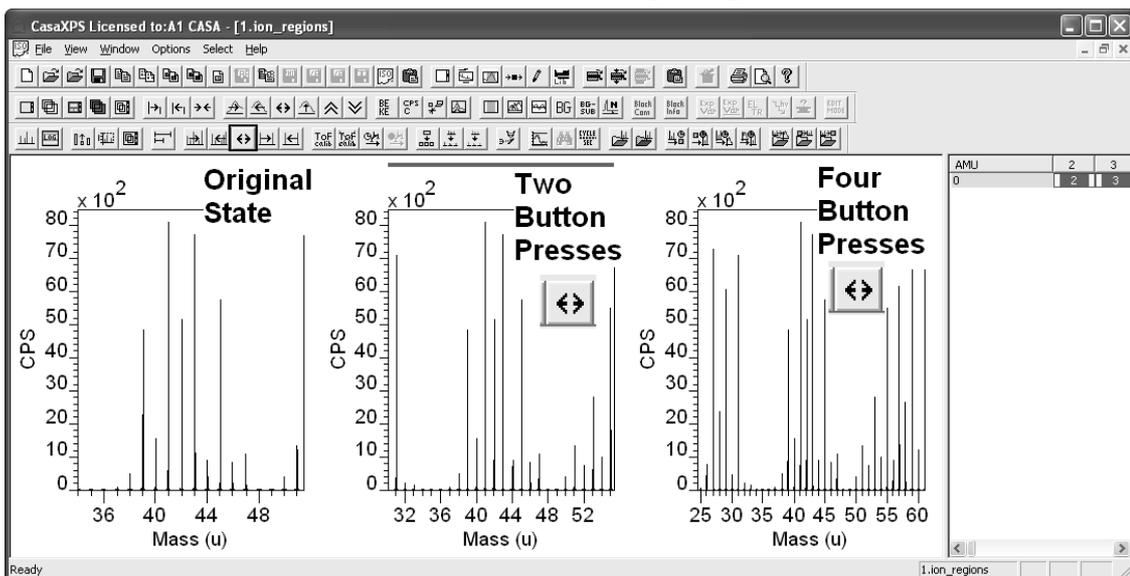


Step the mass range towards higher mass values or towards lower mass values. The current mass range determines the size of the step. On

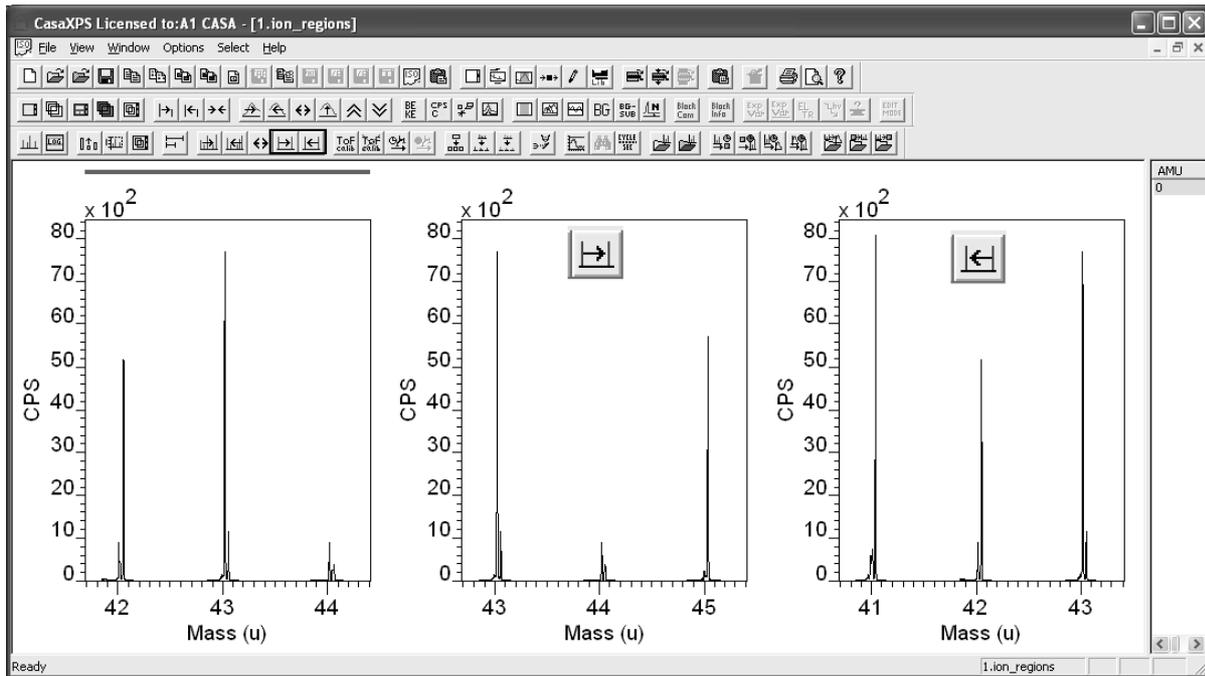
pressing either toolbar button, the mass range is stepped by half the interval currently being displayed.



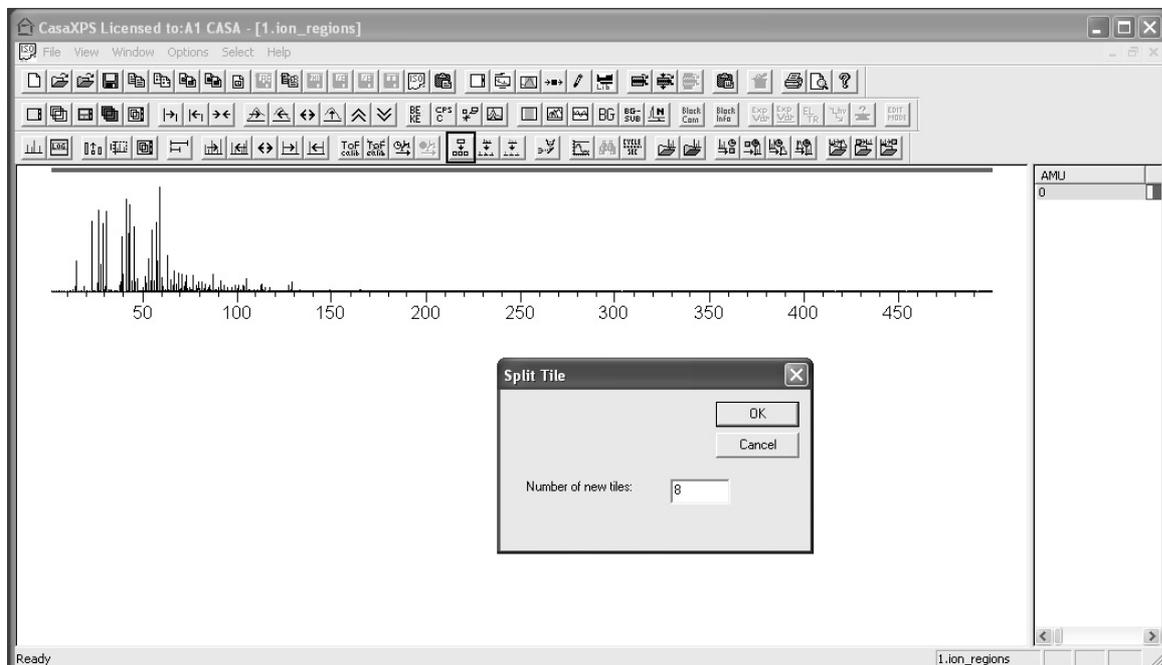
Expand the display range about the central mass defined for the active tile. The SIMS toolbar button increases the mass range about the central mass for each press of the button without rescaling the intensity range. The equivalent button on the second toolbar performs the same operation as the SIMS toolbar button with the exception that the button on the second toolbar also rescales the intensity range.



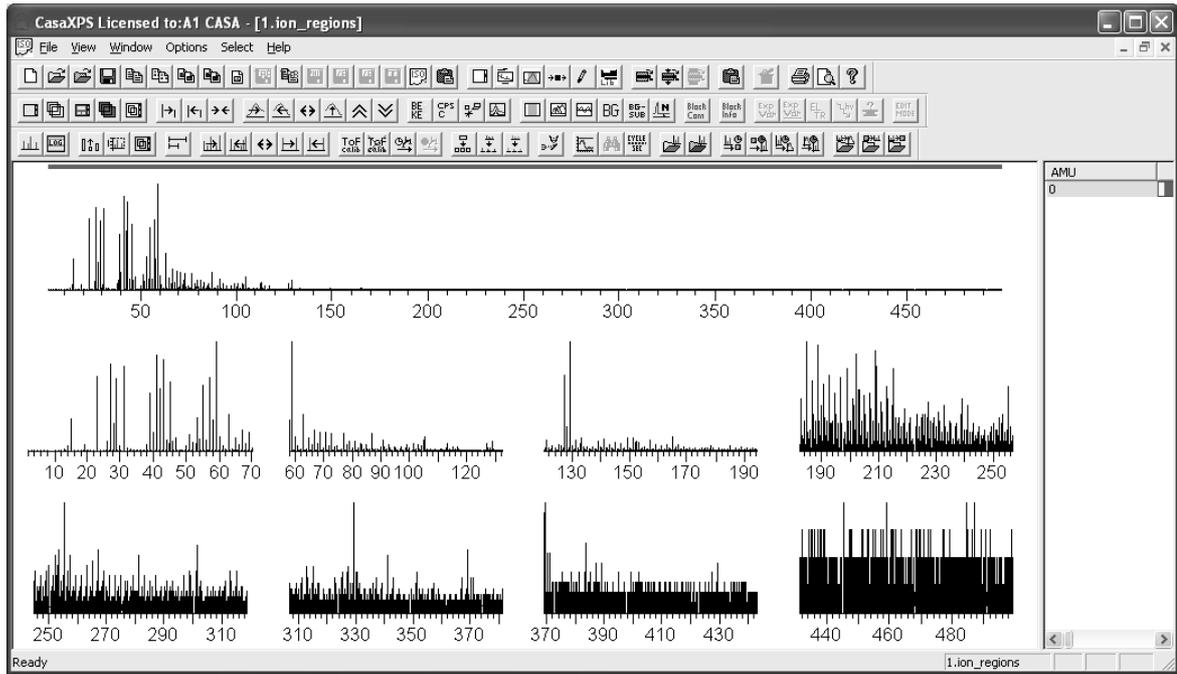
Step the current mass range by one amu. The intensity scale is unaltered by pressing either of these buttons.



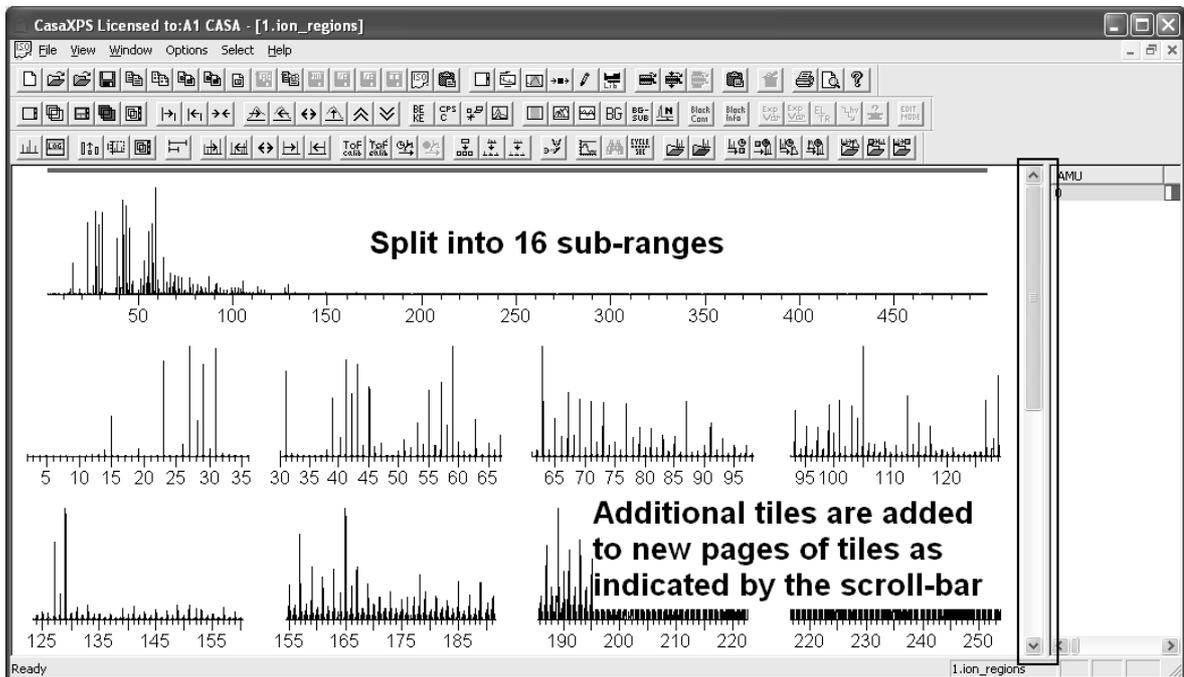
Given a spectrum displayed in the active tile, the toolbar button adds a set of tiles to the scrolled list of tiles in the left-hand pane, where the display range in the active tile is split into sub-ranges, the number of which is define on the dialog window invoked by the toolbar button. The display before pressing the toolbar button:



Result of splitting the full spectrum into eight sub-ranges, one per tile is shown below:



Each sub-range is rescaled within the display tile. Note that if the number of tiles exceeds the number of tiles-per-page in the left-hand pane, the additional tiles cause the scroll-list to expand indicating the existence of further pages of display tiles.

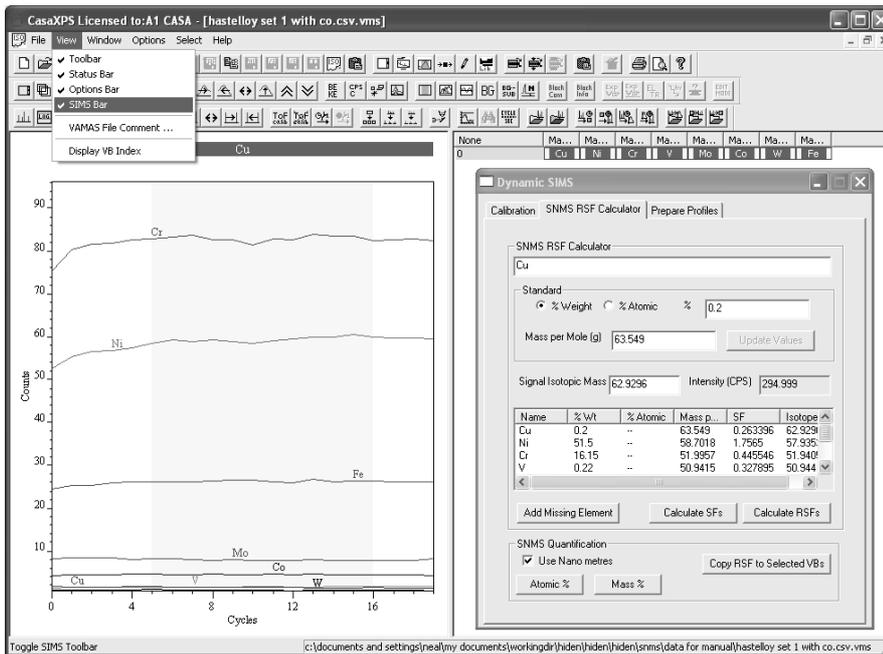


# SNMS in CasaXPS

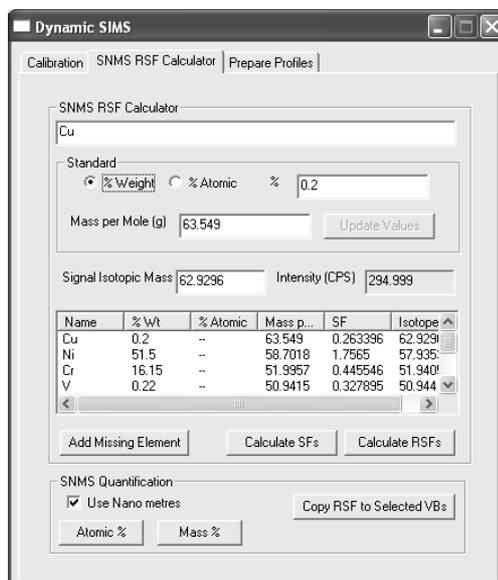
## An Overview

Sputtered Neutrals Mass Spectrometry (SNMS), as a technique related to SIMS, is supported on the Dynamic SIMS dialog window of CasaXPS.

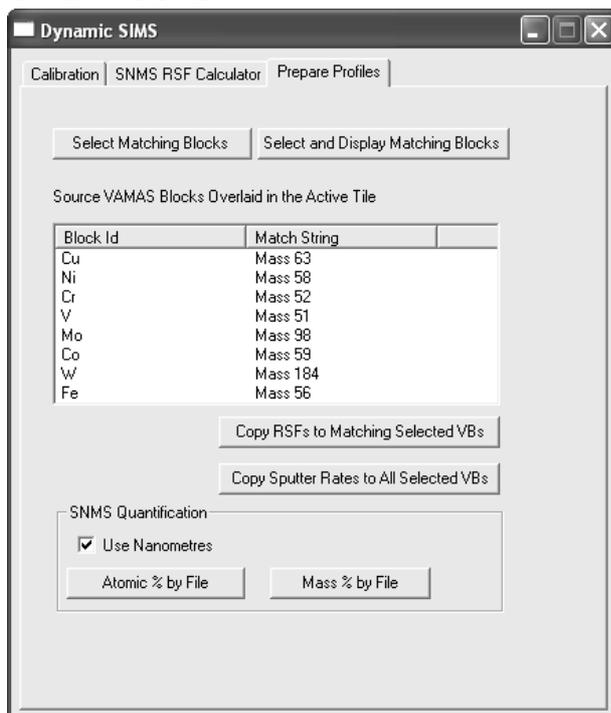
The Dynamic SIMS property page is available from the SIMS toolbar . The SIMS toolbar is displayed using the View menu on the CasaXPS Main Window menu bar.



Quantification of SNMS profiles requires the calculation of sensitivity factors. These SFs are calculated using options on the SNMS RSF Calculator property page.



Relative SFs are SFs normalised with respect to a given isotope. Both SFs and RSFs are determined based on measurements from standard materials. Once established for a set of isotopes, data measured under identical conditions can be quantified in terms of either Atomic concentration or Mass concentration using options on the SNMS RSF Calculator property page. Further tools for transferring RSFs to other measurements are available on the Prepare Profile property page.

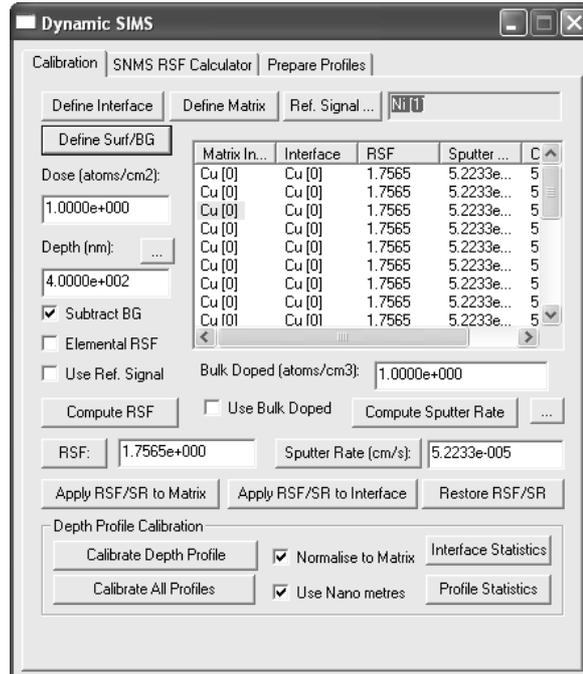


The function of the Prepare Profile property page is to copy RSF and sputter-rates to multiple data files with the view to generating quantified profiles from the raw SNMS data. The buttons on the Prepare Profile property page are designed to work based on selections made within the set of opened files. To this end, other buttons on the Prepare Profile property page provide a means to make selections appropriate for the action buttons.

SNMS and Dynamic SIMS are specified in CasaXPS using an identical framework. The RSF and sputter-rates are assigned on a measurement-cycle by measurement-cycle basis. In both SNMS and Dynamic SIMS, a profile fully prepared for quantification must have each cycle populated with RSF and sputter-rates as viewed via the Calibration property page of the Dynamic SIMS dialog window.

The sputter-rate for a given profile is calculated using the Calibration property page and, using the same mechanisms as for Dynamic SIMS, the

sputter-rate and appropriate RSF entries are updated. The table on the Calibration property page displays the parameters used during quantification.



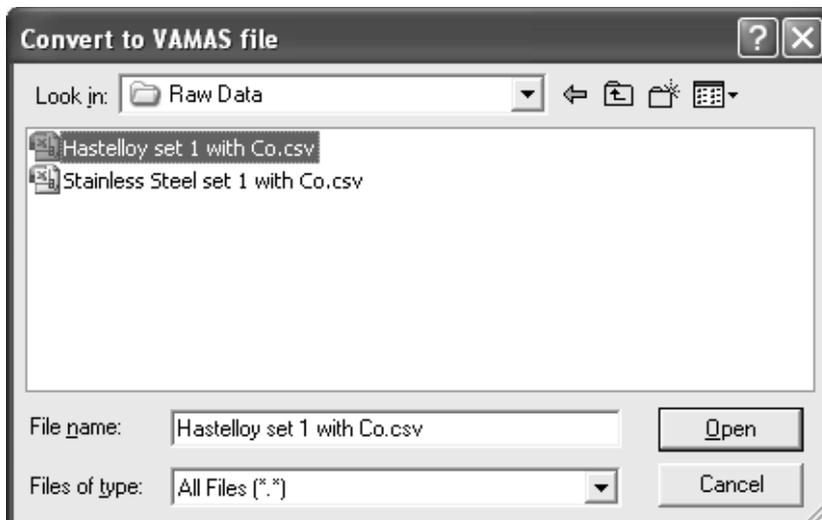
## Basics of CasaXPS

### Converting Data

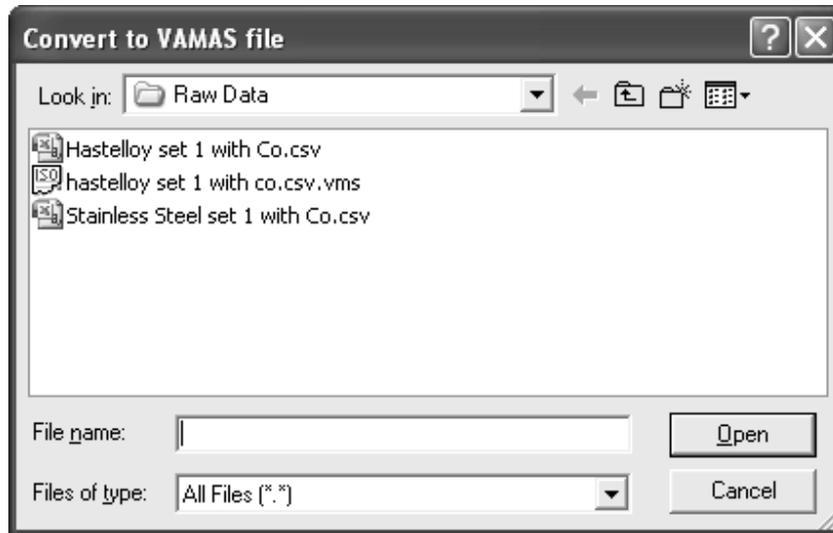
CasaXPS native file format is ISO 14976 VAMAS file. CasaXPS contains many conversion filters available from the Convert menu option on the File menu or via the top toolbar.



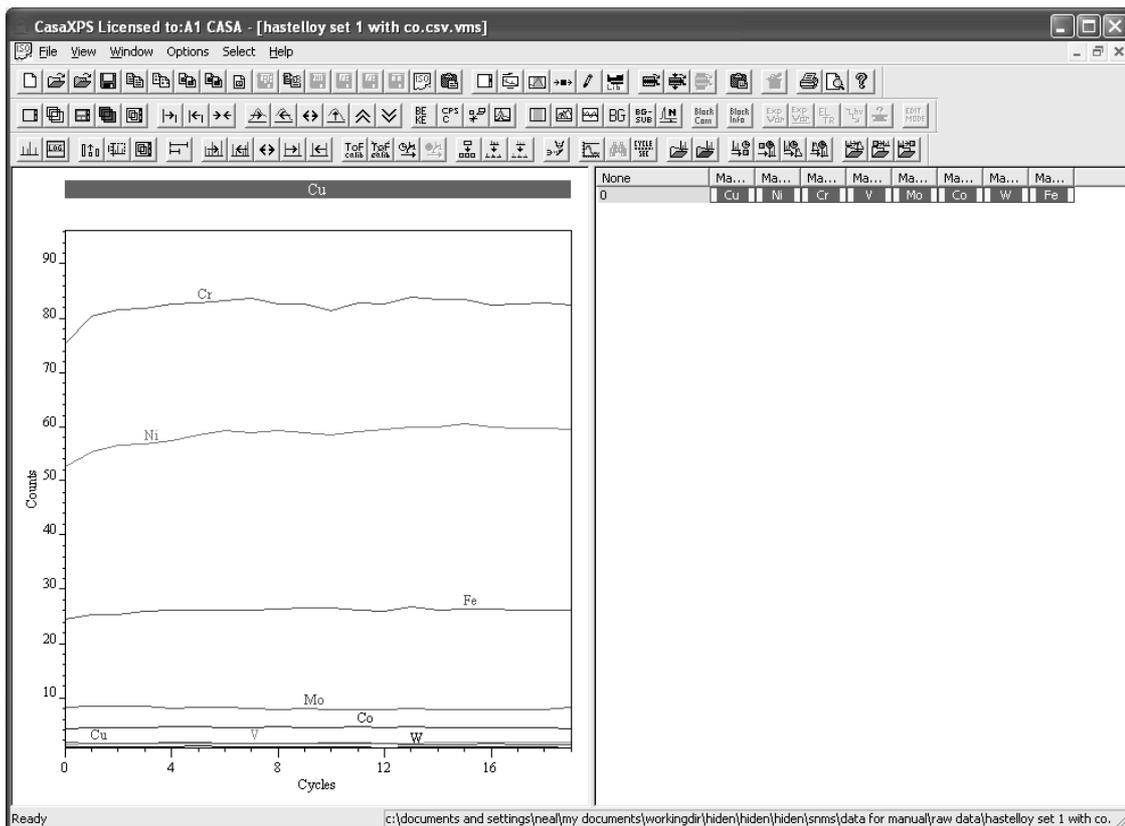
Converting data involves selecting the data file with the appropriate file extension via the Convert to VAMAS file dialog window.



For example, Hiden data is saved in comma separated format with file extension csv. On selecting a file containing Hiden data format with the extension csv, CasaXPS will convert the data to VAMAS format and write a new file into the same directory as the original csv file.



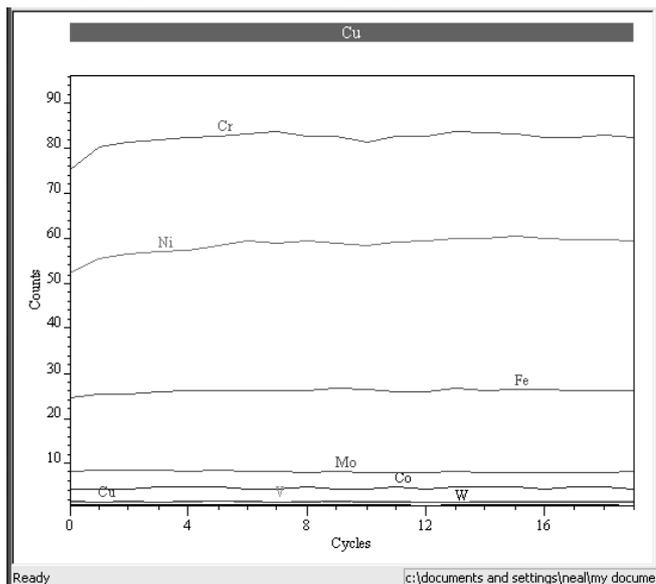
The VAMAS file will then open as an Experiment Frame in CasaXPS.



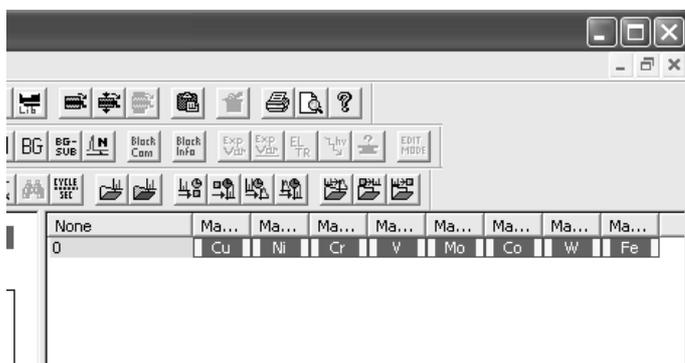
## Data Viewed Via an Experiment Frame

A profile experiment contains one or more traces measured and recorded for each isotope monitored. The Experiment Frame in CasaXPS displays the data using two panes with an adjustable central divider.

The left-hand-pane displays the data in graphical form.



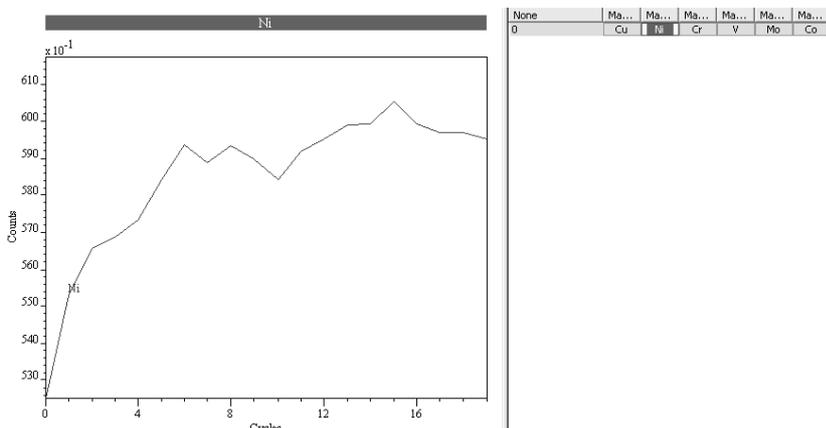
The right-hand pane offers the data blocks within the VAMAS file.



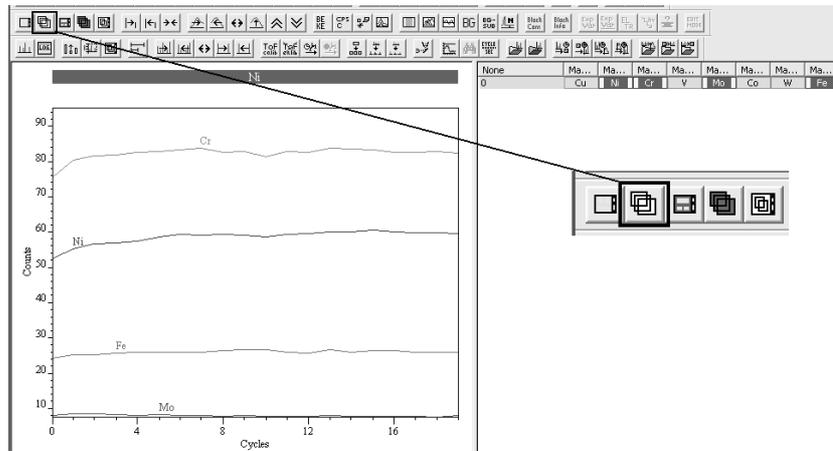
The right-hand pane is used to make selections from the set of VAMAS blocks held within the VAMAS file. These selections are used to display subsets of data within the file and direct processing operations to specific data blocks.

### Displaying Data

Individual VAMAS blocks appearing in the right-hand pane are displayed by double-clicking the left-hand-mouse button with the cursor over the data block.



Selecting more than one VAMAS block in the right-hand pane and using the Overlay toolbar button causes the selected VAMAS blocks to be displayed in the active display tile.



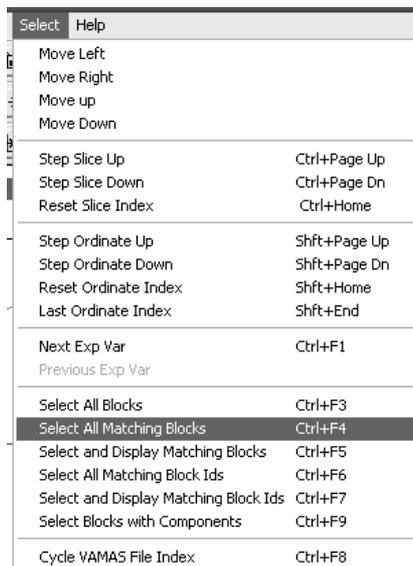
### Selecting VAMAS Blocks

Selections are made using the right-hand pane:

1. Single click the left mouse button over the right-hand pane to select a single block of data.
2. Hold the Shift-Key down and single click the left mouse button over a different block in the right-hand pane to make a range selection.



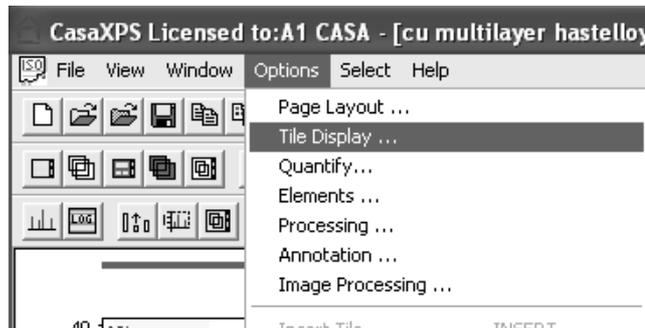
3. To add to or remove from the current set of selected VAMAS blocks, hold the Control-Key down before left clicking the mouse with the cursor over a VAMAS block in the right-hand pane.
4. Use the Select menu to extend a selection to other VAMAS blocks of similar identity in other files.



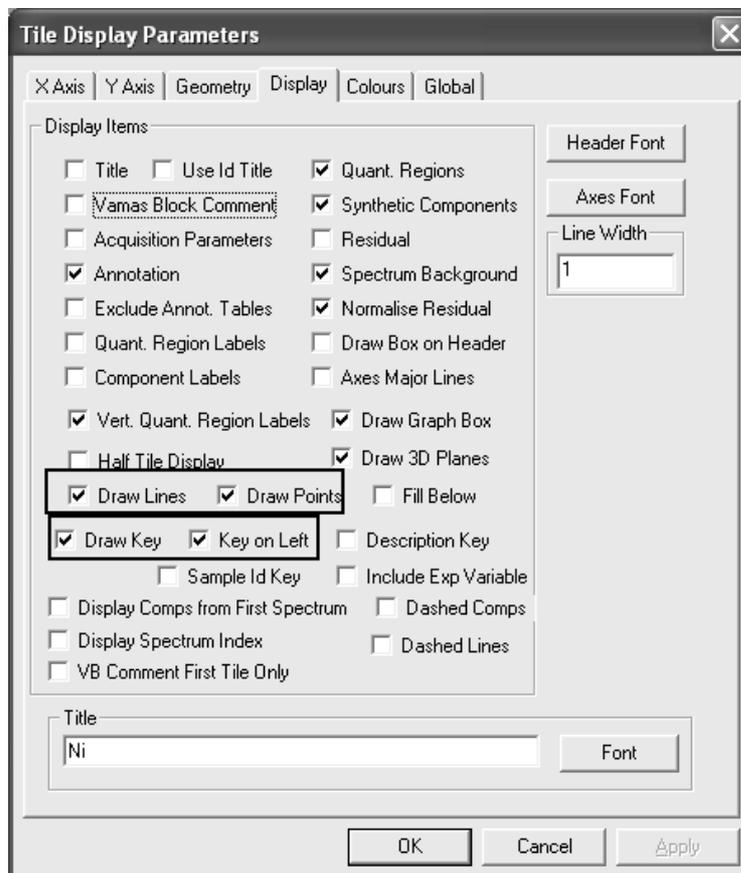
## Tile Display Options

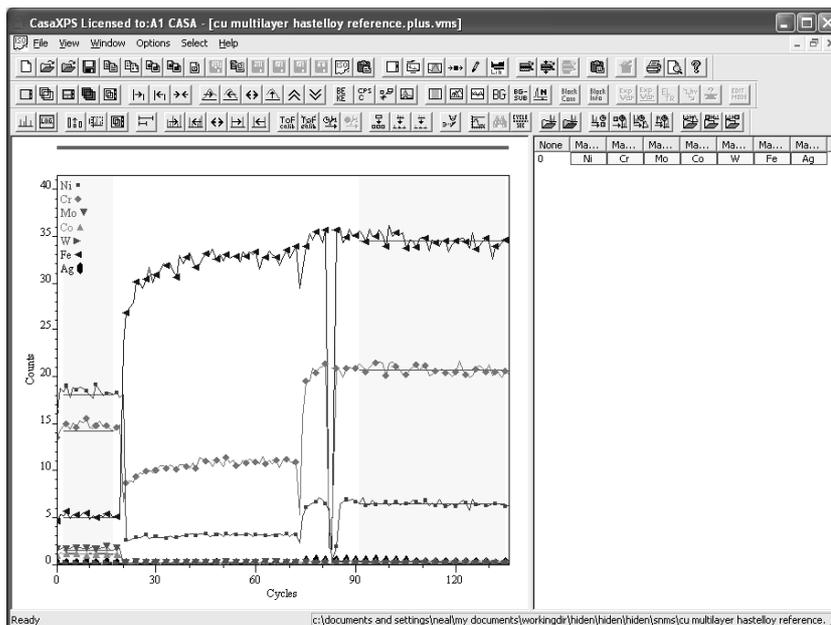
The left-hand pane of an Experiment Frame displays the data in the form of profiles, spectra or images. Options affecting the display are managed using the Tile Display Parameters dialog window. The Tile Display Parameters

dialog window is invoked via the top toolbar  or from the Options menu



When plotting a profile involving multiple traces, a common requirement is to place a Legend or Key within the tile in which the data are plotted. The Display property page on the Tile Parameter dialog window provides control over placing a Key on either the right-hand side of the graph area or alternatively the left side via the **Draw Key** and **Key on Left** tick-boxes.

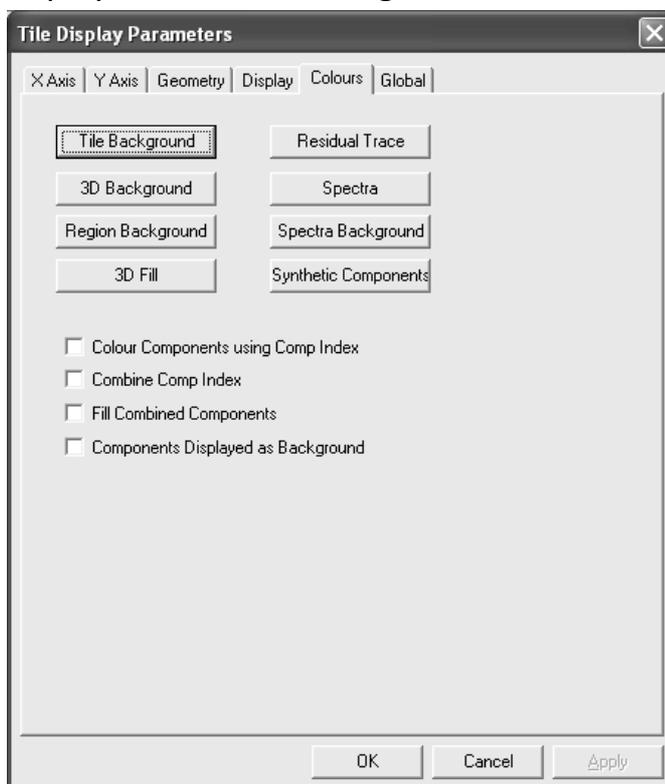




The Display property page also allows the profiles to be plotted using lines, points or both lines and points.

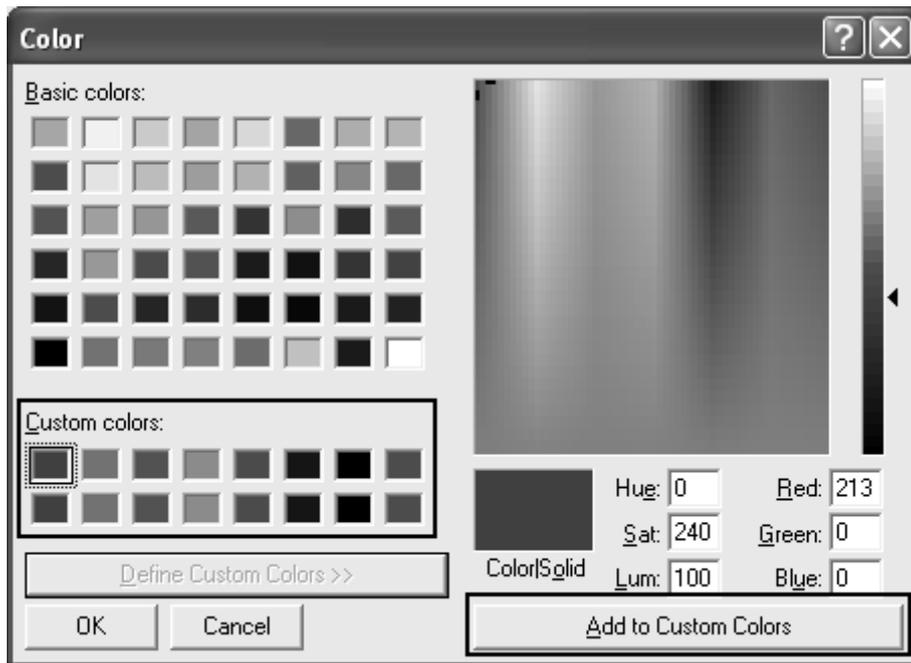
### Display Colours

The colours used to plot the profiles are specified using the Colours property page on the Tile Display Parameters dialog window.

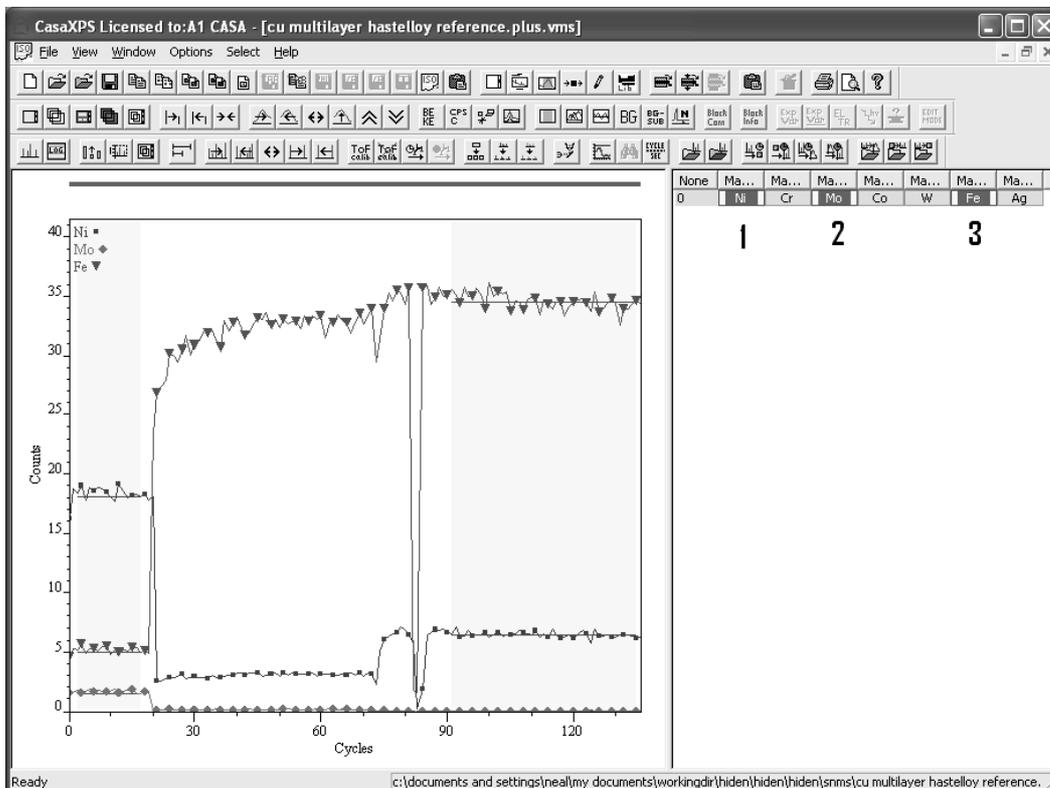


To modify the colours used to display the profiles, press the button on the Colours property page on the Tile Display Parameters dialog window labelled Spectra. Use the Colour dialog window to adjust the Custom Colours palette

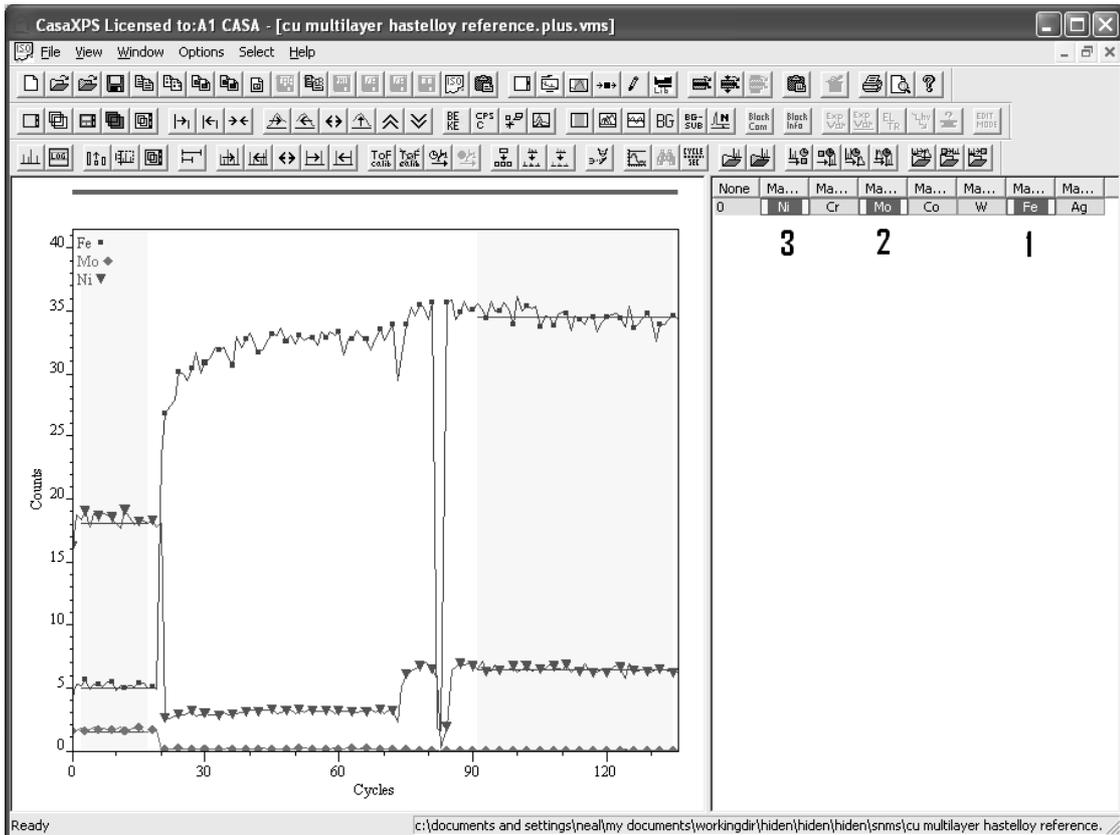
before pressing the OK button on the Colour dialog window followed by Apply or OK on the Tile Display Parameters dialog.



The order for the colours used to display the profiles is determined by the Custom Colours moving left to right then top to bottom as view on the Colours dialog window. Further, the order of the VAMAS blocks displayed in the Active Tile is determined by the order in which the data blocks are selected in the right-hand pane.

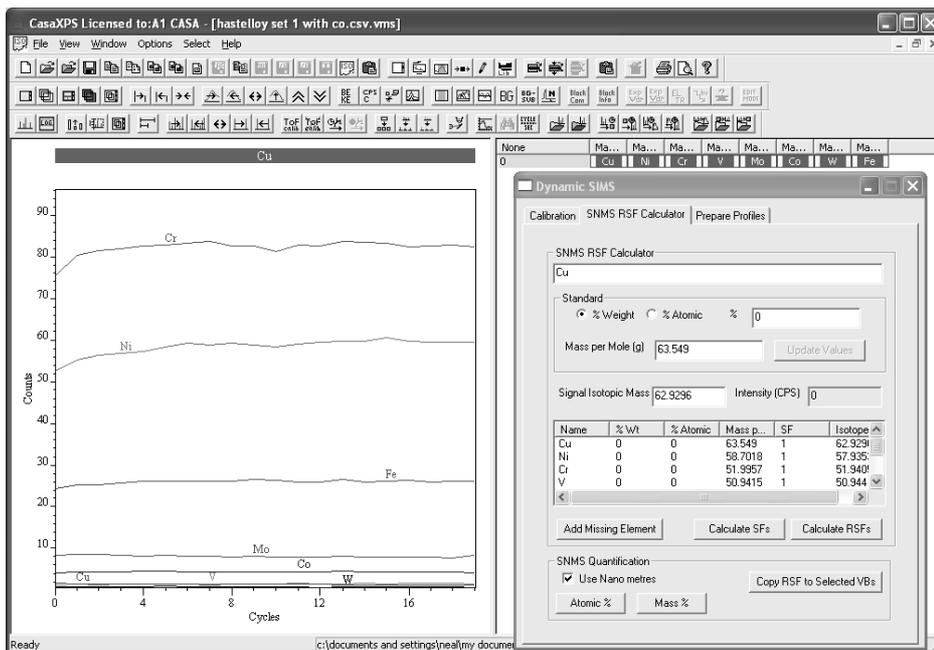


Holding the Control Key down allows the order of the data blocks to change and therefore the colours change accordingly.



## Calculating SNMS Sensitivity Factors

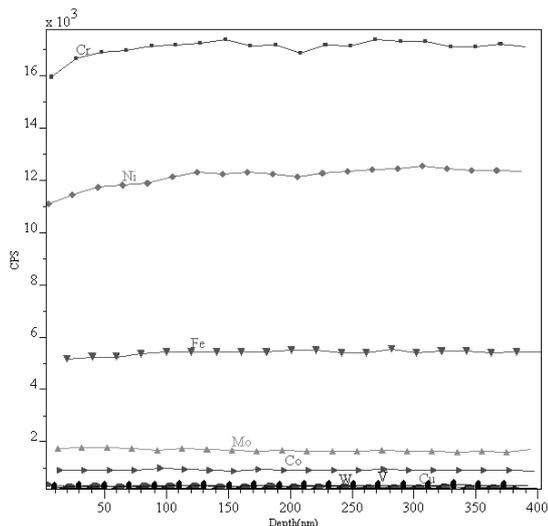
The task of calculating a set of sensitivity factors for SNMS requires a standard sample of known composition and a measurement from the standard sample, where a specific set of isotopes for which sensitivity factors are to be determined is used to monitor the sample-composition in terms of counts per second. The SNMS RSF Calculator determines a set of factors relating the amount of substance to the signal measured. Thus these sensitivity factors provide the scaling factors to convert measured signal to amount of substance for profiles measured from samples of unknown material composition. The calculation of SNMS sensitivity factors is performed using the SNMS RSF Calculator property page on the Dynamic SIMS dialog window.



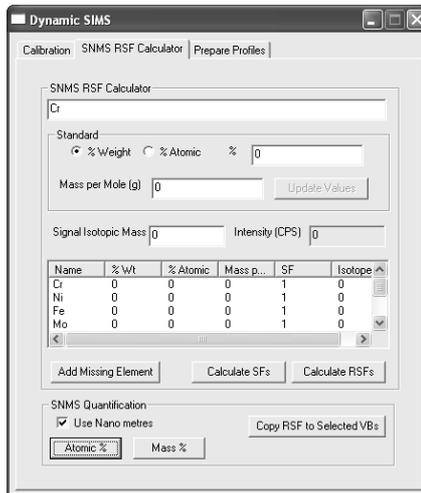
An example of a standard sample is a Hastelloy material for which the composition is known to be:

Element	% Composition by Weight
Cu	0.2
Ni	51.5
Cr	16.15
V	0.22
Mo	17.1
Co	1.5
W	4.29
Fe	7.3

When measured using a quadrupole mass spectrometer, the recorded signal from the Hastelloy sample defines the instrumental response for the given sample composition.



Armed with the experimental data measured from the standard and the table of material compositions, the sensitivity factors for the isotopes used in the experiment are calculated by populating the table on the SNMS RSF Calculator property page and defining a quantification region for each VAMAS block. The quantification region provides a means of estimating representative signal intensity for each profile.

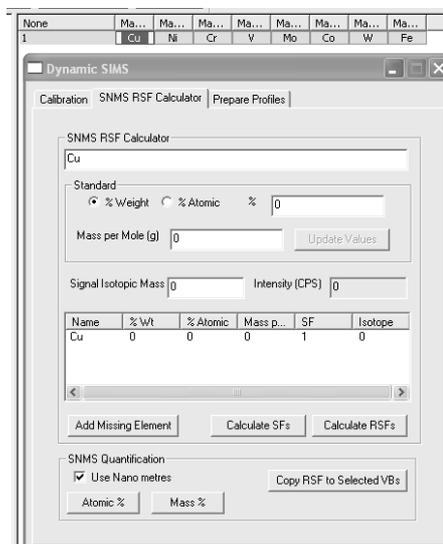


The information used to calculate the sensitivity factors is recorded in the VAMAS blocks for each of the profiles. It is therefore necessary to update the appropriate information for each of the VAMAS blocks representing the data measured from the standard sample.

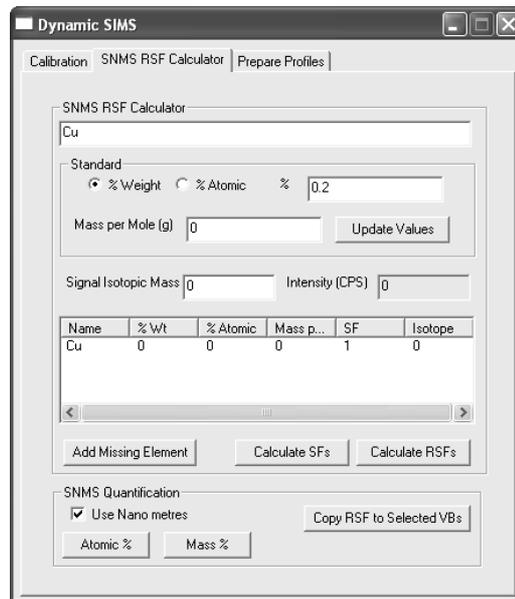
None	Ma...							
1	Cu	Ni	Cr	V	Mo	Co	W	Fe

To update the information needed to compute the sensitivity factors, repeat the following steps for each isotope in the SNMS profile measured from the standard sample.

1. Double-click a VAMAS block in the right-hand pane.



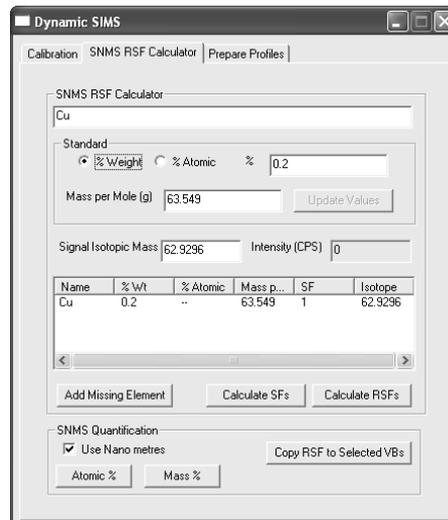
2. Select the type of percentage known about the composition of the sample and enter the value for the percentage in the text-field.



The Update Value button becomes active as soon as a value is entered for the percentage composition.

3. Check that the correct mass per mole and isotopic mass are displayed and press the Update Value button.

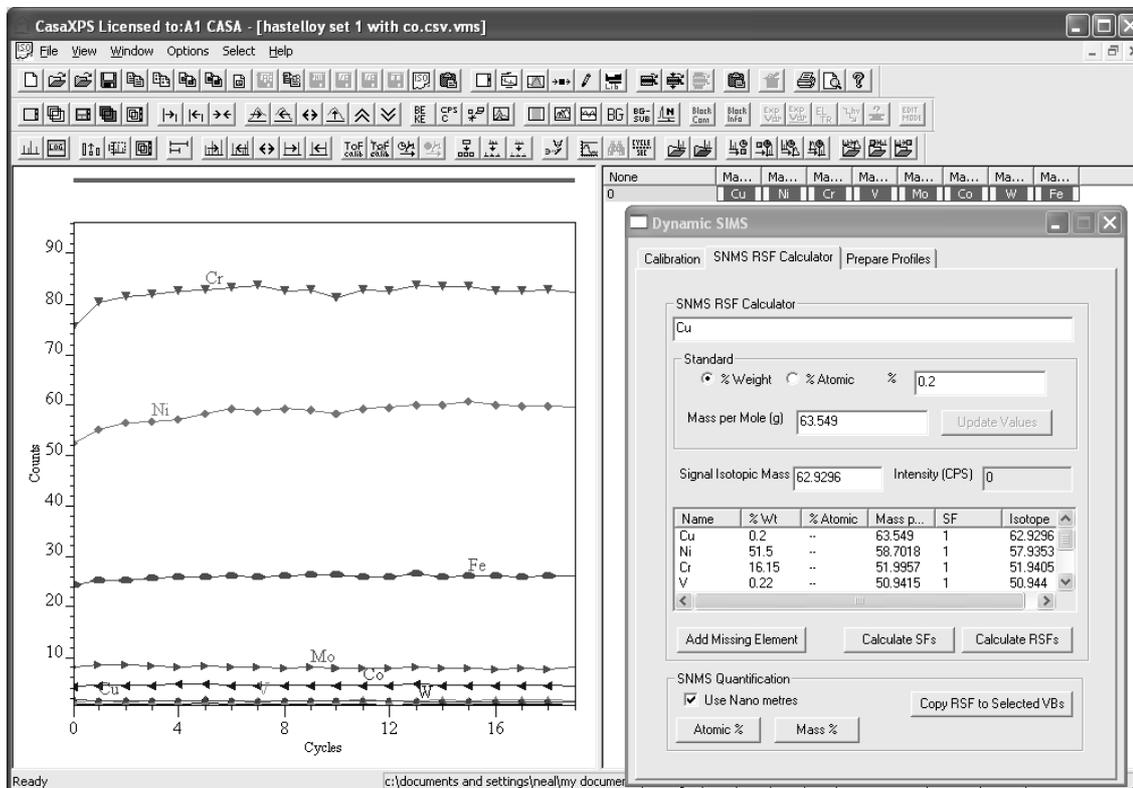
The table on the property page displays the values currently available for profiles displayed in the active tile.



The mass per mole is determined from the average mass for a given element, while the isotopic mass represents the mass of the peak used to measure the profile signal.

The table is only updated when the Update Values button is pressed.

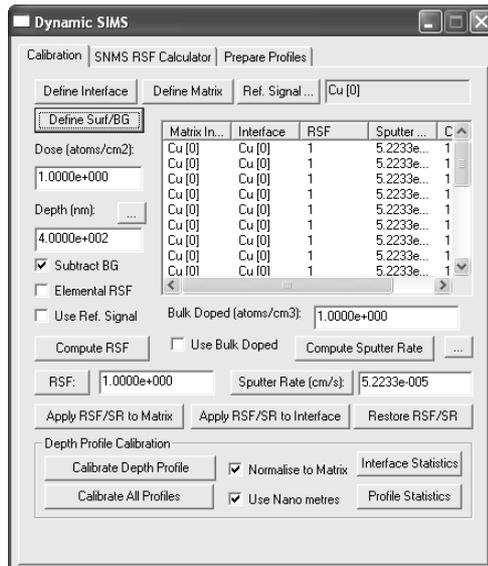
Each VAMAS block holding the data from a profile must be updated with the composition information. Overlaying the VAMAS blocks for the full profile in the active tile causes the table on the SNMS RSF Calculator to display the full list of quantification information.



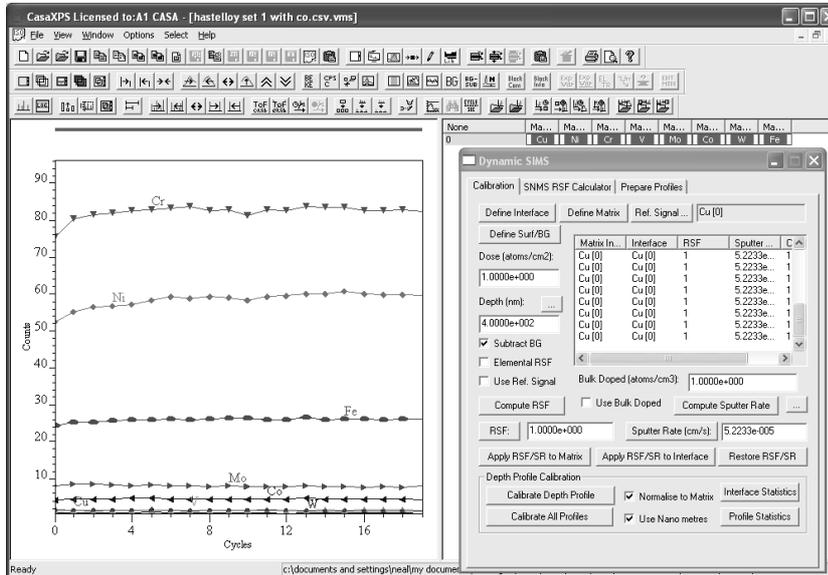
The table reflects the percentage composition for the standard sample. To relate these percentage compositions to the signal intensities for the set of profiles, it is necessary to specify a representative intensity for each isotope. The representative intensity is determined as the average over a set of acquisition cycles as specified via a quantification region. Specifically, the signal intensity is the average intensity over the set of data cycles defined by the first quantification region for each VAMAS block in the experiment.

4. Create a quantification region for each VAMAS block, where the limits to the region define a set of data channels over which the intensity can be averaged and assumed to be representative of the signal measured for the isotope being profiled.

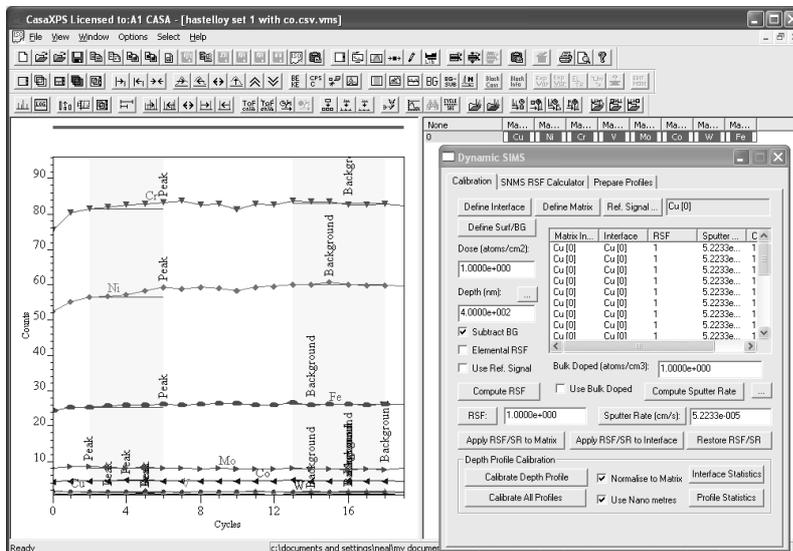
The quickest means of creating quantification regions on SNMS/SIMS data is to use the Calibration property page on the Dynamic SIMS dialog window.



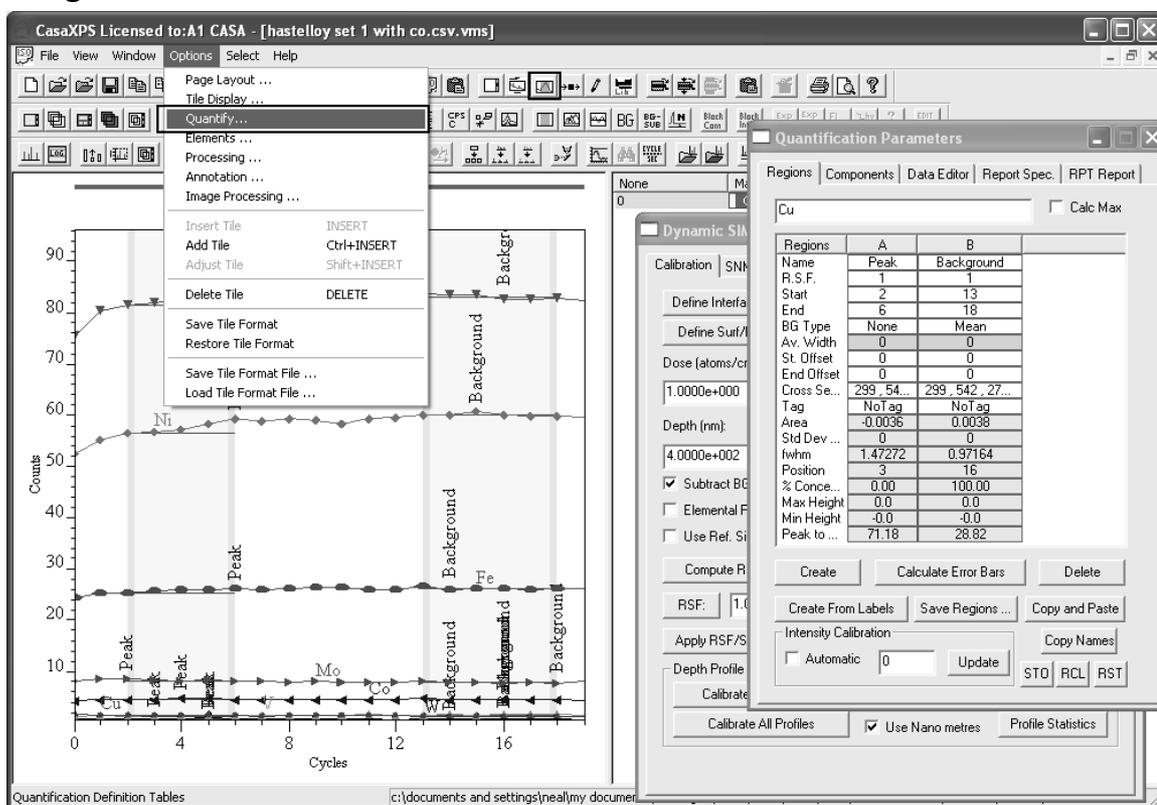
Overlay all the VAMAS blocks in the active tile before pressing the Define Surf/BG button on the Calibration property page.



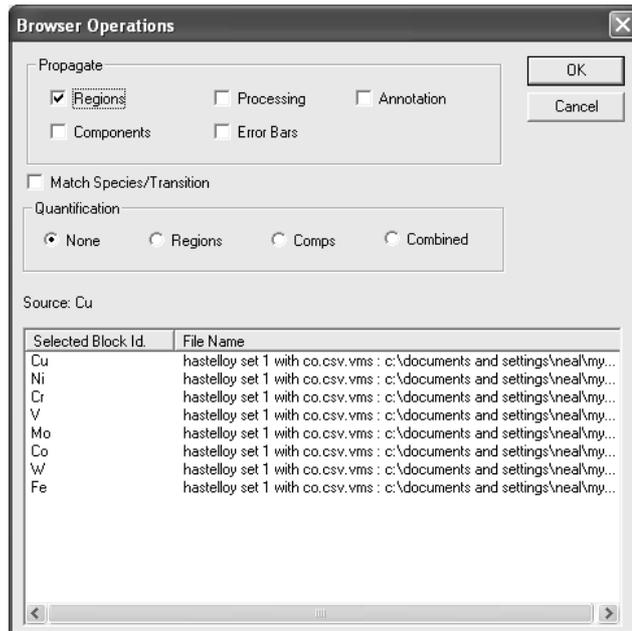
Define Surf/BG



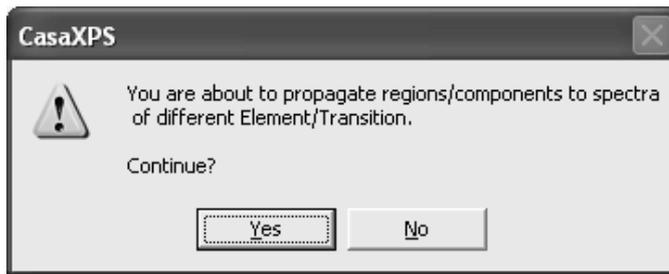
The Define Surf/BG button creates two quantification regions per VAMAS block overlaid in the active tile. Only the first region, assigned the name Peak, is used to determine the signal intensity for the SNMS data. The reason two regions are created is to allow dynamic SIMS experiments to define a surface zone and a zone representative of the background signal to a SIMS profile. The quantification regions are so named because of their use in XPS data analysis. For the purposes of SIMS and SNMS, the regions only define intervals. Should these intervals need changing from the default values obtained by pressing the Define Surf/BG button, the Regions property page on the Quantification Parameters dialog window provides a means of making changes to these interval limits.



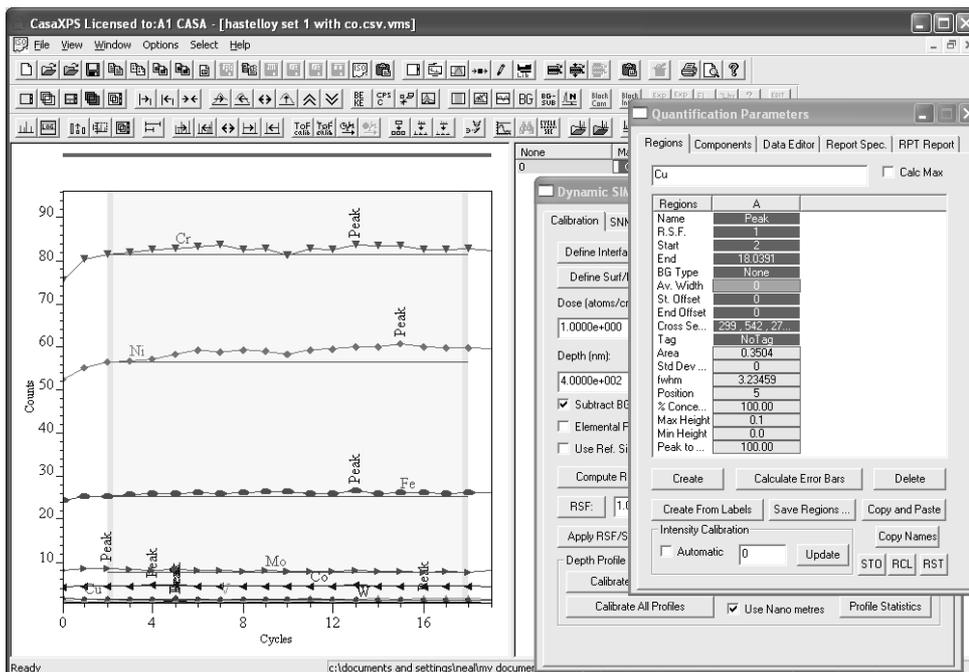
Each VAMAS block must be updated with any changes to the region limits. Quantification regions are propagated from one VAMAS block to others by selecting the range of VAMAS blocks in the right-hand pane of the experiment frame and right-clicking the mouse over the left-hand pane displaying the data with the modified regions. A dialog window appears offering the ability to propagate the regions to other VAMAS blocks listed on the dialog.



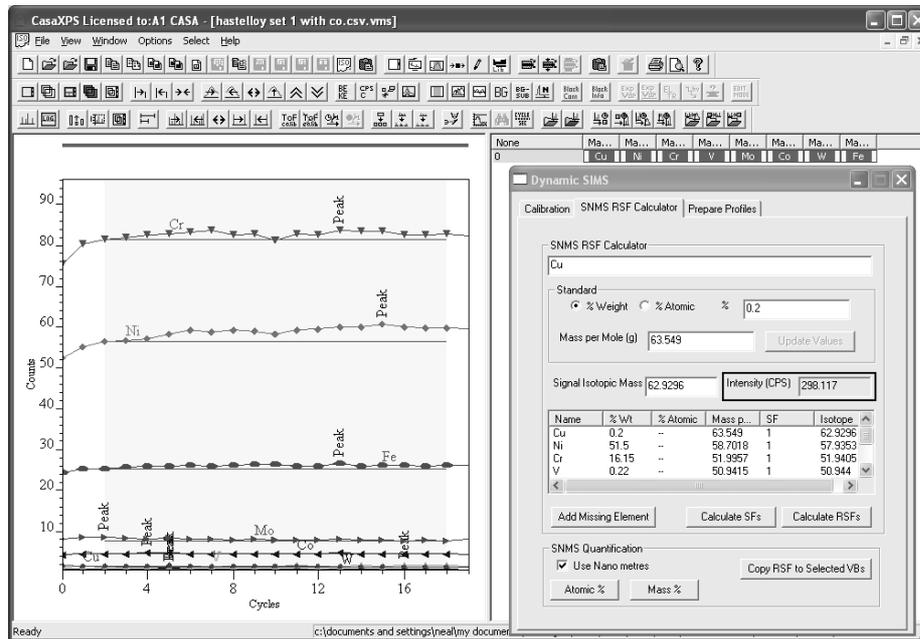
Tick the tick-box in the propagate section and press the OK button. A further dialog window appears requesting confirmation, which should be accepted by pressing the Yes button.



Assuming that the background region is deleted and the Peak region adjusted to provide a representative average signal from each profile, the appearance of the set of profiles changes as follows.



Following the creation of an appropriate quantification region, the SNMS RSF Calculator property page will show the average value determined from the region for the first VAMAS block displayed in the active tile.

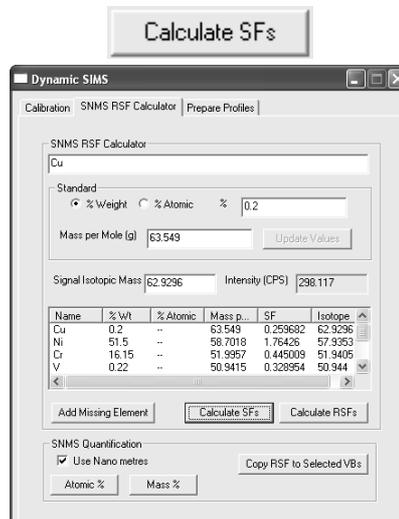


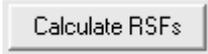
The VAMAS file for the standard sample is now ready to calculate the sensitivity factors for the measured isotopes.

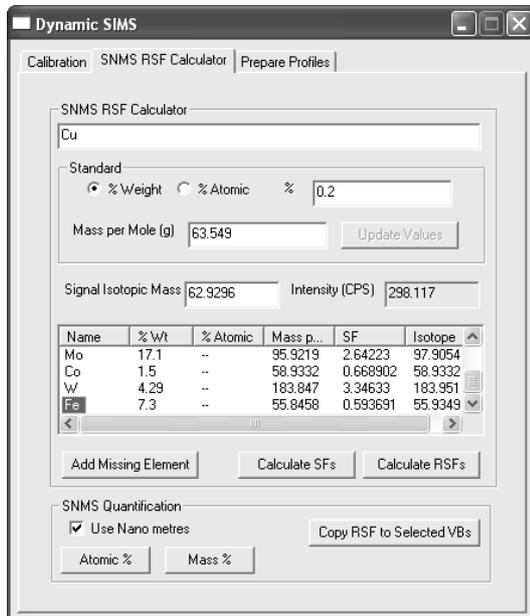
VAMAS blocks used in the calculation of the sensitivity factors must be:

1. All overlaid in the active tile
2. The table on the SNMS RSF Calculator property page displays the correct percentage compositions, Mass per Mole and signal isotopic mass
3. A region is defined on each VAMAS block.

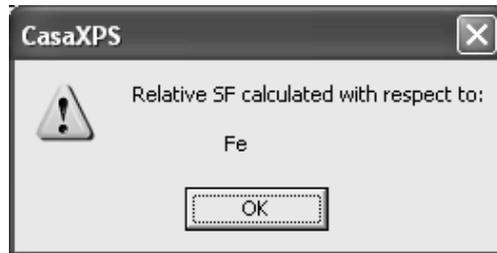
Once the data are prepared appropriately, pressing the Calculate SF button calculates and adds sensitivity factors to the table on the property page.



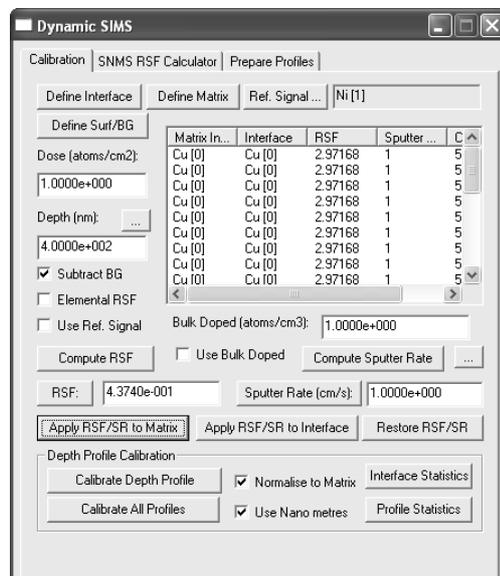
Alternatively, relative sensitivity factors are calculated by first selecting an entry in the Name column of the table before pressing the Calculate RSFs button .



A dialog window report the reference isotope by name and on pressing OK, the table is populated with RSF with respect to the indicated VAMAS block.



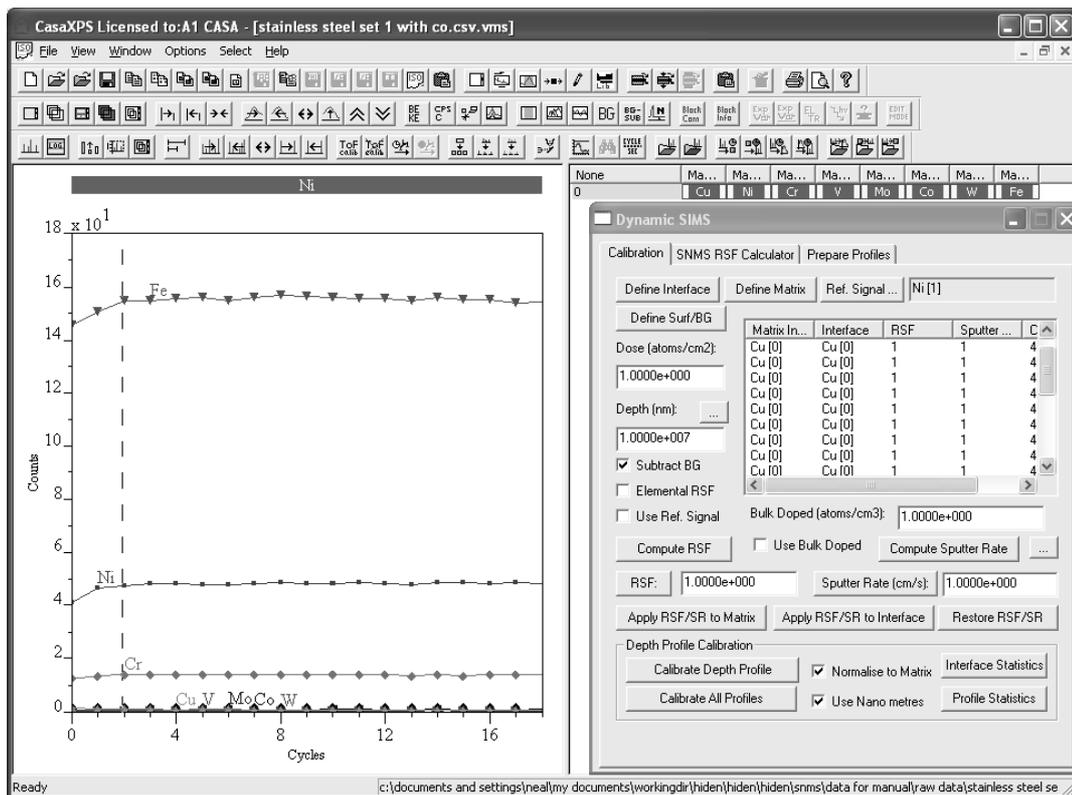
In both cases, the RSF or SF values are also entered into the VAMAS blocks on a cycle-by-cycle basis, which can be verified via the Calibration property page of the Dynamic SIMS dialog window.



## Quantification of SNMS Profiles

Isotopic profiles are quantified by applying the sensitivity factors to the intensities measured from the sample. These sensitivity factors are maintained within profiles measured from standard materials of known composition. The quantification of a profile is therefore achieved by transferring the appropriate sensitivity factors from these standard materials to the unknown material, establishing the sputter-rate for the material under analysis, followed by calculation of the percentage atomic or mass concentrations. The result is a new experiment frame containing the quantified profile. The process will be illustrated by quantifying a stainless steel sample using sensitivity factors determined from a Hastelloy material of known composition.

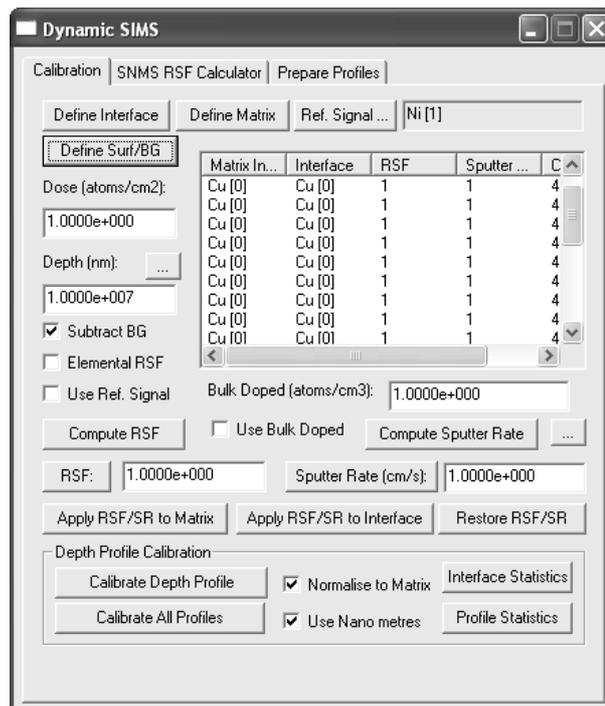
### Quantification of Stainless Steel using SNMS: an Example



On conversion, the data from a stainless steel sample appears in CasaXPS, viewed via the Calibration property page of the Dynamic SIMS dialog window, as a set of VAMAS blocks in the right-hand pane of an experiment frame.

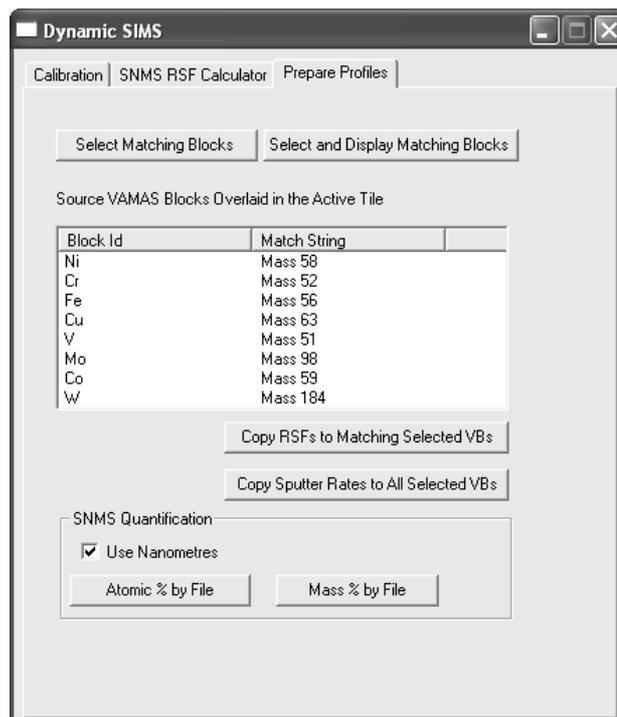
None	Ma...							
0	Cu	Ni	Cr	V	Mo	Co	W	Fe

The Calibration property page shows that initially the profiles are all assigned an RSF of unity and a unit sputter-rate.



RSFs and sputter-rates are defined on a cycle-by-cycle basis. This allows values to be adjusted depending on the point in a profile at which the intensities are measured. In multilayer materials permitting differing RSFs and sputter-rates may be important; however for a uniform stainless steel sample all cycles will be assigned the same RSFs and sputter-rates independent of depth.

The Prepare Profile property page on the Dynamic SIMS dialog window provides the tools for transferring RSFs and sputter-rates between profiles.

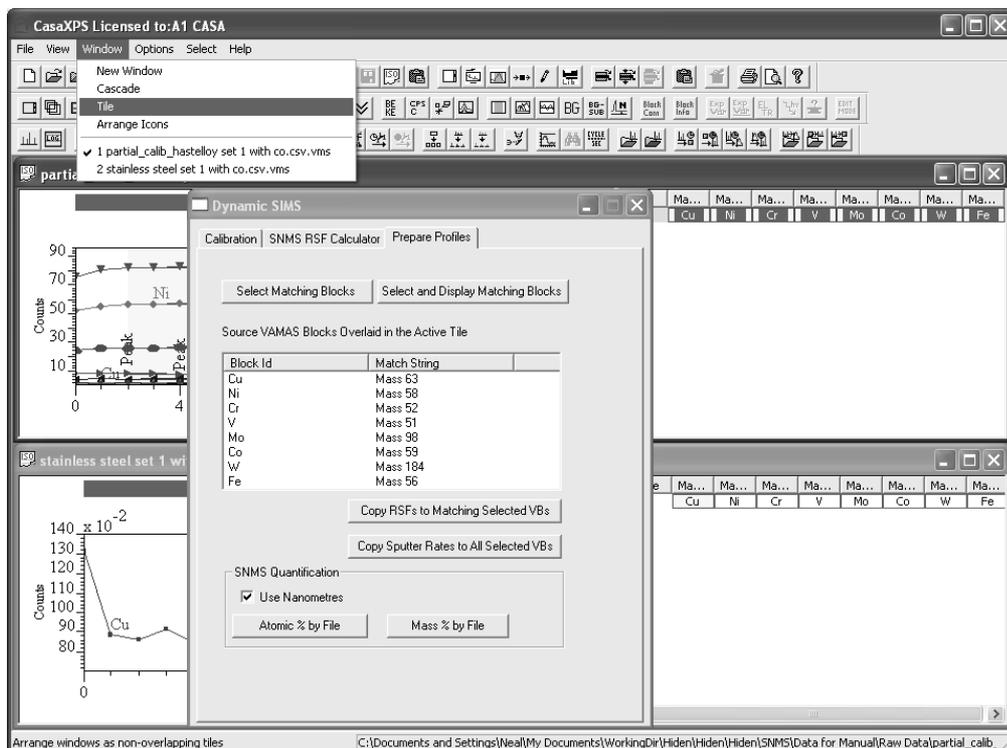


To transfer the RSFs from the Hastelloy standard to calibrate a stainless steel sample:

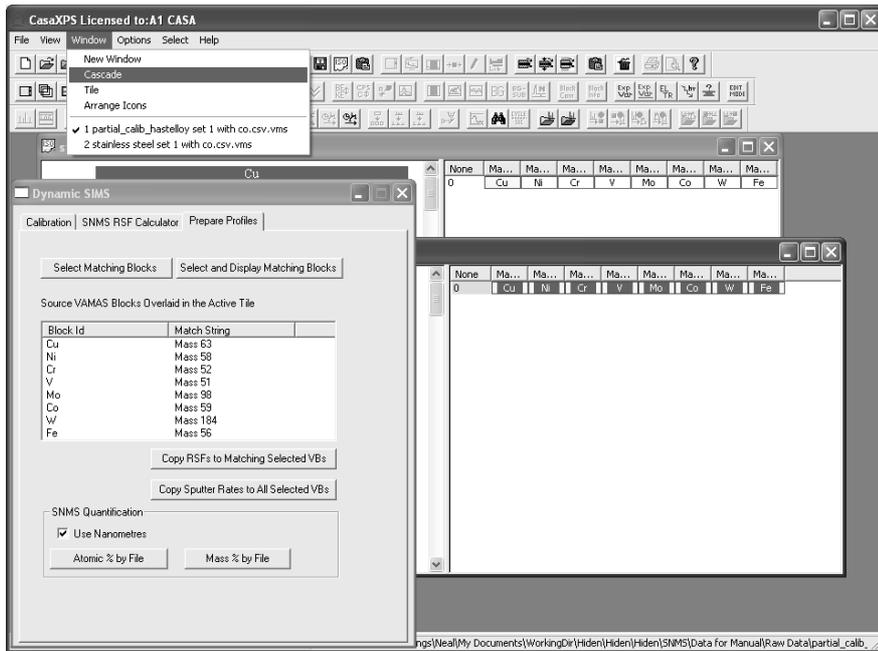
1. Load both the Hastelloy profile (previously processed to include the sensitivity factors) and the stainless steel profile.

Data converted from Hiden files include VAMAS fields defining the element and species for the VAMAS blocks. While these strings are only important in as much as profiles from the same isotopic peaks must be assigned identical strings, the actual strings are at the users discretion. The Hiden data labels the mass peaks with the nominal mass such as “Mass 58”. These element and transition strings are used to make global selections within the set of open VAMAS files; also the transfer of RSF and sputter-rate values is achieved via the Prepare Profile property page based on these strings. Therefore, a consistent assignment for these fields significantly aids the speed of data preparation leading to quantified profiles.

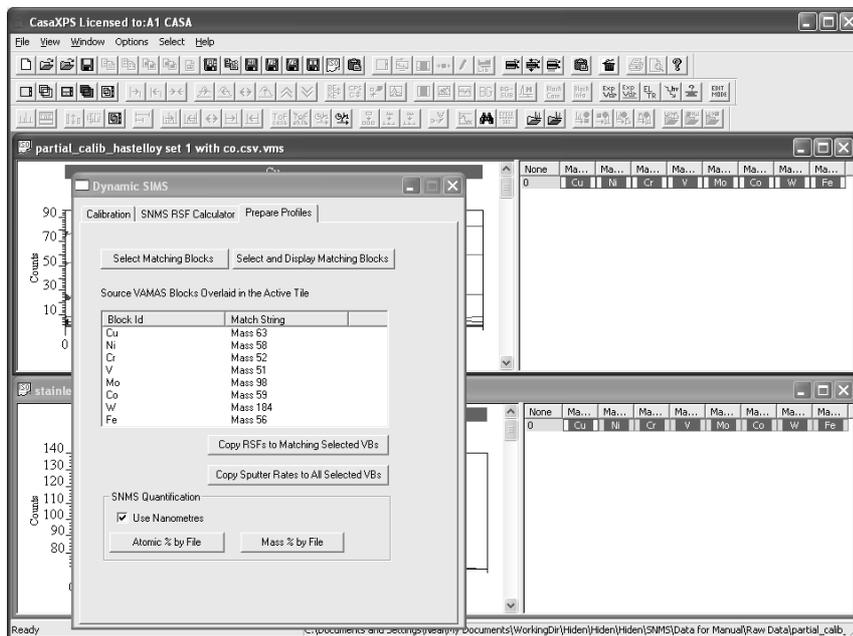
2. Tile the experiment frames within CasaXPS so that the right-hand panes can easily be seen



In this example only two files are in use so tiling the opened files using the Window menu is relatively easy. When more files are involved, a cascade of experiment frames can be more useful a means of monitoring the selections within the file set.



3. Select the VAMAS blocks within the Hastelloy standard previously prepared with appropriate sensitivity factors.
4. Press the **Select Matching Blocks** button to match the selection from the Hastelloy experiment frame throughout the opened VAMAS files.

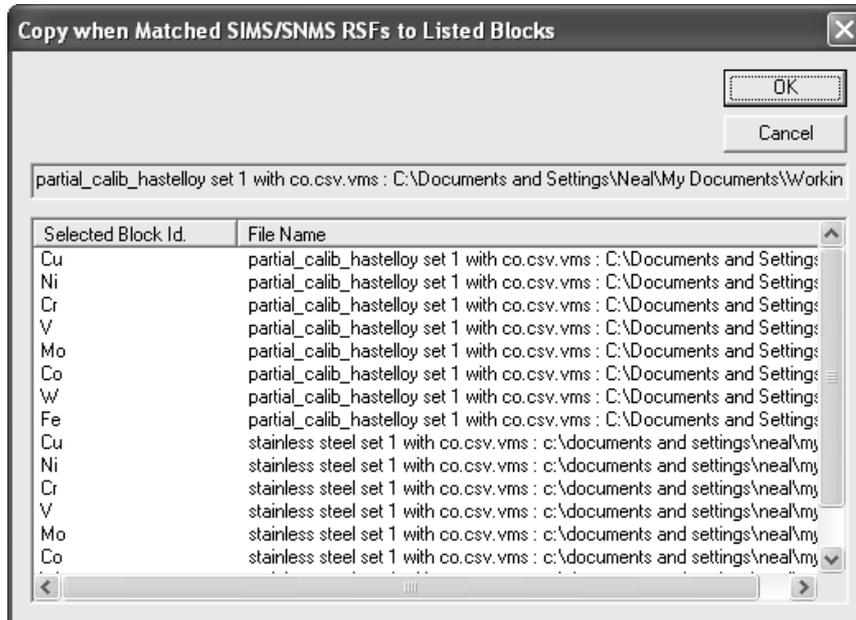


5. Ensure that the source experiment frame is the experiment frame with focus.



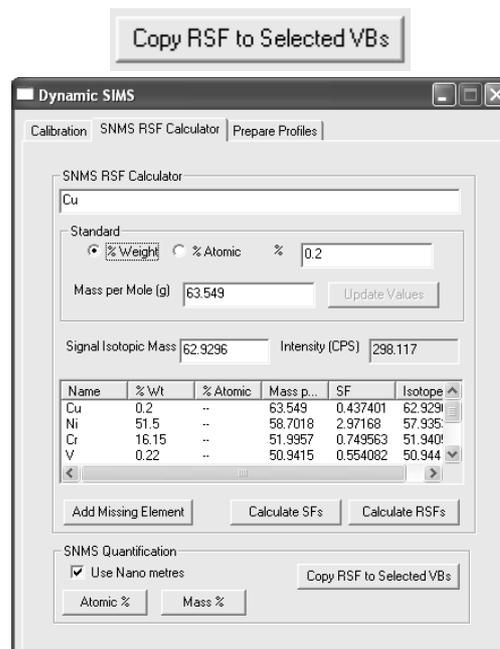
6. Press the  button.

A dialog appears listing the set of VAMAS blocks together with the file names from which the VAMAS blocks belong.

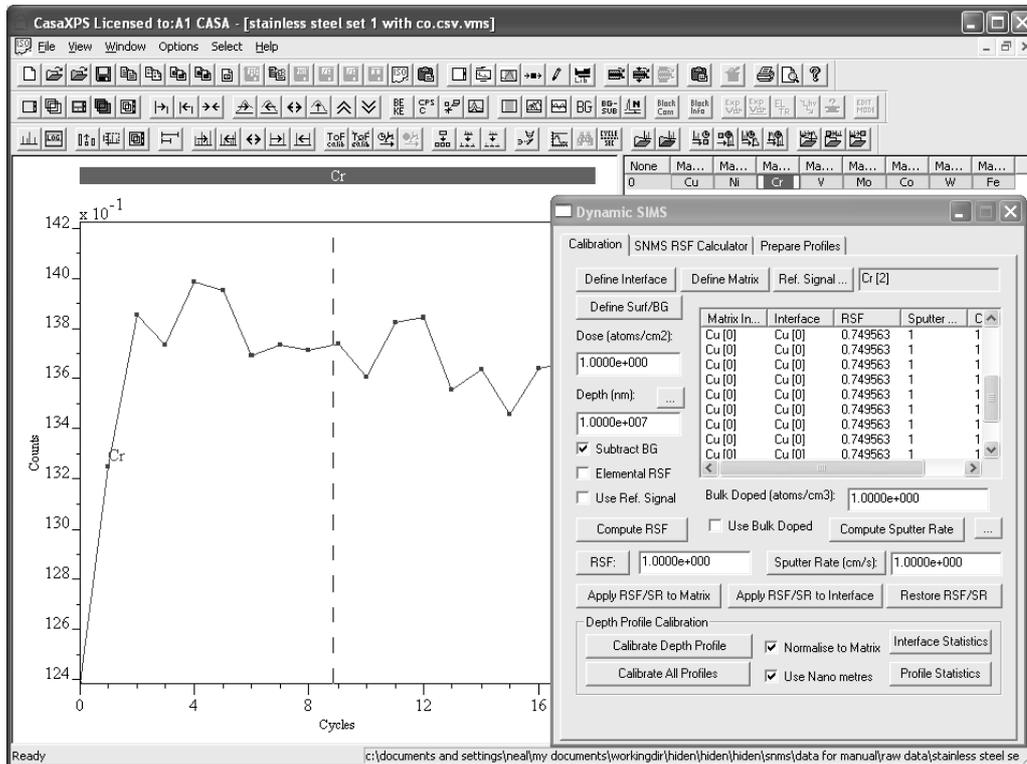


7. To transfer the RSF from the source file to the destination VAMAS blocks, press the OK button on the dialog.

The key point to note is that the RSFs are copied only to those VAMAS blocks for which the source VAMAS block element/species strings match the target element/species strings. To force the transfer of RSF values to other VAMAS blocks regardless of such constraints, use the button on the SNMS RSF Calculator property page.



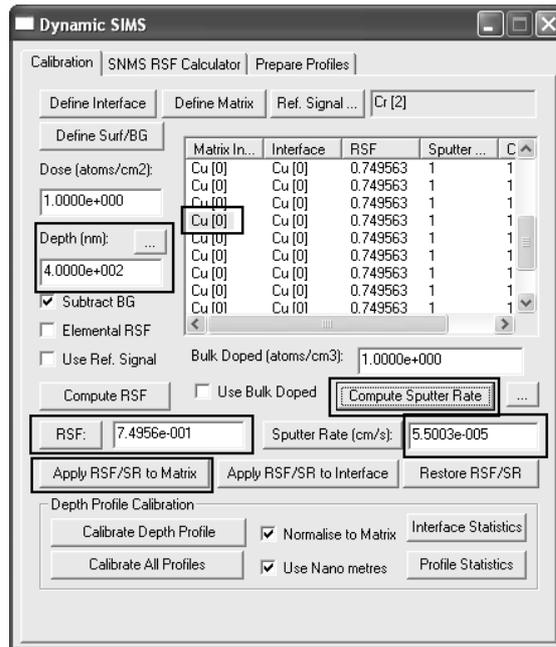
Following these operations the VAMAS blocks in stainless steel sample is populated with RSFs from the Hastelloy standard. These values can be viewed via the Calibration property page, where the table lists both the RSF per cycle and also the sputter rate per cycle. The remaining step is to assign a sputter rate for the stainless steel sample using the Calibration property page.



## Specifying the Sputter-Rate

The sputter rate for a profile is updated on the Calibration property page of the Dynamic SIMS dialog window. The information presented on the Calibration property page is designed for calibrating dynamic SIMS profiles. The mechanism allows the specification of sputter rates and RSFs based on matrix materials. Since the RSF is already added to the SNMS data via the Prepare Profiles or SNMS RSF Calculator property pages, the RSF must be retrieved before applying the newly calculated sputter-rate to the SNMS profile. Note that all VAMAS blocks in the row containing the block used to enter the sputter rate are also updated.

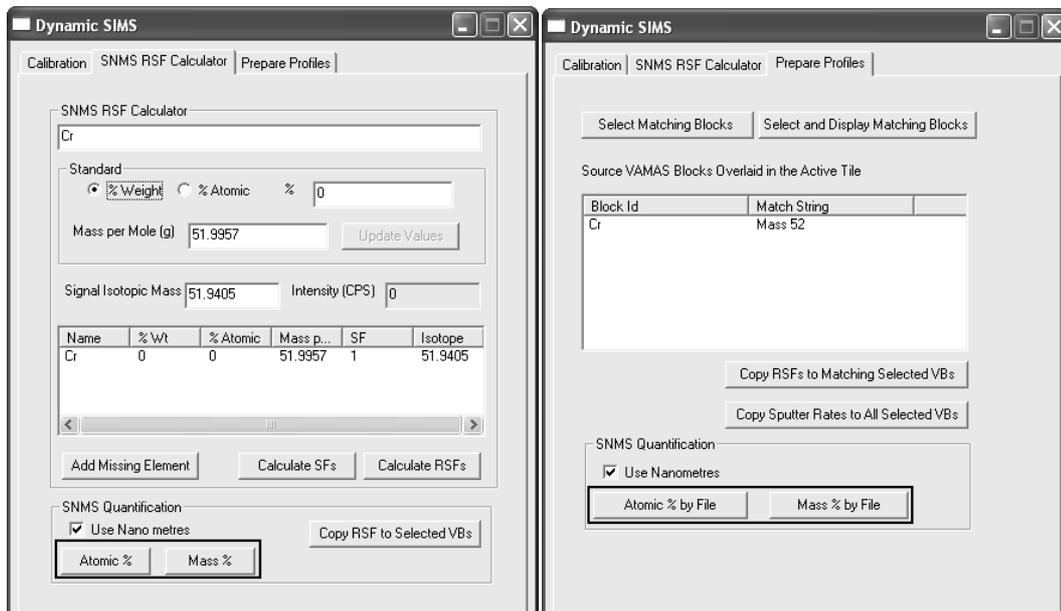
To update the sputter rate for a profile, perform the following steps using the Calibration property page.



1. Select an entry from the Matrix Index column as shown.
2. Press the RSF button to retrieve the RSF value from the table.
3. Enter the Crater depth in the text-field just below the Depth (nm) label before pressing the Compute Sputter Rate button.
4. Press the Apply RSF/SR to Matrix button.

### Creating a Calibrated SNMS Profile

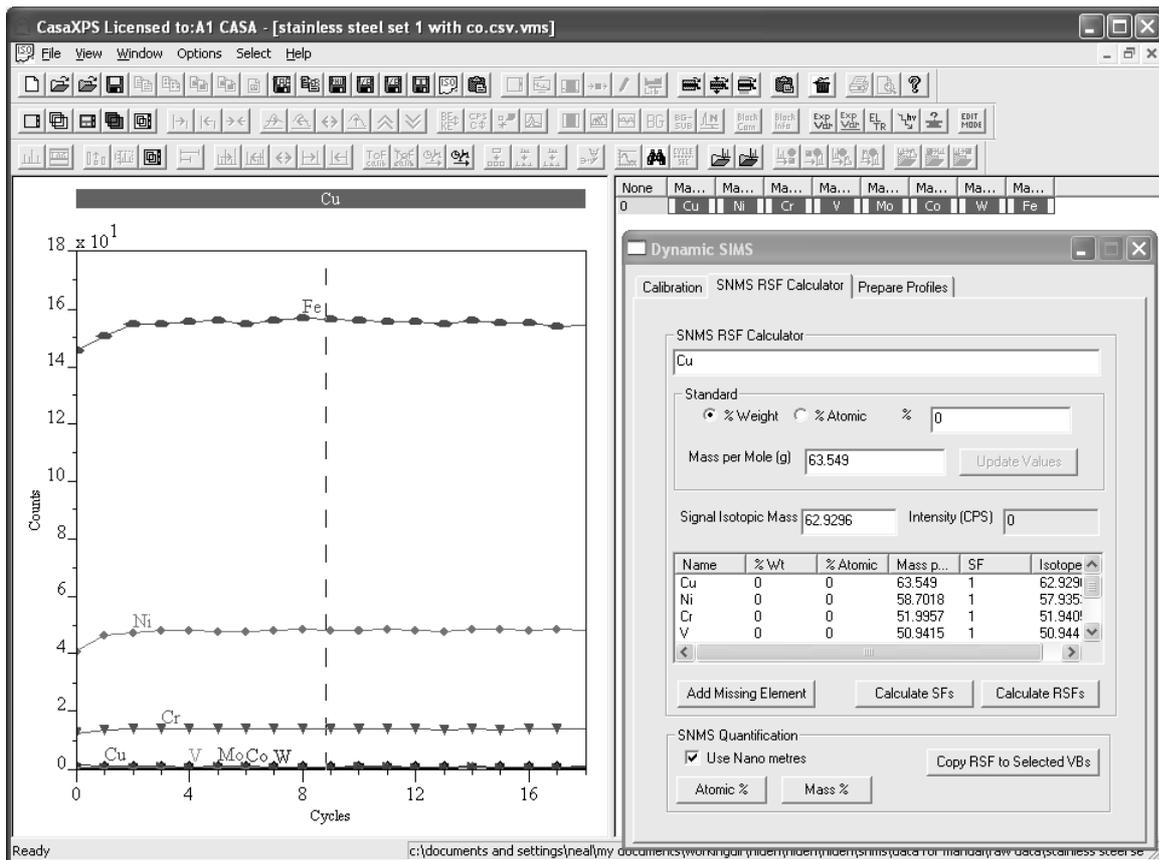
Once the set of VAMAS blocks containing the SNMS profile have been populated with RSFs and the sputter-rate, quantification in terms of Atomic or Mass concentrations is achieved by pressing the appropriate buttons on the either the SNMS RSF Calculator property page or the Prepare Profile property page.



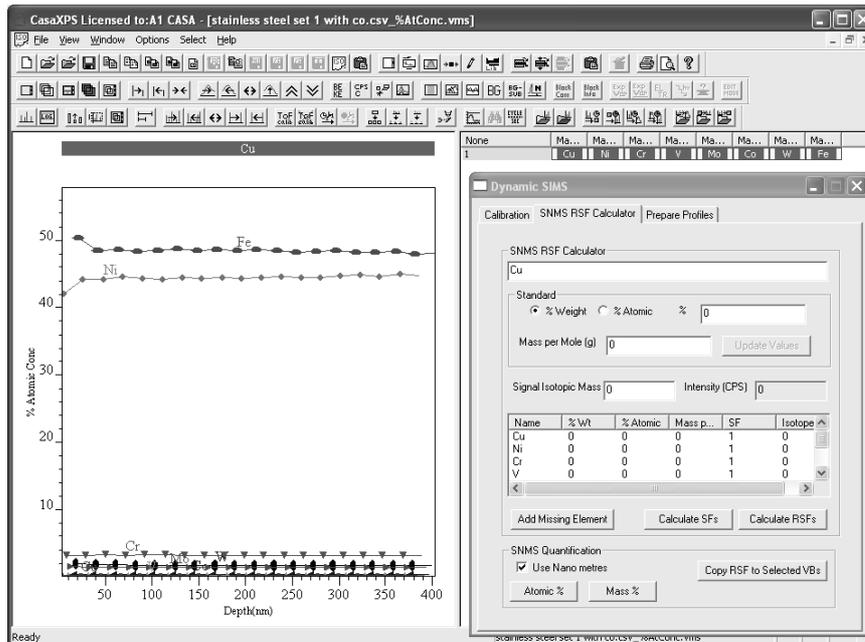
These two property pages provide a means of quantifying SNMS data either one file at a time or multiple files in one operation.

The SNMS RSF Calculator property page provides a means of quantifying the SNMS profile in the active tile. To perform the quantification step, display one or more VAMAS blocks in the active tile. Ensure the RSF and sputter-rates are correctly assigned for each of the VAMAS blocks by inspecting the table on the Calibration property page. To quantify the profile, press the % Atomic or % Mass buttons on the SNMS RSF Calculator property page. A new experiment frame is created containing a set of VAMAS blocks in which the data are scaled by the sensitivity factors and offered as a percentage of the total scaled intensities. The profiles are therefore presented in the form of an amount of substance rather than the raw signal.

Before quantification the signal is displayed in raw counts against acquisition cycle number.



After quantification, the data are presented in percentage of material against depth in nanometres.

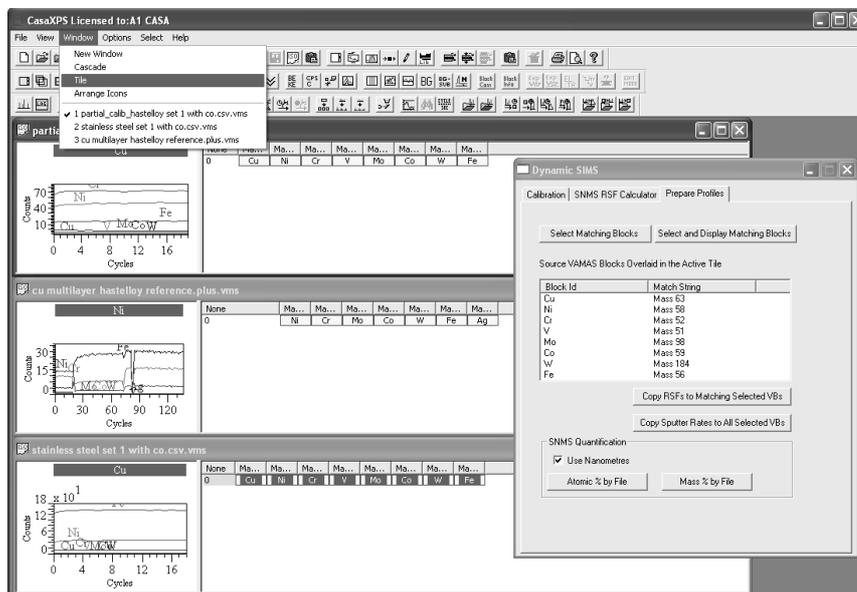


The alternative to performing the quantification on a file by file basis is to prepare a set of SNMS profiles and then use the Prepare Profile property page to quantify the data in one operation.

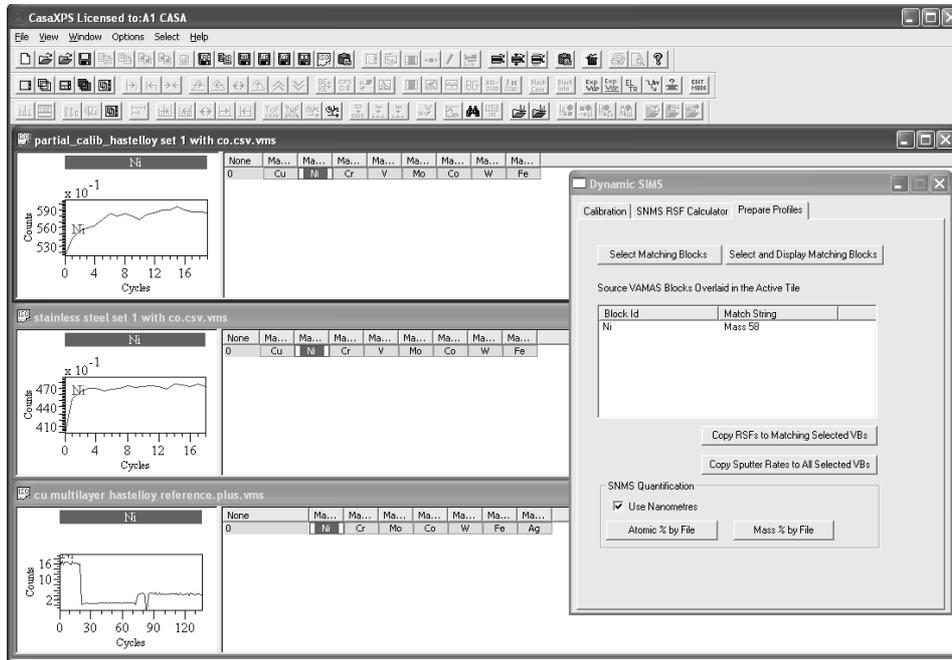
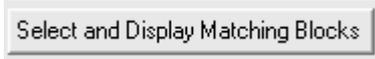
Sputter rates may be transferred to other profiles using the Prepare Profile property page in an analogous way to the RSF mechanism.

When multiple VAMAS files are opened in CasaXPS and prepared with appropriate RSF and sputter-rates, the Atomic % by File button or the Mass % by File button may be used to quantify the profiles in each opened file for which at least one VAMAS block is selected and the active tile displays data from one profile in the file. The following steps lead to quantification for two profiles.

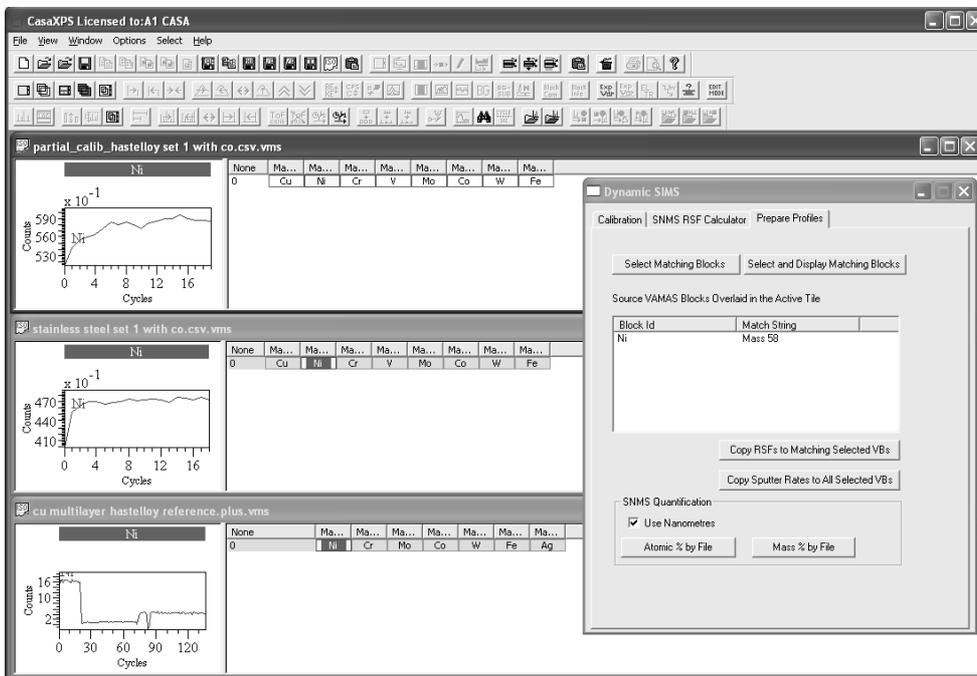
1. Tile the experiment frames within the CasaXPS main window



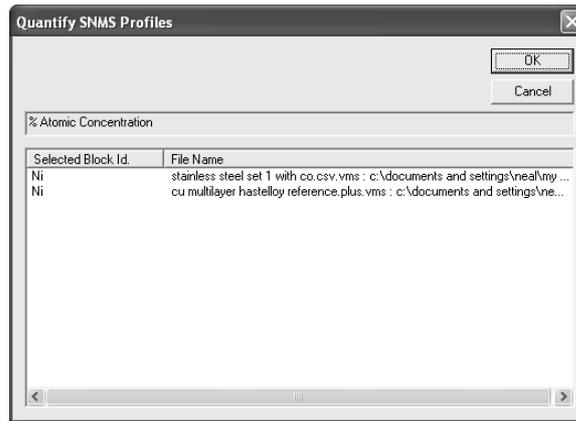
- Select one of the VAMAS blocks common to both profiles to be quantified and press the Select and Display Matching Blocks button



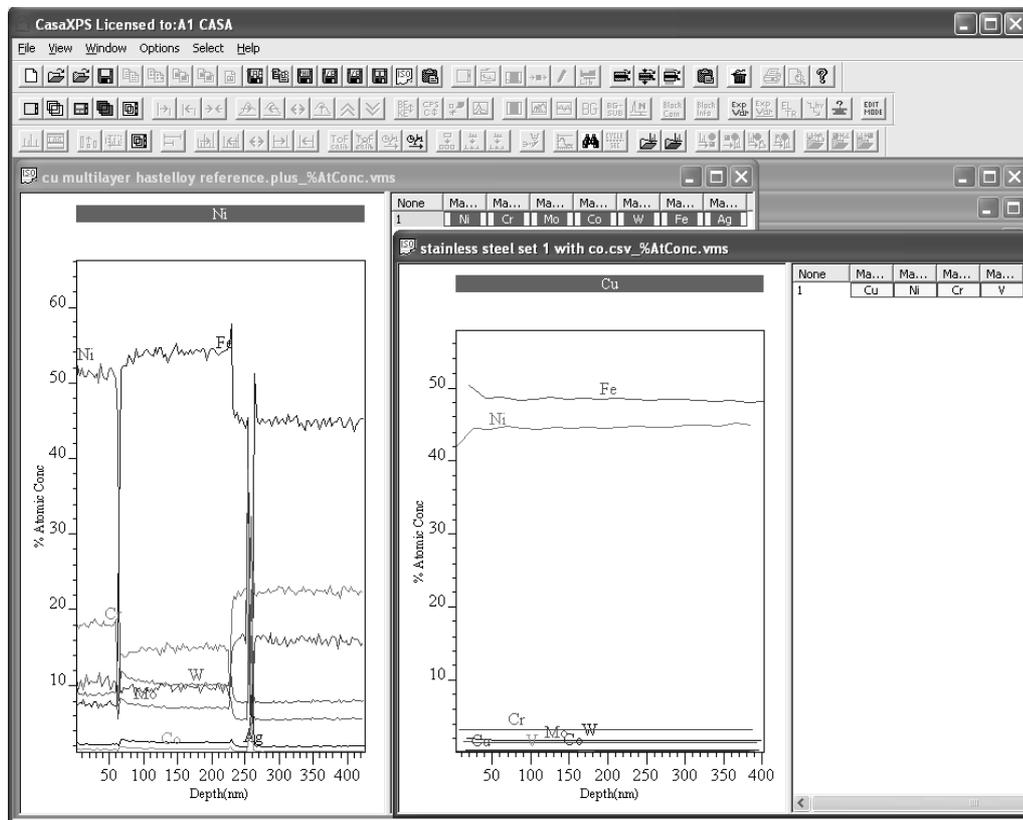
- De-select the VAMAS block in the experiment frame for which no quantification is required.



- Press the Atomic % by File button.
- Review the list of files displayed in the resulting dialog window and press OK if all is well.



Two new experiment frames appear containing the quantified profiles from the two files for which at least one VAMAS block is selected.



Note that:

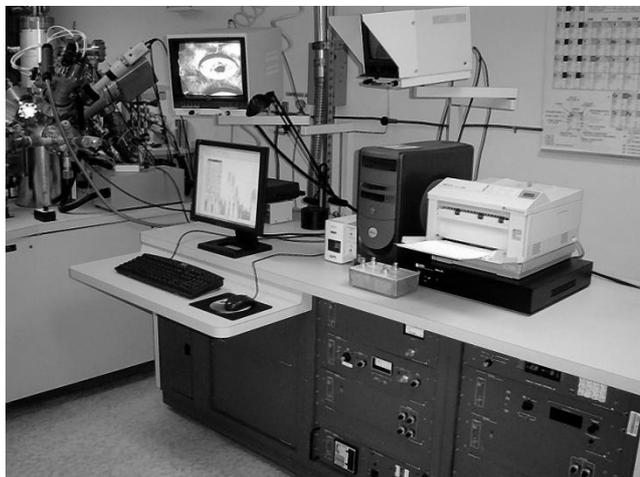
- Only files in which a VAMAS block is selected are quantified.
- Each raw file contains the information required to perform the quantification and therefore any number of different files can be quantified at once provided the RSF and sputter-rates are prepared appropriately and a selection includes at least one VAMAS block.
- The Control-Key and the mouse can be used to add to the selection across experiment frames, so the operation is not limited by the functionality of the selection options on the Prepare Profile property page.



Hiden SIMS/SNMS Workstation

## Dynamic SIMS

The Dynamic SIMS technique etches a sample using an ion gun whilst monitoring the signal for a set of isotopes. The resulting profile represents a measure for the composition of the sample as a function of depth, where raw data takes the form of counts per acquisition cycle as a function of acquisition cycle time. These raw data are calibrated using the tools on the Dynamic SIMS dialog window to provide profiles in terms of atomic density plotted against depth in nanometres.



Quantification of SIMS data is complicated by virtue of measuring the intensity of the secondary ions generated by the interaction of the primary beam on the sample surface. The complexity results from the dependence of the signal intensity on the bulk properties of the sample. That is, a change in the material etched by the ion beam may alter the signal intensity for the secondary ions regardless of the concentration of the element within the surface. It is therefore important to identify the essential structure of a sample, referred to as the *matrix* material, with the understanding that should the matrix material change, both the signal intensity for mass peaks may change as well as possible changes to the etch rate. SIMS analysis is highly sensitive and ideal for the analysis of dopants, diffusion studies and contamination. Quantification schemes for SIMS generally assume that the impurity being measured is dilute (less than a few percent). Above this dilute limit the probability of ionisation becomes dependent upon the impurity concentration itself, as well as the chemistry of the matrix.

### ***Notes on Dynamic SIMS RSF Calculation***

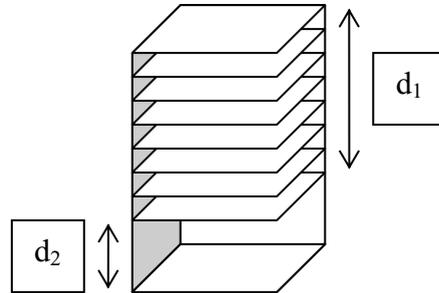
#### **Reference Signal Measured during the Course of Profile**

Dynamic SIMS relative sensitivity factors (RSFs) are the means by which measured implant signals are scaled to permit meaningful comparisons of profile data. During the course of a measurement, the signal may change for a variety of reasons and as a result a common practise is to measure both the implant signal and also the matrix signal. The matrix signal provides the experimental context for the implant signal, therefore the calculation of an RSF from a standard sample includes the matrix signal measured in counts per second. Since an RSF is essentially a scale factor and the matrix monitored during the course of the profile is a sequence of measurement, the value included in the RSF calculation is determined from an average of the matrix acquisition cycles.

An alternative to measuring the matrix signal at the same time as the implant is to monitor the matrix signal following the profile completion. The structure of the experiment changes slightly when the matrix signal is determined following the implant measurement, and since the RSF calculation for both scenarios are generalised by the reference signal estimation following the

profile, the discussion of the RSF computation will be based on the more general case.

### Reference Signal Measured at End of Acquisition Cycles



Consider a sample created from a matrix material A implanted with a material B using a fluence  $\phi$  atoms per  $\text{cm}^2$ . If the resulting sample is profiled using C data acquisition cycles followed by a matrix signal measurement, where each acquisition cycle takes  $t$  seconds per cycle and the matrix signal is measured for a further  $T$  seconds resulting in a crater of depth  $d$  cm, then the RSF for equivalent samples can be determined as follows.

The reference signal measured during the period  $T$  corresponding to the etch volume characterized by the depth  $d_2$  is assumed to be representative of the matrix signal throughout the profiled volume characterized by the depth  $d_1$ . Further, the sputter rate is determined from the total depth of the crater equal to  $d_1+d_2$  divided by the total etch time. Hence  $d_1 = td / (t+T)$ . The RSF for the given experiment is:

$$RSF = \phi \left[ \frac{tCI_A}{I_B - I_{bg}C} \right] \frac{1}{d_1} \quad (1)$$

where

1.  $I_A$  is the matrix signal in counts per second,
2.  $I_B$  is the sum of the signal from the implant over the acquisition cycles

$$I_B = \sum_{i=1}^C I_i \text{ in counts,}$$

3.  $I_i$  are the counts record for the implant in each cycle and
4.  $I_{bg}$  is the background counts for the implant signal.

The formula for the RSF in Equation (1) is defined in terms of parameters determined from an experiment. There are assumptions within this formula regarding the nature of the experiment, which become clear when the parameters are rearranged as follows:

$$RSF = I_A \left[ \frac{\phi}{d_1 \frac{1}{C} \sum_{i=1}^C \left[ \frac{I_i - I_{bg}}{t} \right]} \right] \quad (2)$$

The denominator in equation (2) is an approximation to the integral of the background subtracted implant counts per second integrated over the depth of the profiled volume. That is:

$$d_1 \frac{1}{C} \sum_{i=1}^C \left[ \frac{I_i - I_{bg}}{t} \right] \approx \int_0^{d_1} \frac{(I(x) - I_{bg})}{t} dx \quad (3)$$

where the approximation in Equation (1) assumes a uniform step-size  $\Delta x = d_1/C$  for a rectangular integration scheme. If the step-size as a function of depth changes during a calibration profile, the RSF calculated from Equation (1) will be less representative of the measured uncalibrated implant dose. Since the objective of calibrating an implant signal is to ensure that profiles obtained from identical implantation conditions return identical areal densities, or stated mathematically, integrals of the form in (3) for RSF scaled intensities are all the same when calculated from profile data measured for samples with identical implant dose, computation of the integral in Equation (3) is preferable to the summation in the same Equation. Therefore, the RSF calculation in version 2.3.15 of CasaXPS is now performed using:

$$RSF = I_A \left[ \frac{\phi}{\int_0^{d_1} \frac{(I(x) - I_{bg})}{t} dx} \right] \quad (4)$$

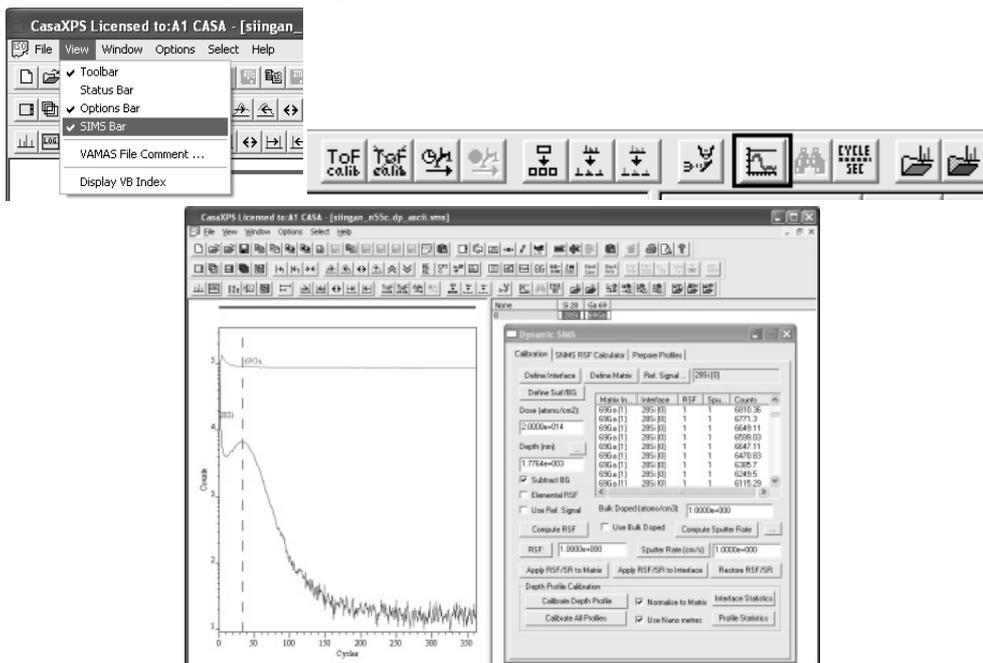
Equation (4) better represents the nature of the dynamic SIMS RSF as a scaling factor for adjusting implant intensities relative to a known fluence  $\phi$ . The inclusion of the matrix signal  $I_A$  in the RSF calculation is to allow the implant intensity to be further normalised with respect to the matrix signal as a means of removing instrumental variations possible during the course of a profile, or in the case of the reference signal at the end of the profile, between different profile measurements.

### **Quantification of Dynamic SIMS Profiles**

The options on the Calibration property page of the Dynamic SIMS dialog window are designed to permit the analysis of samples for which the matrix material changes in the course of the experiment. Although multilayer

materials are analysed using dynamic SIMS, the typical sample consists of a single matrix and one or two impurities appearing in dilute quantities compared to the matrix. For this reason, the first perspective of the Calibration property page will be that of these more common and simple samples.

Most data systems used to acquire dynamic SIMS profiles provide a means of exporting the data in an ASCII format. These data files must be converted to VAMAS format by CasaXPS using a very specific structure within the ISO 14976 definition. The experimental context for the dynamic SIMS profiles is collected into a VAMAS file by CasaXPS and presented as a set of VAMAS blocks. Each VAMAS block within a file manages the quantification information in a set of corresponding variables (as specified by the ISO format). The Calibration property page on the Dynamic SIMS dialog window displays these corresponding variables in a table.



Data file supported by CasaXPS include:

1. Hiden Analytical Limited
2. Two formats for Cameca IMS instruments.
3. RBD Instruments Inc. PHI-upgrade system.

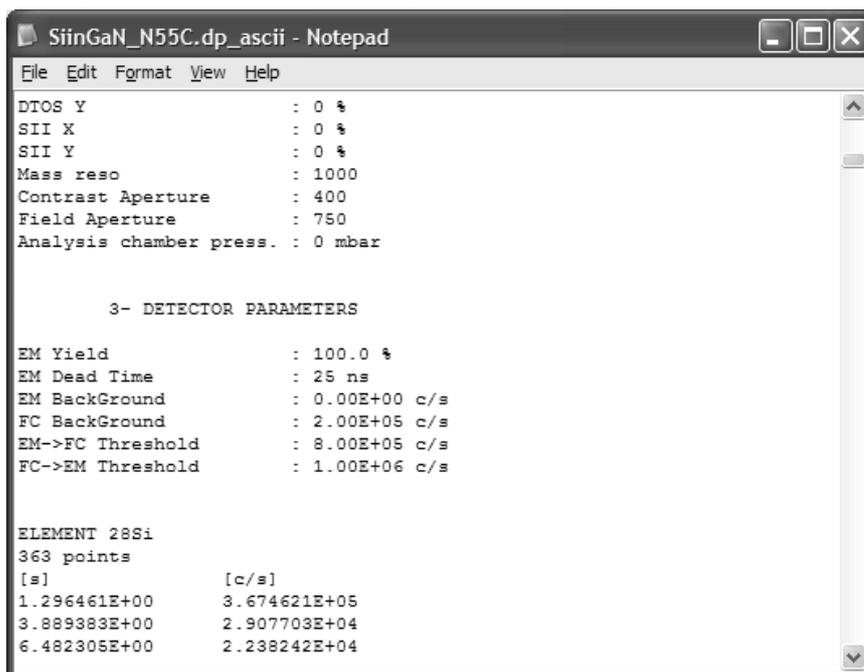
To convert a native ASCII format to VAMAS format suitable for quantification in CasaXPS, convert the data using the Convert option on the File menu or the Convert toolbar option .

## Quantification of Basic Profiles

An example based on Cameca IMS-6f old ASCII format.

### *Converting Cameca Depth Profiles*

Depth profile data from Cameca IMS-6f SIMS instruments can be exported via ASCII formatted files. These files, when written to disk, are assigned a file extension of `.dp_ascii` and, if exported from the raw data, include experimental parameters plus two columns of X/Y pairs representing the etch-time per cycle and the secondary ion intensity in counts per second.



```

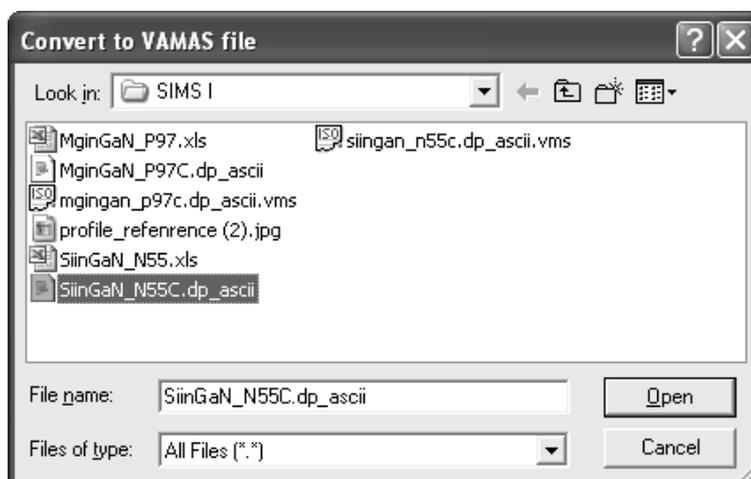
SiinGaN_N55C.dp_ascii - Notepad
File Edit Format View Help
DTOS Y : 0 %
SII X : 0 %
SII Y : 0 %
Mass reso : 1000
Contrast Aperture : 400
Field Aperture : 750
Analysis chamber press. : 0 mbar

3- DETECTOR PARAMETERS

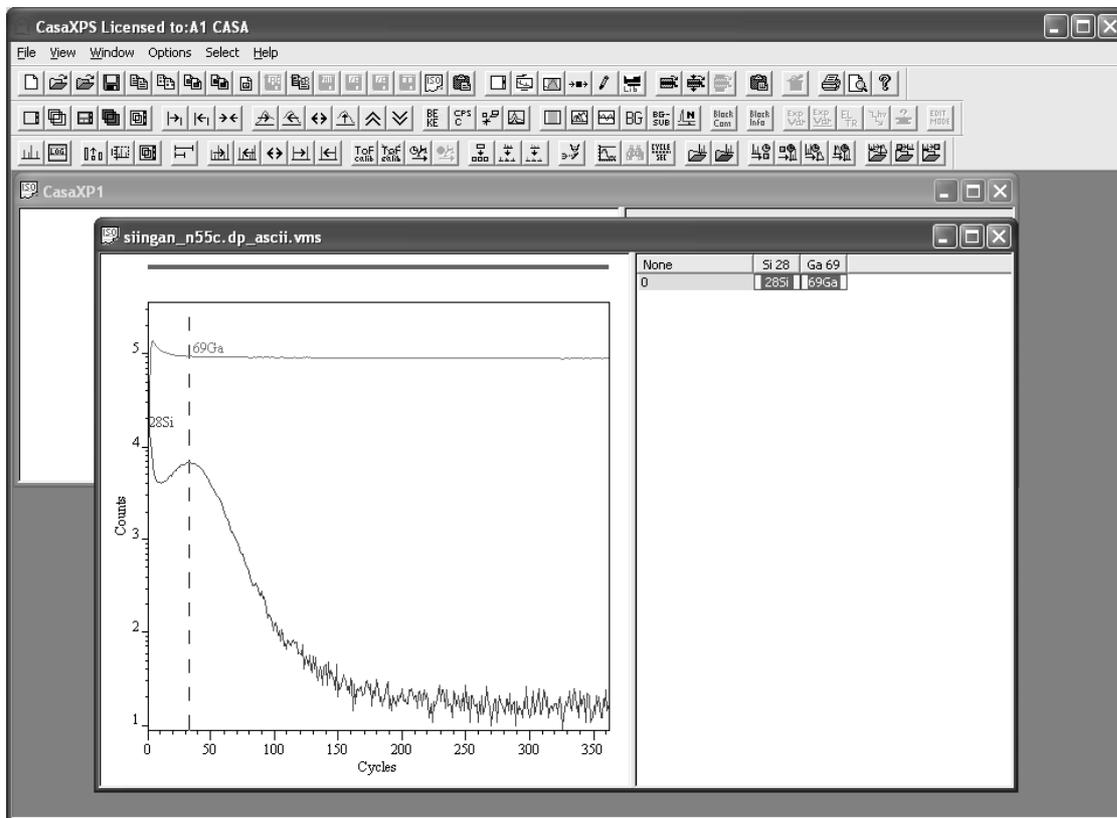
EM Yield : 100.0 %
EM Dead Time : 25 ns
EM BackGround : 0.00E+00 c/s
FC BackGround : 2.00E+05 c/s
EM->FC Threshold : 8.00E+05 c/s
FC->EM Threshold : 1.00E+06 c/s

ELEMENT 28Si
363 points
[s] [c/s]
1.296461E+00 3.674621E+05
3.889383E+00 2.907703E+04
6.482305E+00 2.238242E+04
  
```

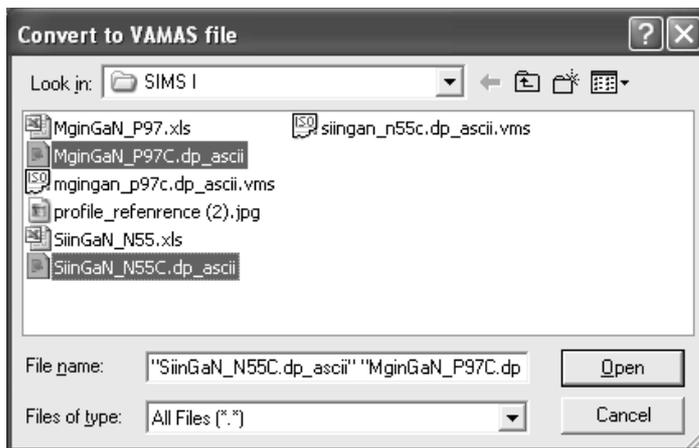
CasaXPS will convert these `.dp_ascii` files only when the raw data is exported. Conversion is performed using the Convert option on the File menu or via the toolbar button. A File dialog window is invoked by these options, in which the `.dp_ascii` file containing the raw data is selected and the Open button pressed.



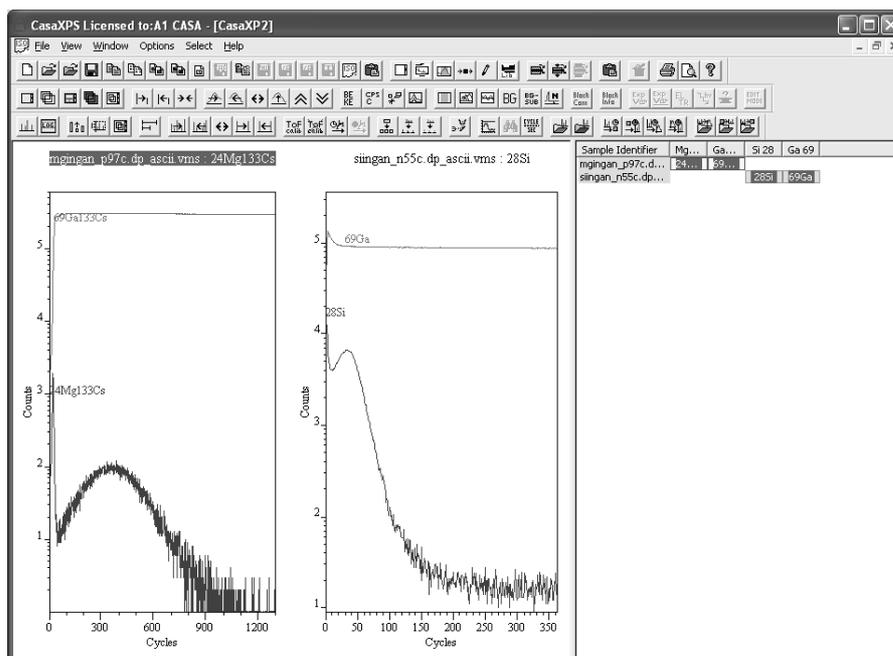
A new VAMAS file will be written to the same directory containing the original ASCII data after which the profile appears in a new experiment frame in CasaXPS.



When more than one profile is of interest, the data can be combined into a single experiment frame via the Convert and Merge option on the File menu.



Again a File dialog window appears, in which each .dp\_ascii file within the current directory can be selected using the mouse and the Control Key; on pressing the Open button on the dialog window the entire set of selected dp\_ascii files are converted to VAMAS files and the resulting files loaded into a single experiment frame.



The directory containing the original dp\_ascii files will also contain corresponding VAMAS files. Since the conversion process involves writing new VAMAS files, it is important that the directory containing the data must have write permission and there is sufficient space on the disk to receive the new VAMAS file.

### ***Quantification Information***

After conversion to VAMAS format, both the timing information and the intensity units are adjusted to those used internally by CasaXPS. Most notably, the intensity unit in the .dp\_ascii file is counts per second, however the intensity in the VAMAS file will be measured in counts per cycle and the abscissa becomes cycle index. All the associated timing information is also save with these abscissa and ordinates so that the calibration to depth and atomic density can be computed later.

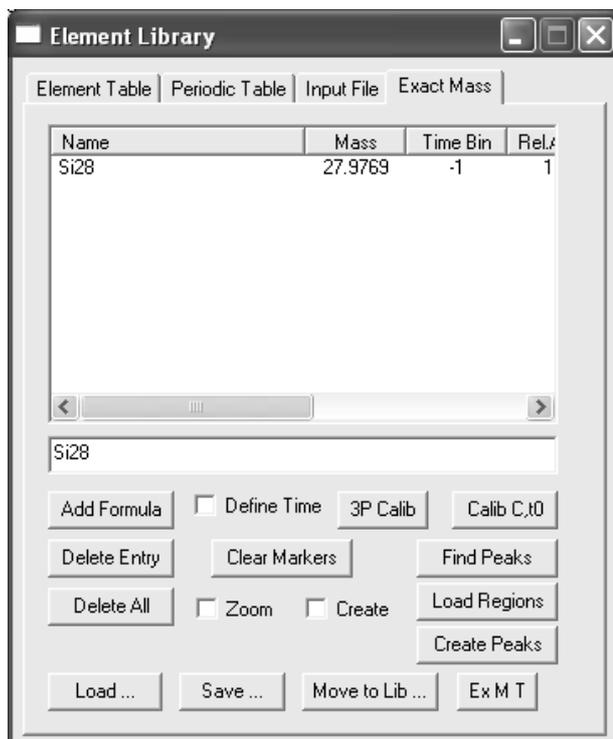
Mass channels used to measure the secondary ion intensity are labelled within the .dp\_ascii file using the nominal mass and the element name abbreviation. When entered into the VAMAS file, the block identifier is assigned the original string used to label the mass channel, however CasaXPS attempts to extract the nominal mass and the element abbreviation for use in the element and transition fields used by the VAMAS format. The concatenation of these element and transition fields provides the information used to align the VAMAS blocks within the experiment frame and is also used to determine the isotopic abundance ratio, which in turn is used to determine elemental from isotopic relative sensitivity factors. If the

element/transition fields for a profile are not correctly assigned, should the user request elemental sensitivity factors an error message will result. In the event that the element and transition fields do not contain the element and isotopic information required to determine the relative abundance for an isotope, then these fields must be edited to reflect the true isotope used to measure the profile. To edit these fields:

1. Select the VAMAS block(s) in the right-hand pane of the experiment frame.
2. Press the  toolbar button and, on the resulting dialog window, enter the correct element abbreviation and nominal mass for the isotope of those VAMAS blocks in the selection.

When the information on the dialog window is accepted, the VAMAS blocks in the right-hand pane of the experiment frame are re-organised to reflect the new assignment.

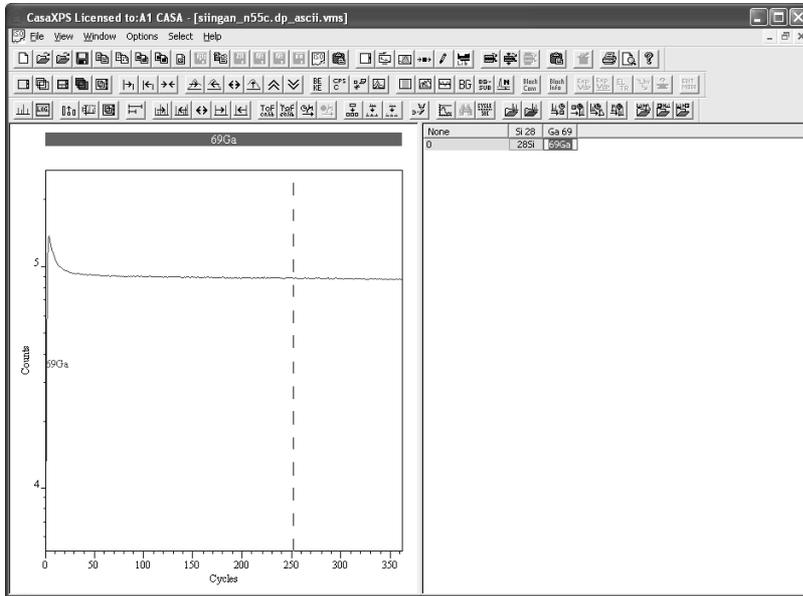
One way to check the possible values for the element/transition entries is to use the Exact Mass Calculator property page on the Element Library dialog window.



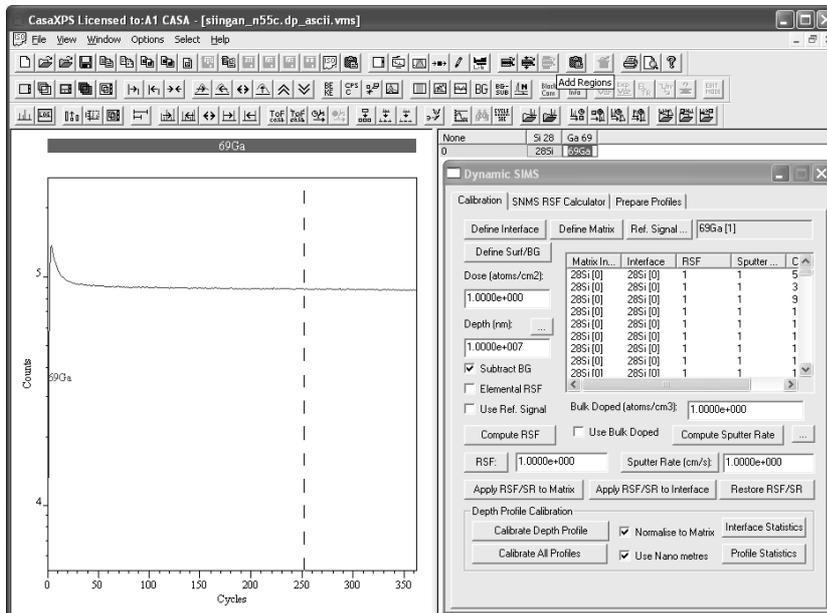
Enter a string such as “Si28” into the text-edit field on the Exact Mass property page and press return or the Add Formula button. If a valid isotope string has been entered, then the string will be entered into the scrolled list above the text-field. Otherwise, an error dialog indicated an error occurred. If



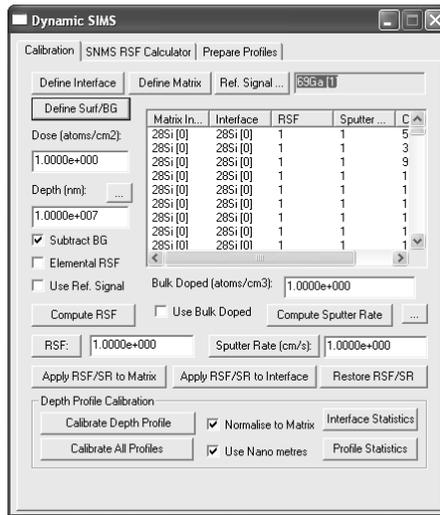
1. Convert the .dp\_ascii file using the **Convert** option on the **File** menu.
2. Display the 69Ga data in the active display tile
3. Left-click on the active tile to enable the toolbar buttons.



4. Invoke the Dynamic SIMS Calibration dialog window by pressing the Dynamic SIMS toolbar button .



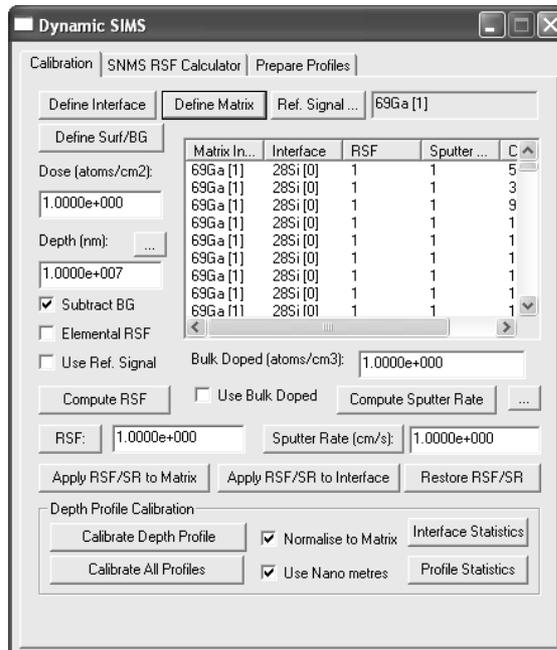
The top left-most text-field displays the Block Id for the data which is the current focus of the Dynamic SIMS dialog window.



5. Press the **Define Matrix** button.

Provided no cycles are selected in the scrolled list below the **Define Matrix** button, a dialog window indicates that no selection is active and asks whether all cycles should be updated for the profile in the active tile.

6. Press the **Yes** button and observe that the **Matrix Index** column of the scrolled list is updated with the string 69Ga.

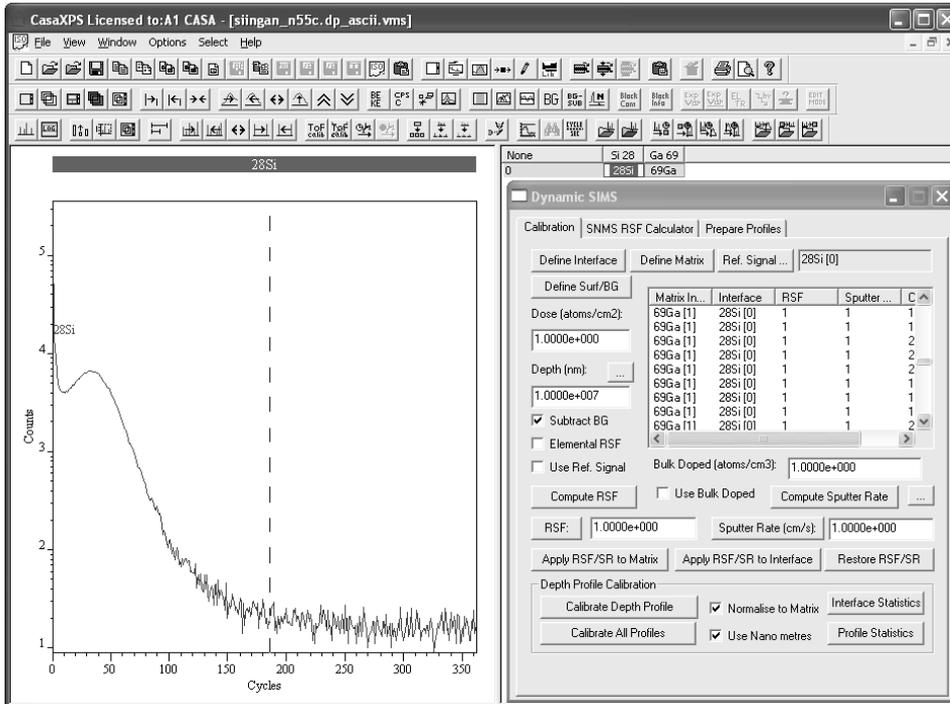


If a cycle selection has been made within the scrolled list, then all cycles must be selected before pressing the **Define Matrix** button is pressed.

The second column in the scrolled list is labelled **Interface**. For this particular profile, the same matrix is present throughout the etch cycles and therefore the use of the Interface column is unnecessary. If the material were a multilayer sample, where RSF and sputter-rates varied between layers, then

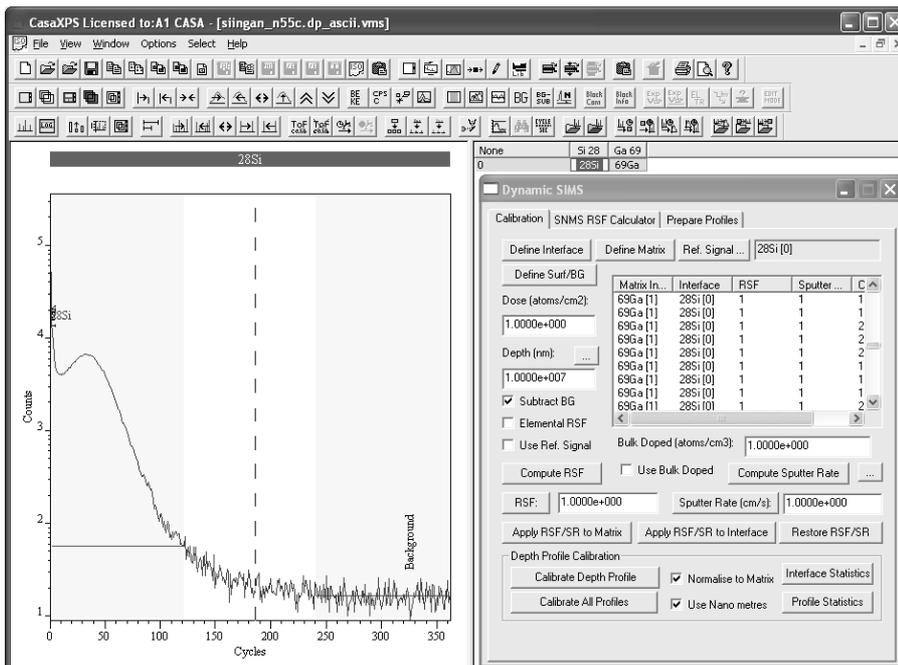
the Interface column would need to be populated with strings corresponding to the different materials characterising the layer structure. Once the layers are established, the Interface definition allows the assignment of RSF and sputter-rates to the individual layers.

7. Double-click on the 28Si VAMAS block so that the silicon profile is displayed in the Active Tile.



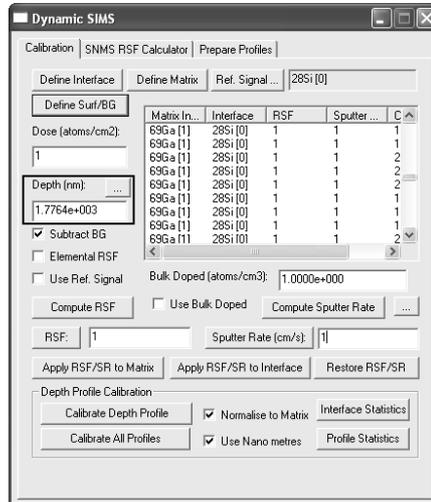
8. Press the **Define Surf/BG** button.

Two regions are created on the 28Si profile and these mark the surface limit and the background to the secondary ion signal.

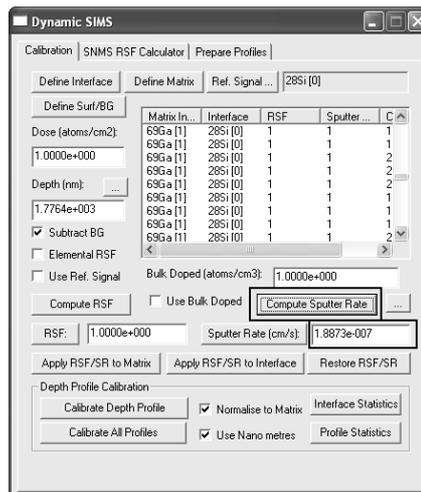


Adjustments to these regions are performed using the Quantification Parameters dialog window.

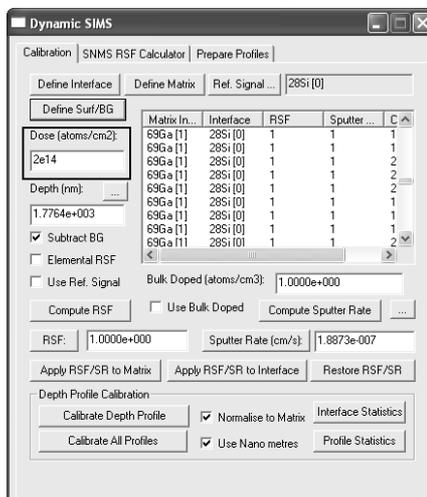
- On the Calibration property page, enter the crater depth value measured for the standard (crater depth = 1776.4 nm)



- Press the Compute Sputter Rate button.

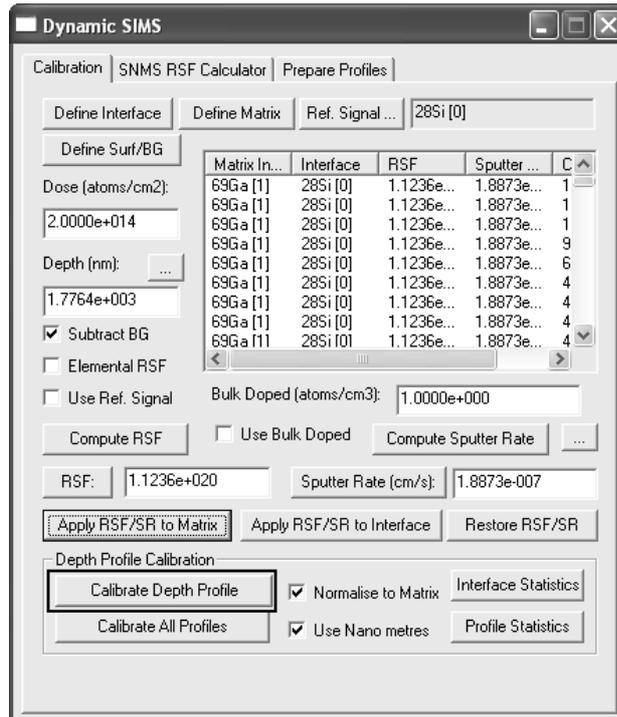


- On the Calibration property page, enter the dose value known for the standard (dose =  $2 \times 10^{14}$  atoms per cm<sup>2</sup>)

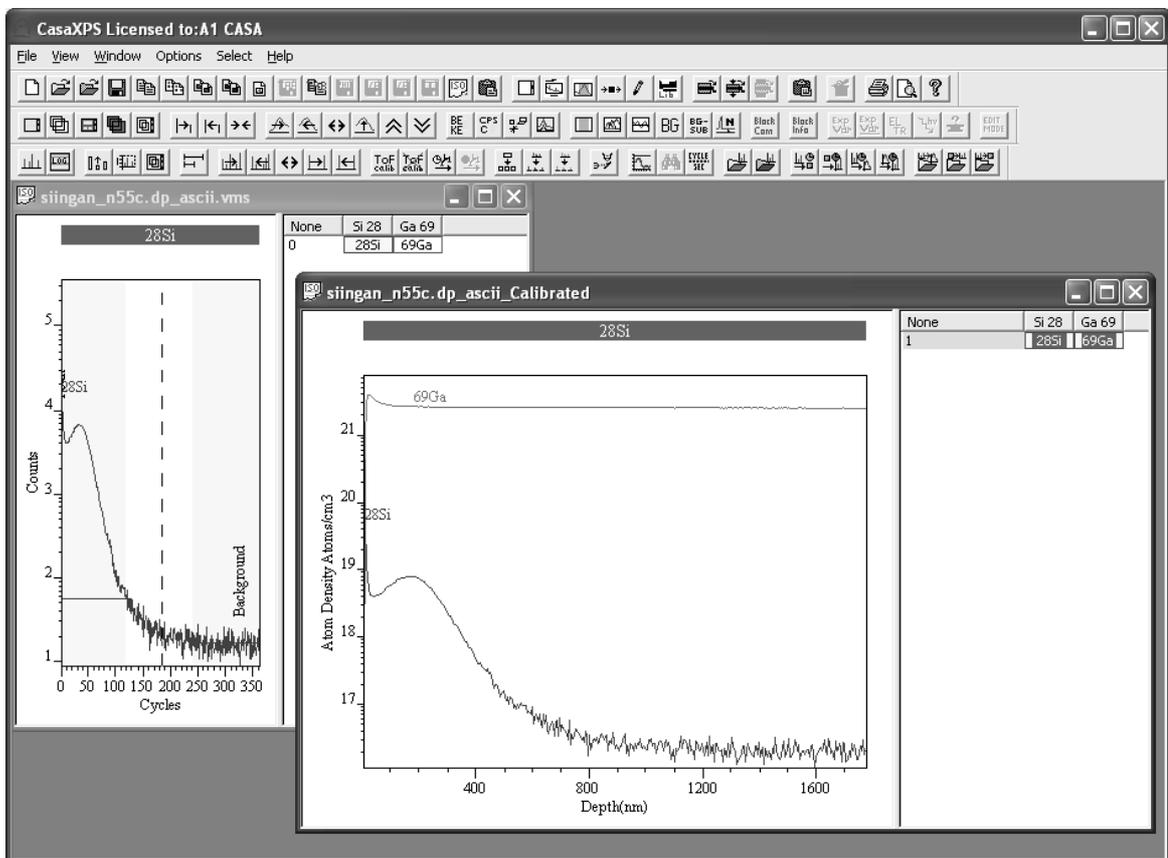




14. Press the button labelled Calibrate Depth Profile.



The RSF and sputter-rate entered into the 28Si table are used to compute the atomic density and the depth; the computed profiles are entered into a new experiment frame.



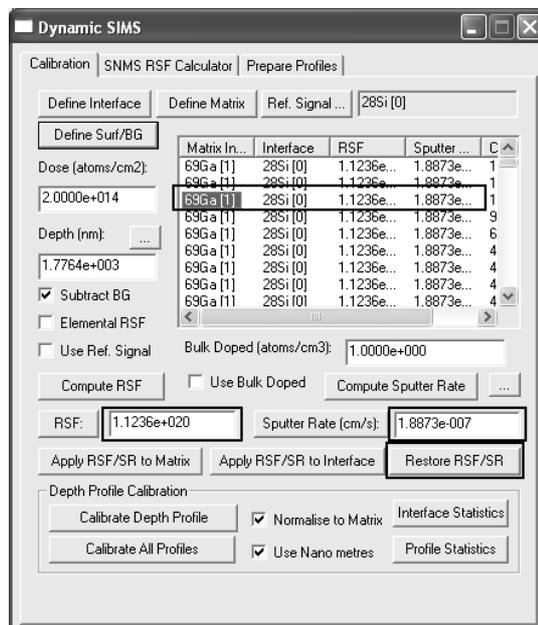
The new experiment frame contains a VAMAS block for each VAMAS block in the original file. Within these new VAMAS blocks, several corresponding variables are defined which are assigned values for the intensity in counts per second plus the RSF and sputter-rate used to calibrate the profile. These values can be viewed using the Ctrl PageUp/Ctrl PageDown mechanism for stepping through the corresponding variables in a VAMAS block.

NB: To compute the elemental RSF from an isotope profile, the tick-box labelled **Elemental RSF** must be ticked and the element/transition field for the VAMAS block in use must be set appropriately.

## Making Adjustments to the Sputter Rate

A depth profile prepared for calibration must have an RSF and sputter rate defined for each matrix within the analysis volume. If at a later time it is desired to alter the RSF or sputter rate for a given matrix, the following sequence of steps should be used:

1. Select a cycle from the scrolled-list to identify the matrix for which the RSF or sputter-rate requires adjusting.
2. Press the pushbutton labelled **Restore RSF/SR**.

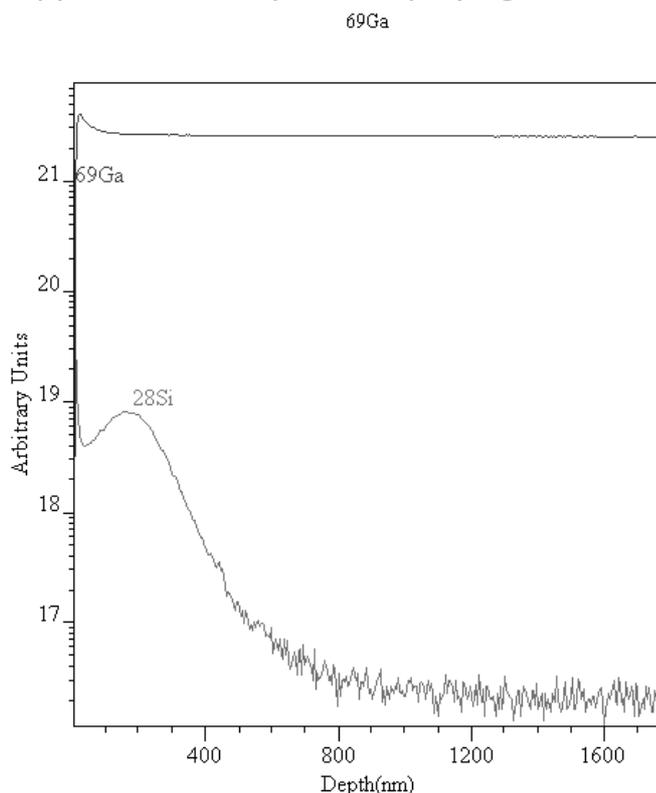


The values for the matrix identified by the chosen cycle are entered into the corresponding text-fields for the **RSF** and **Sputter Rate** on the dialog window.

3. Either the RSF, the sputter rate or both the RSF and the sputter rate can be recalculated before again pressing the **Apply RSF/SR to Matrix** button. The matrix defined by the selected cycle will be updated with the modified values.

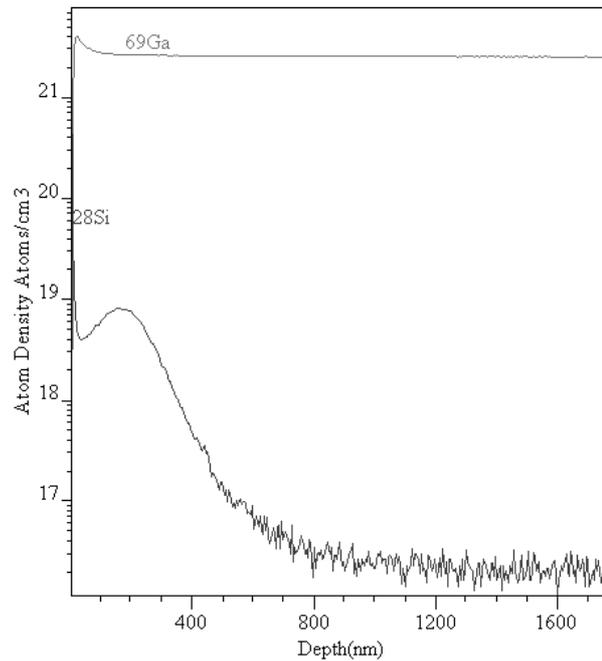
## Display of Calibrated Profiles

The labels for identifying the x and y axes in a display tile are determined from the first VAMAS block with respect to the order of selection in the right-hand pane of the experiment frame at the time the VAMAS blocks are overlaid in the display tile. If a row of VAMAS blocks are selected by clicking on the experimental-variable value for the row, then the left-most VAMAS block will determine the axes labels. Matrix signals are typically not calibrated and in the event the first VAMAS block contains the matrix signal, the profile would appear with the y-axis displaying an arbitrary scale.



When calibration is performed, only those profiles for which quantification information is supplied are converted to atom density. Profiles with an RSF of unity are scaled to ensure the profiles appear within the range for the calibrated profiles; hence the y-axis label is assigned the string “Arbitrary Units”. To display an overlay of the profiles where the Y axis is labelled with respect to a calibrated profile, namely “Atomic Density”, it is necessary that a calibrated VAMAS block is selected first. To select VAMAS block in an arbitrary order, left-click the first VAMAS block, then hold the Control Key down and left click the other blocks required for the display. The traces are displayed in the active tile by pressing the overlay toolbar button  and are ordered with respect to the selection sequence.

28Si

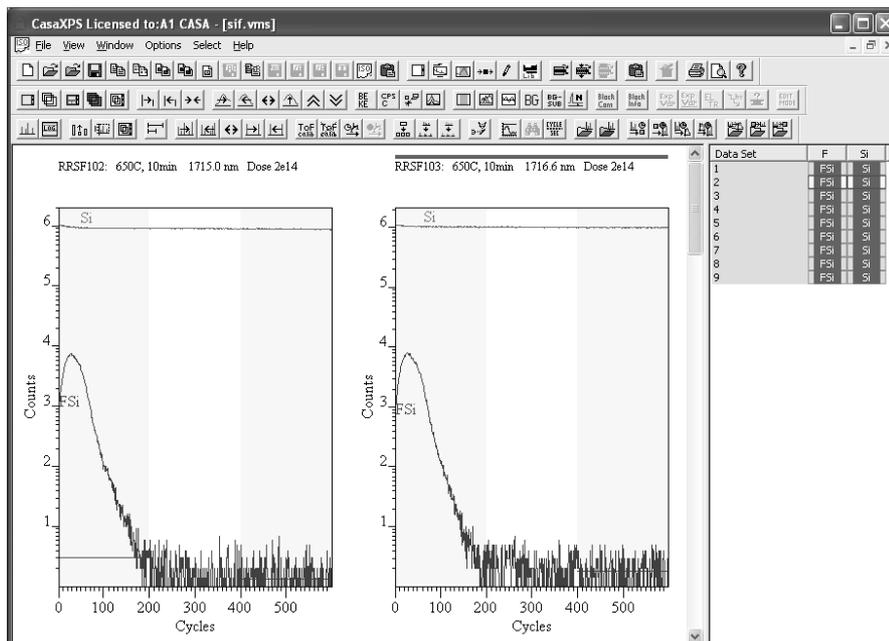


The VAMAS block for the impurity 28Si is selected before the matrix 69Ga.

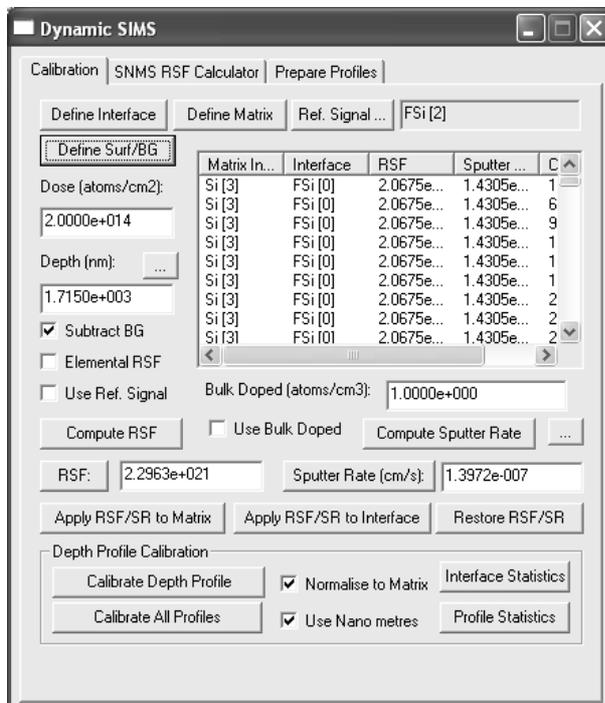
### ***Further Aspects of Dynamic SIMS Quantification***

#### **Logical Structure of a SIMS Depth Profile within CasaXPS**

A depth profile is a collection of VAMAS block all assigned to the same experimental variable value; typically the experimental variable will be an index number for a given file of data. There may be more than one profile per VAMAS file, where each profile will occupy a row as viewed via the right hand pane of the experiment frame.



For each VAMAS block within a raw depth profile, a number of corresponding variables are setup to offer fields for use in the quantification step. The important fields for quantification are displayed in the Matrix Index table on the Calibration property page of the Dynamic SIMS dialog window.



## Methods for Computation of RSF and Sputter Rate Values

RSF values are computed from standard materials using one of three approaches:

1. Matrix, dopant and crater depth.
2. Matrix, known bulk doped atomic density and crater depth.
3. Interface assignment with respect to depth and atomic density.

The computation of the RSF requires the determination of values from the Matrix signal and also the Implant. To support the determination of these quantities the matrices within a profile must be identified and a pair of regions defined to specify the surface zone as well as the appropriate background signal for a given mass.

## Identification of the Matrix and Interface Cycles

Defining the matrix for experiments involving a **Single matrix material** is achieved as follows:

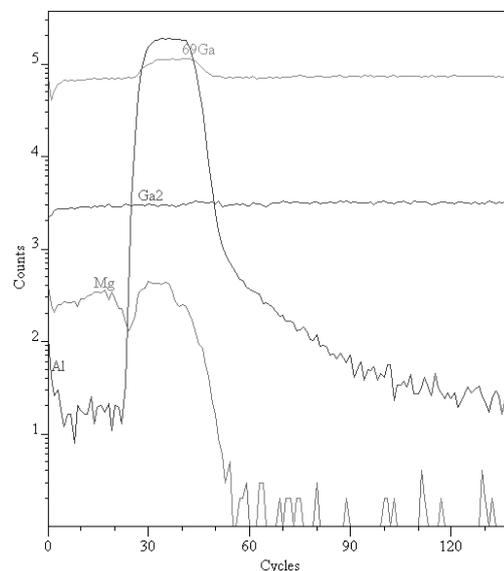
1. Display the matrix signal for each profile in the active display tile.
2. Press the Define Matrix button on the Calibration property page on the Dynamic SIMS dialog window.

A pop-up window will inform you that no matrix index is selected and asks whether the displayed matrix should be applied to all Cycles. Answer by pressing the Yes button. To avoid the warning message, before pressing the Define Matrix push button, first select all the table entries by pressing the header button for the column labelled Matrix Index. If there are any rows currently selected it will be necessary to de-select these rows before pressing the header Matrix Index.

If the file contains more than one depth profile and the matrix for each profile is overlaid in the active tile, then the operation of defining the matrix for each depth profile is performed in one go.

Defining the matrix for **Layered materials** is achieved as follows:

A key point for SIMS is that the signal from a given mass peak depends on the environment in which the isotope is found. As the crater bottom moves through an interface between differing materials there is potential for both the relative sensitivity and the etch rate to change during the course of the acquisition. The example used to illustrate a layered material involves profiling magnesium in gallium with an aluminium layer in the form of GaN : AlGaN : GaN (Dr Shadi Shahedipour, University of Albany, New York).



The secondary ion yield for Mg differs between the GaN and the AlGaN layers. Presentation of these types of samples requires a means of adjusting the Mg RSF for acquisition cycles depending on the aluminium signal strength.

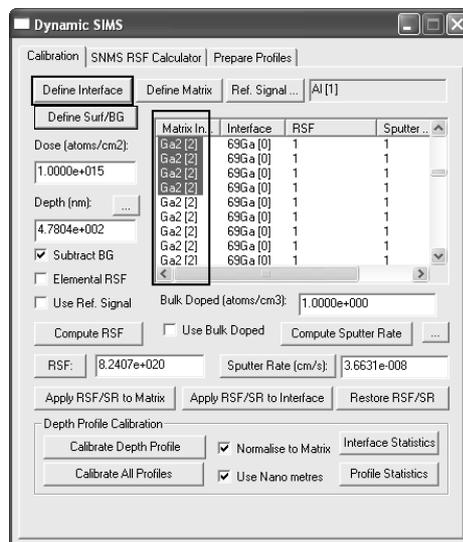
The table on the Calibration property page provides two columns headed Matrix Index and Interface. These columns specify the matrix material and



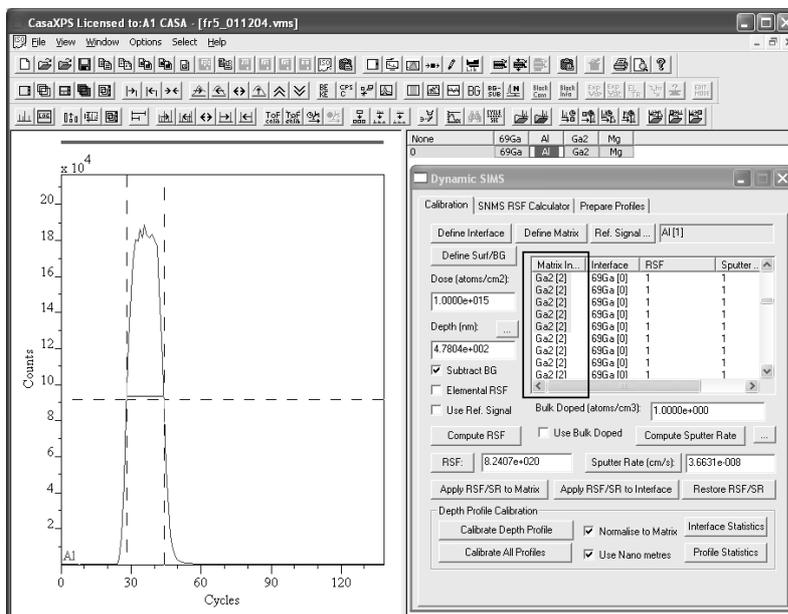
All VAMAS blocks from the same row in the right-hand pane will now show the same Ga2[2] matrix for each cycle throughout the profile.

At this point the Interface column is populated with the 69Ga[0] reference, that is, the matrix and interface columns are initialised to the first VAMAS block in the file. Only the matrix has so far been replaced by a reference to the Ga2[2] VAMAS block. Since the depth profile includes two environments from which the Mg signal is measured, to distinguish between these two environments the cycles corresponding to the AlGaN layer must be identified. The Al signal provides the means of specifying the appropriate set of cycles for which AlGaN is significant compared to the GaN layers.

1. Display the signal for Al in the active display tile.



2. Either using the table or the mouse (see below), select ranges of cycles within the Matrix Index column of the table on the Calibration property page.





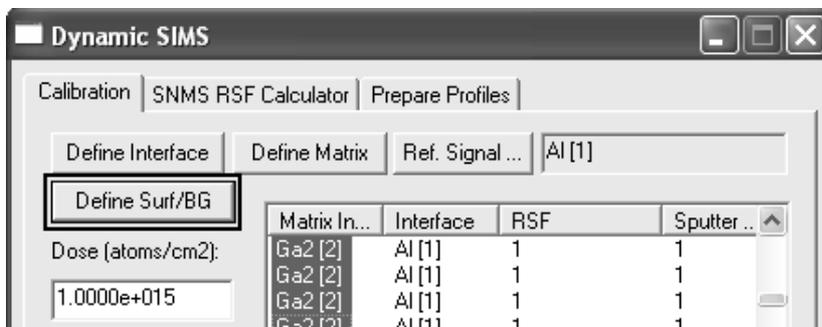
The use of the cursor and Shift key aids the identification of layered structures viewed via a profile signal. Once a set of layers are so indicated, the assignment is made by pressing the Define Matrix or Define Interface button, as appropriate.

## Surface Data and Background Signal

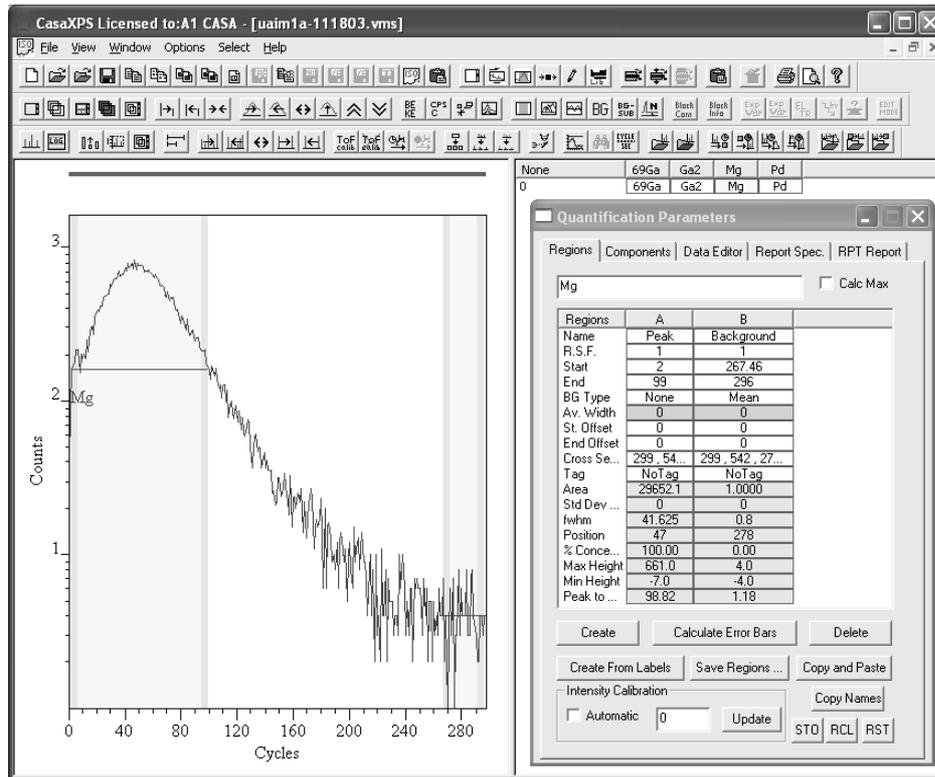
Since SIMS signal intensity depends on the matrix material, adventitious carbon or other surface contaminants may result in signal from the surface deviating from the bulk behaviour. It is therefore sometime appropriate to exclude surface acquisition cycles from the RSF determination. Further a bulk material may also cause a residual signal for the implant and therefore removal of a background count rate is also appropriate. To aid the specification of these two limitations when calculating RSF values, two regions must me defined for each VAMAS block before an RSF can be computed.

Defining the Surface and Background Regions:

1. Display any number of VAMAS blocks in the active display tile.
2. Press the Define Surf/BG button.



Two regions will appear on each profile; the left most region indicates the peak and should be adjusted to start just after cycles associated with any surface spike. The second right-most region defines the background to the tail of an implant. Both regions can be adjusted using the Quantification Parameters dialog window when viewing the Regions property page. The left mouse button may be used to drag the start and end position of these regions whenever the Region property page is active. Adjustment under mouse control is available when grey vertical lines at either end of the regions are displayed which appear when the Region property page is top-most on the dialog window.

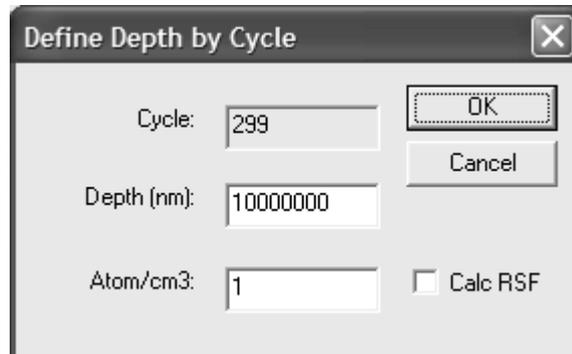


### Three Ways to Calculate RSF Values from Standard Samples

Once the matrix and regions have been defined, the RSF can be computed by the appropriate method:

- Either: enter the Implant dose in Atoms/cm<sup>2</sup> and the measured crater depth in nanometres then press the Compute Sputter Rate button before pressing the Compute RSF button. Pressing these buttons will result in the corresponding values appearing in the boxes below the buttons.
- Alternatively, if a bulk doped standard is in use, tick the box labelled **Use Bulk Doped** and enter the known atom density into the above data input field. When a bulk doped standard is used to compute the RSF, both the implant and matrix require regions.
- The third method for computing the RSF is via a known implant depth and atom density. The button to the right of the Depth field, namely,  ... results in a dialog window in which a depth and/or a peak intensity can be entered. The position of the implant is defined using the Matrix Index table by making a single selection in that table. The appropriate cycle can be identified by left-clicking on the peak in the left-hand pane active tile. The Matrix Index table scrolls to show the cycle corresponding to the mouse selection and the table entry is

therefore offered for selection prior to invoking the Define Depth by Cycle dialog window. If the correct depth and corresponding atoms per  $\text{cm}^3$  are entered, the Calc RSF tick box is ticked and the OK button is pressed, the RSF, Depth and Sputter Rate fields will be updated.



### Adding RSF and Sputter Rates to Profile Data

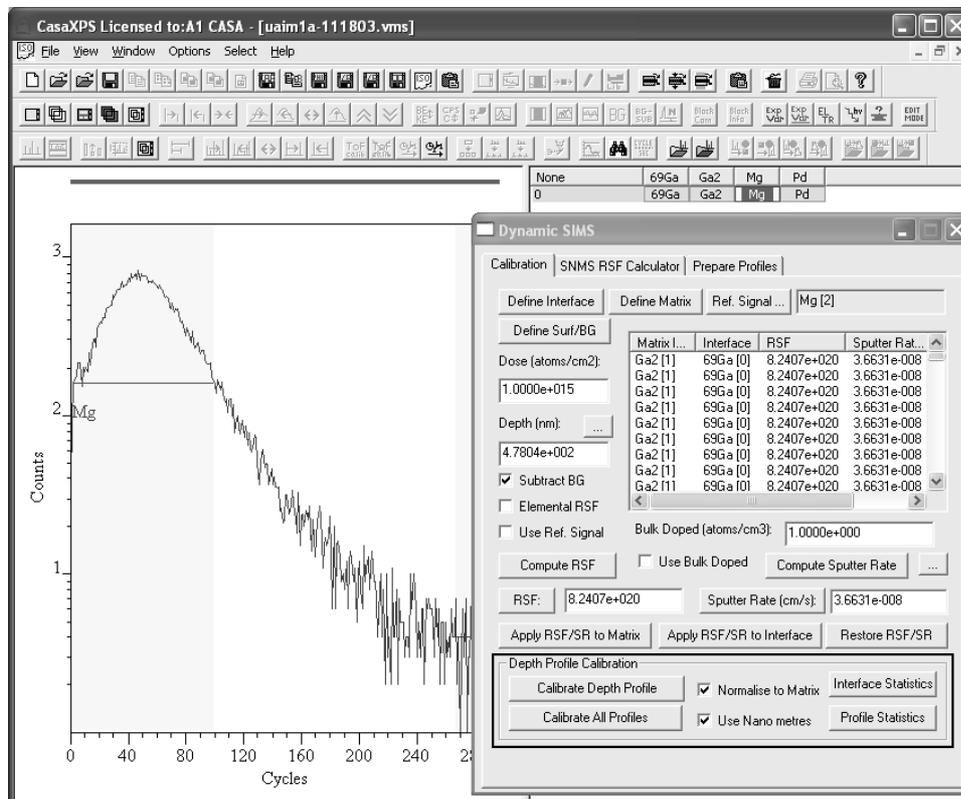
Once an RSF is computed and the appropriate Sputter Rate entered for an implant in a given matrix, the profile can be update with these values: select a cycle from the Matrix Index table with the appropriate matrix entry and press either the **Apply RSF/SR to Matrix** button or the **Apply RSF/SR to Interface** button. Each cycle within the profile with the same entry as the selected matrix index will be updated with both the Sputter Rate and the RSF. If the material is a multilayer structure the procedure should be repeated for each layer, where the RSF and Sputter Rates are first determined from a standard profile. An RSF/Sputter Rate pair can be extracted from another profile by first displaying the profile, making a selection in the Matrix Index table and pressing the **Restore RSF/SR** button. The RSF/Sputter Rate from the indicated matrix index will be entered into the fields on the dialog window, thus allowing the unknown to be subsequently displayed and these restored values from the standard used to update the unknown profile. Note, the Dose and depth for single matrix material are computed when the button **Apply to Selected Matrix** is pressed.

### Applying Calibration Parameters to One or More Profiles

Once RSF and Sputter Rates have been assigned to each depth profile, the data are calibrated by pressing the Calibrate Depth Profile button. If multiple profiles are prepared and overlaid in the active tile, pressing the Calibrate All Profiles button results in each profile, so selected, being calibrated and

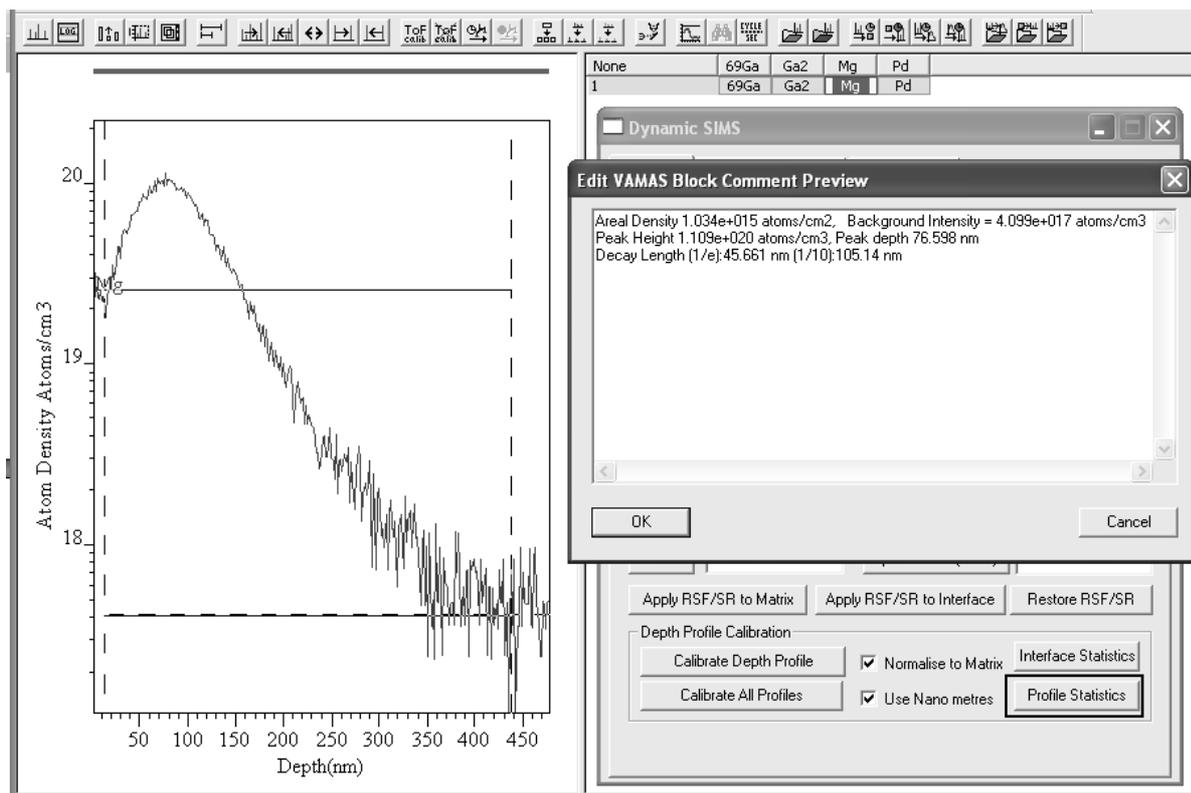
entered into a single experiment frame. The depth scale units must be selected prior to calibration using the tick box **Use Nanometres**.

Note: If normalization to the matrix is not required, it is necessary to compute the RSF with the same selection of the Normalize tick box.



## Depth Profile Statistics: Areal Density and Decay Length

Areal Density and Decay Length are computed as part of the Depth Profile Statistics. The procedure for calculating these statistics requires a pair of cursors to be defined on the displayed profile in the active tile. The aim is to mark the region over which the profile peak appears. To mark the cursors on the profile: hold the Shift Key down and drag a box starting from the left of the peak and ending at the right-hand end with the mouse positioned at the intensity of the background. On pressing the Profile Statistics button a dialog window appears showing the current text in the VAMAS block comment plus a set of lines offering the new calculated profile statistics. If it is desired to include these new lines in the VAMAS block comment, then the OK button should be pressed, otherwise the Cancel button will exit without altering the VAMAS block comment. Note, the text in the VAMAS block comment can be edited within this window leaving only the information so required.



## Maintaining Standards Library Files

Once standards have been prepared and RSF/Sputter Rates computed, these depth profiles can be moved to other files containing profiles from standards.

The toolbar buttons   allow VAMAS blocks to be copied into an existing file and also delete from a file. If a number of standard material profiles are located in a single file, the  button offers a means of searching the strings within a VAMAS block comment and those matched are both selected in the right-hand pane of the experiment frame and are also displayed in the scrolled list of display tiles. VAMAS block comments can be edited using the  toolbar button.

## Step-by-Step Description of Quantification for a Multi-Layer Sample

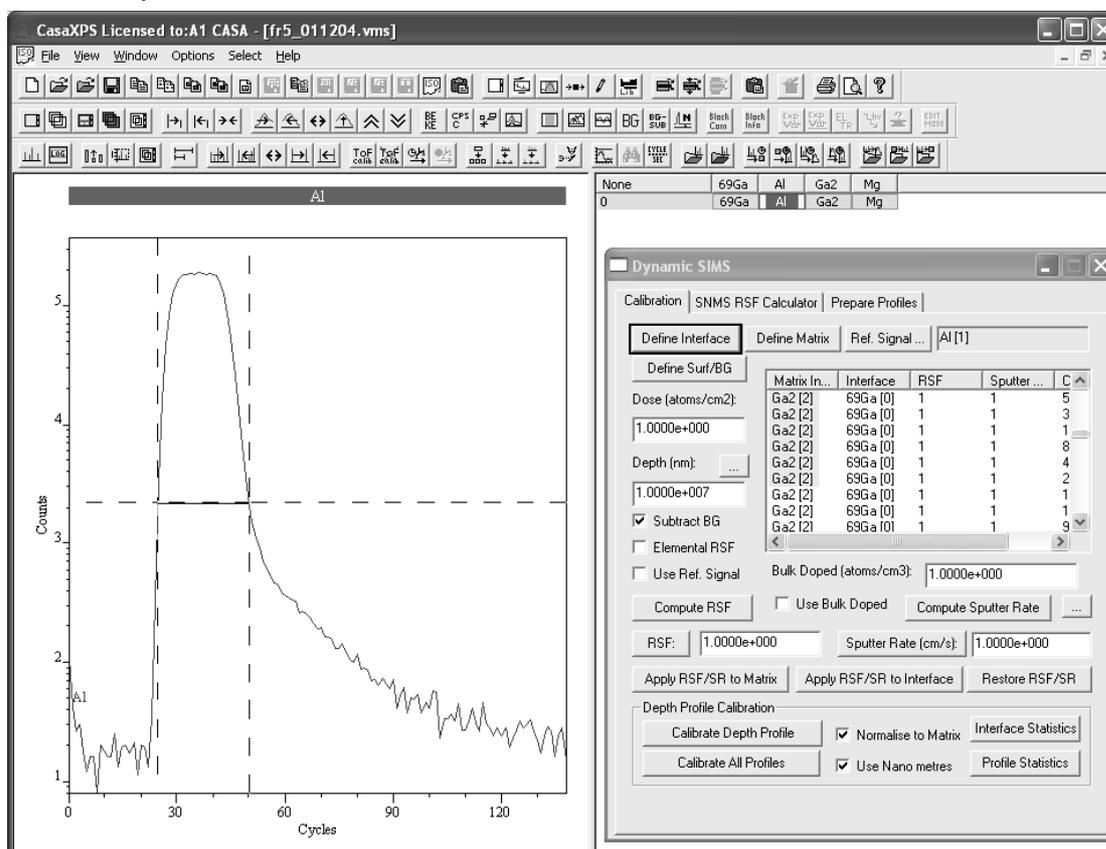
In this example, the desired result is to plot atomic density verses depth for Mg implanted in Gallium. To achieve this end and owing to the layered structure, four masses were monitored, where two labelled 69Ga and Al define the layer structure while the trace labelled Ga<sub>2</sub> represents a constant matrix signal, to which the Mg signal is normalized.



Select all the cycles under the Matrix Index column in the table on the Calibration property page and press the Define Matrix button; the selected entries under the Matrix Index column will change to Ga2[2], thereby showing the matrix is defined.

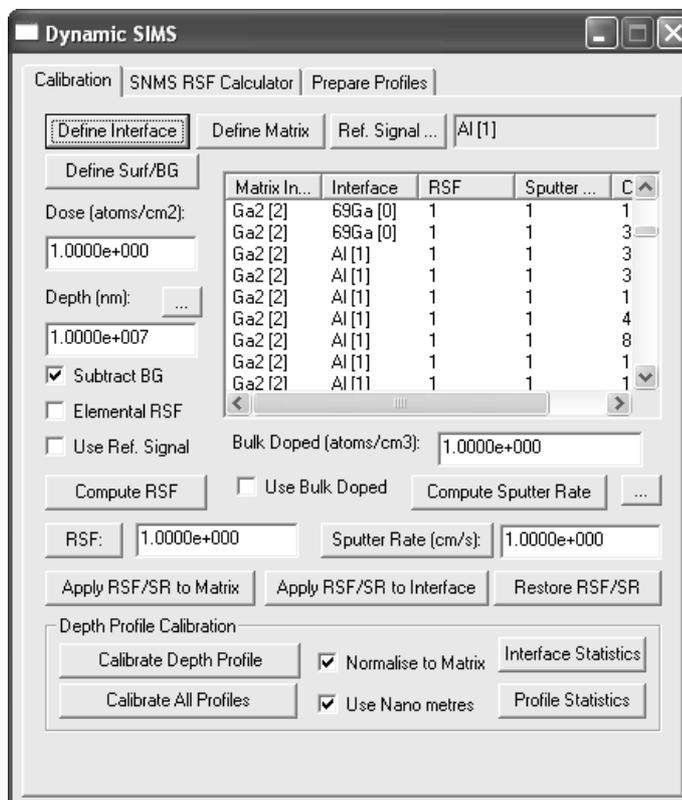
### Step 2: Define the Layer Structure

The structure of the material is GaN : AlGa<sub>N</sub> : GaN (Dr Shadi Shahedipour, University of Albany, New York) therefore the matrix definition alone is not sufficient to specify the cycles for which different sputter rates and RSF must be assigned. Thus a sample such as this one requires the definition of quantification information using the interface column within the table on the Calibration property page. The AlGa<sub>N</sub> layer is characterized by the trace labelled Al. To define a layer within the profile, the signal Al is used to select the set of cycles recorded between the two interfaces.



Before using the mouse to indicate the interfaces, ensure there are no selected cycles in the table on the Calibration property page. Clicking on any column away from the Matrix Index column will de-select all cycles. Note, repeated use of the mouse will add to the current selection, allowing complex multilayer materials to be specified. Mark the AlGa<sub>N</sub> layer by holding the Shift-Key down and then dragging a box from the left to the right

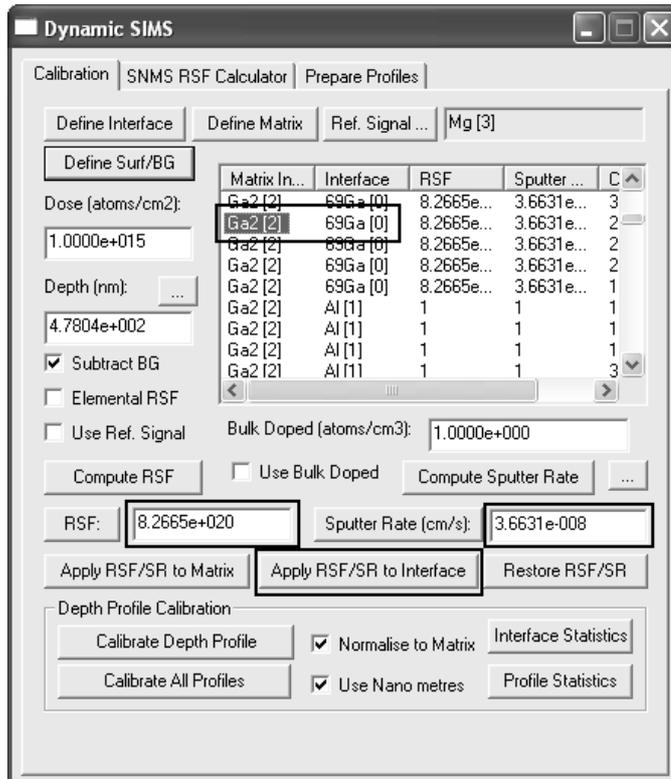
of the AlGa<sub>N</sub> peak. The result of such an action is shown in above. All the cycles within the table on the Calibration property page between the vertical cursors shown above are selected by the mouse action and so pressing the **Define Interface** button on the same property page will cause the Interface column in the table to be updated.



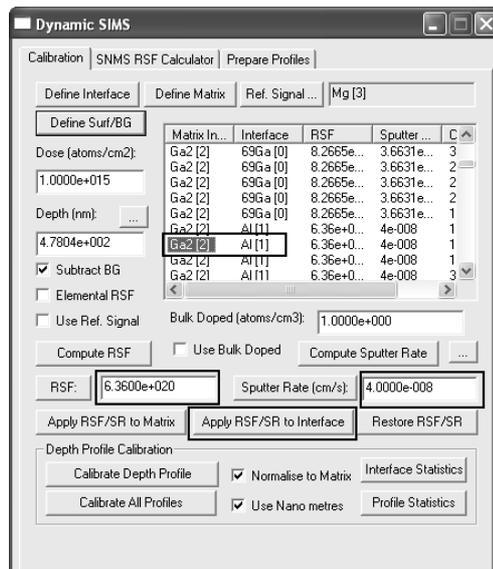
### **Step 3: Enter RSF and Sputter Rate Values**

In this example the RSF and Sputter Rate for the two layers are assumed to be known. All that is required is to add sputter rates and RSF for each of the three layers; the values are entered on the Calibration property page. The required information for quantification are two RSF and SR pairs, which must be entered correspondingly for the GaN and AlGa<sub>N</sub> layers. Since the matrix does not define the layer structure, the assignments are made by using the **Apply RSF/SR to Interface** button. After displaying the Mg trace in the active tile the RSF and sputter rate for each layer can be entered in turn. Since the Interface column was initially all assigned 69Ga[0], the layer assignment based on the Al signal only altered the range of cycles specified by the vertical cursors. As a result the GaN layers are identified by the Interface entries 69Ga[0]. Thus, both the GaN layers are assigned RSF and sputter rates by selecting one cycle for which the interface column contains 69Ga[0], entering the appropriate RSF/SR and pressing the **Apply RSF/SR to Interface**

button. Each cycle previously designated as part of the 69G [0] layer will receive the RSF/SR pair.

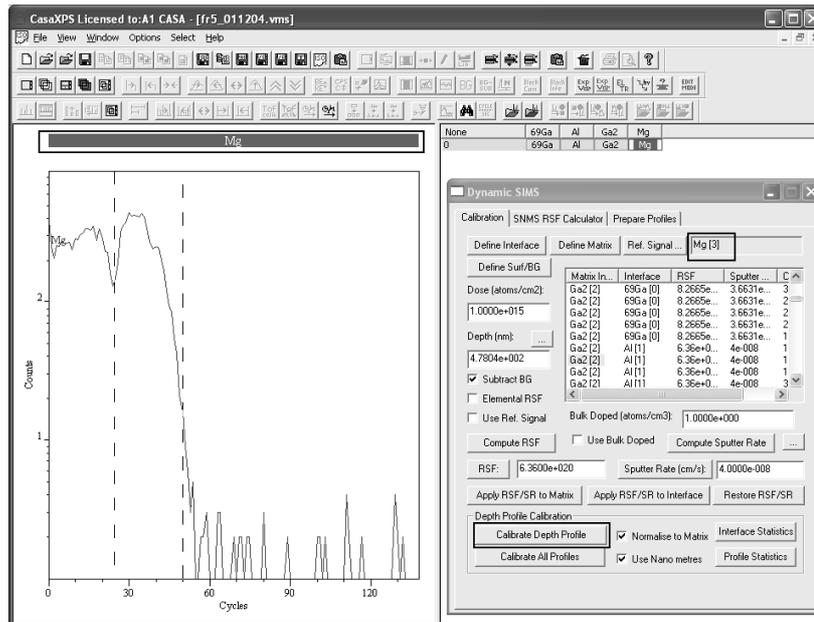


Similarly, the AlGaN RSF/SR values are entered in the text-fields, one cycle with an Interface column of Al[1] selected and the **Apply RSF/SR to Interface** button pressed a second time. Again, each cycle designated as Interface Al[1] will receive the RSF/SR pair.

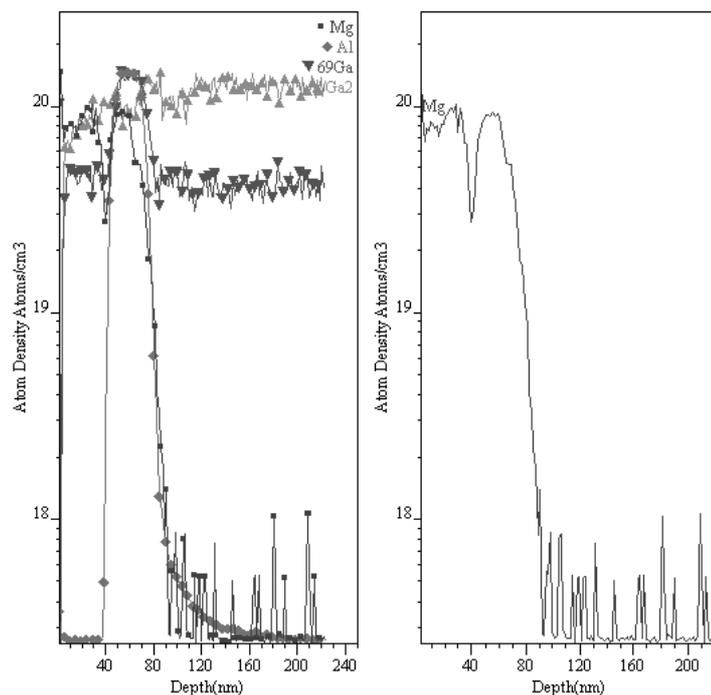


#### Step 4: Calibrate Mg Profile

Calibration is performed by displaying the Mg profile in the active tile and pressing the Calibrate Depth Profile button.

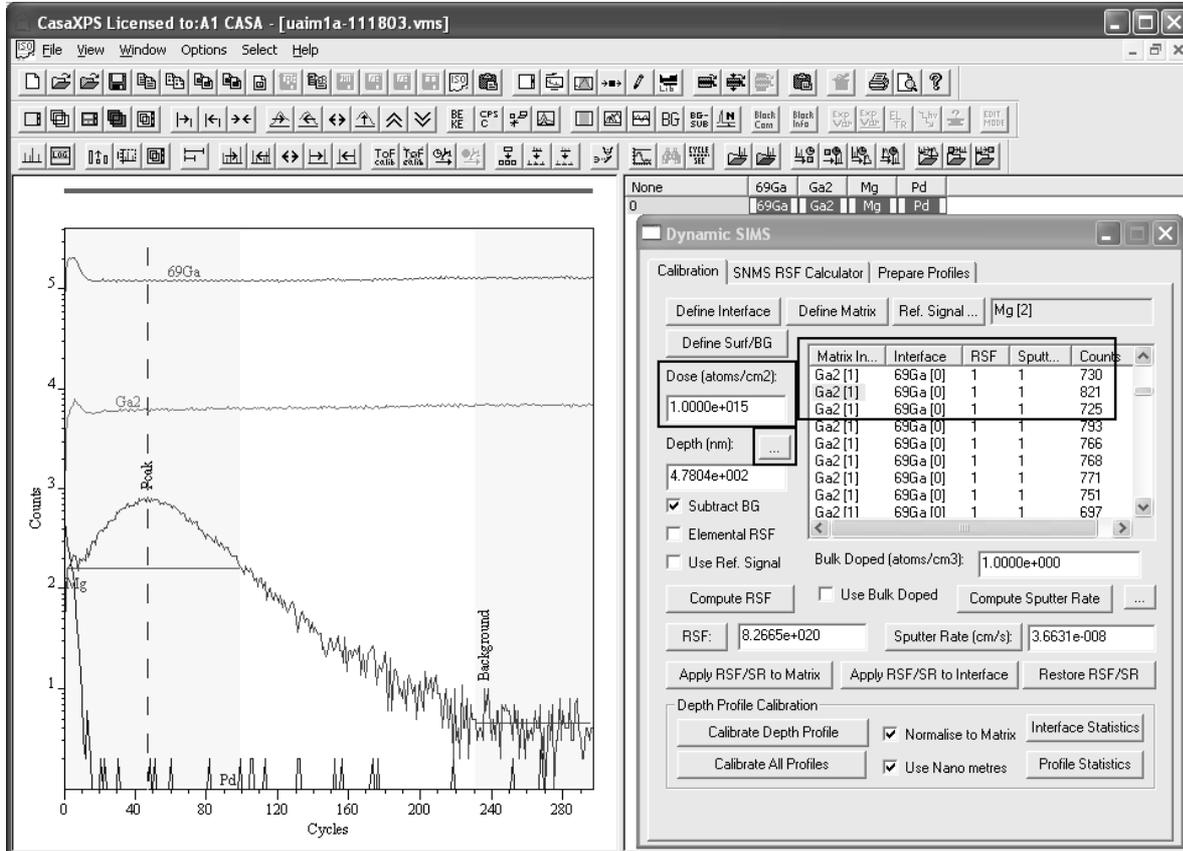


In this example, the only mass for which RSF/SR pairs are entered is Mg. The SR are automatically assigned to all masses, however the RSF values for masses other than Mg remain set equal to unity. A consequence of leaving an RSF equal to unity is that on Calibration to atomic density and depth, masses for which the RSF is equal to unity will be scaled to the atomic density range of any properly calibrated masses. This allows an overlay with respect to the calibrated traces, without requiring the RSF for all masses to be assigned prior to calibration. Counts per second traces are available in the calibrated experiment frame as the second corresponding variable (Ctrl PageUp/Ctrl Page Down).



## An Example of Computing an RSF using Dose and Implant Peak Depth

A profile was obtained from GaN undoped epi growth ion implanted with  $^{24}\text{Mg}$  at a dose of  $1.0\text{e}15$  atoms per  $\text{cm}^2$ . The depth at the peak of the Mg counts is 77 nm. Computation of an appropriate RSF is performed as follows:



### Step 1: Define the Matrix

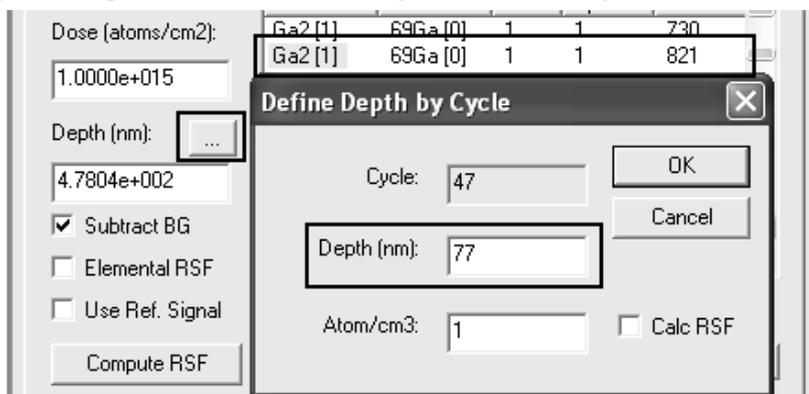
Display the Ga2 matrix profile in the Active Tile, press the header button labeled Matrix Index in the table to select all cycles and press the Define Matrix push button on the Calibration property page. The table on the same property page will update to show that the Matrix index for each cycle is now assigned to the Ga2 profile.

### Step 2: Define the Surface Layers and also the Background for the Mg Profile

Display the Mg profile in the active tile and press the button labeled Define Surf/BG. Two regions are created on the Mg profile. The left-most end of the left-most region defines the surface layers, while the background to the right-most of the two regions estimates the background to the Mg signal.

### ***Step 3: Define the Depth Scale***

In this example, the depth scale is defined to be 77nm at the maximum signal for the Mg profile. Using the left-mouse button, click on the profile to indicate the position of the Mg maximum values. The table entries on the Calibration property page will scroll so that the cycle corresponding to the position of the vertical cursor, which is located at the top of the visible portion of the list. Select the entry at the top of the visible portion and press the button next to the Depth (nm): label. A dialog window appears in which the selected cycle index is already entered and a text-field for the Depth (nm) corresponding to the indicated cycle can be input.



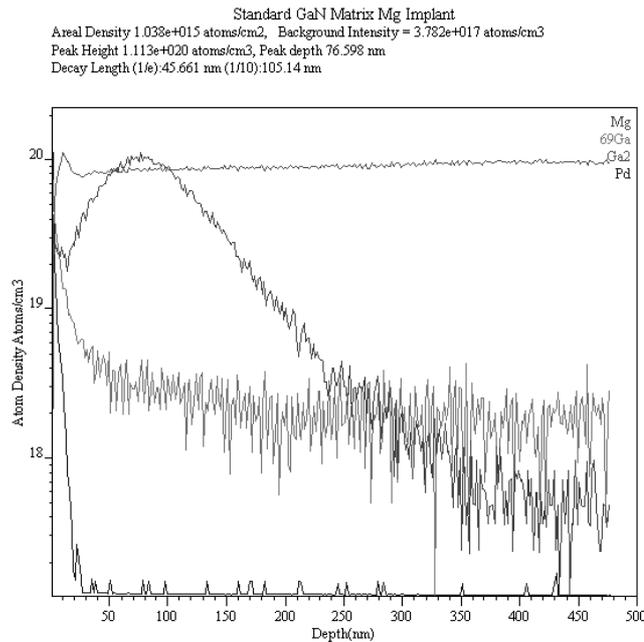
On pressing the OK button, the Calibration property page is updated with the depth computed from the **Define Depth by Cycle** dialog window values.

### ***Step 4: Enter the Dose and Compute the RSF***

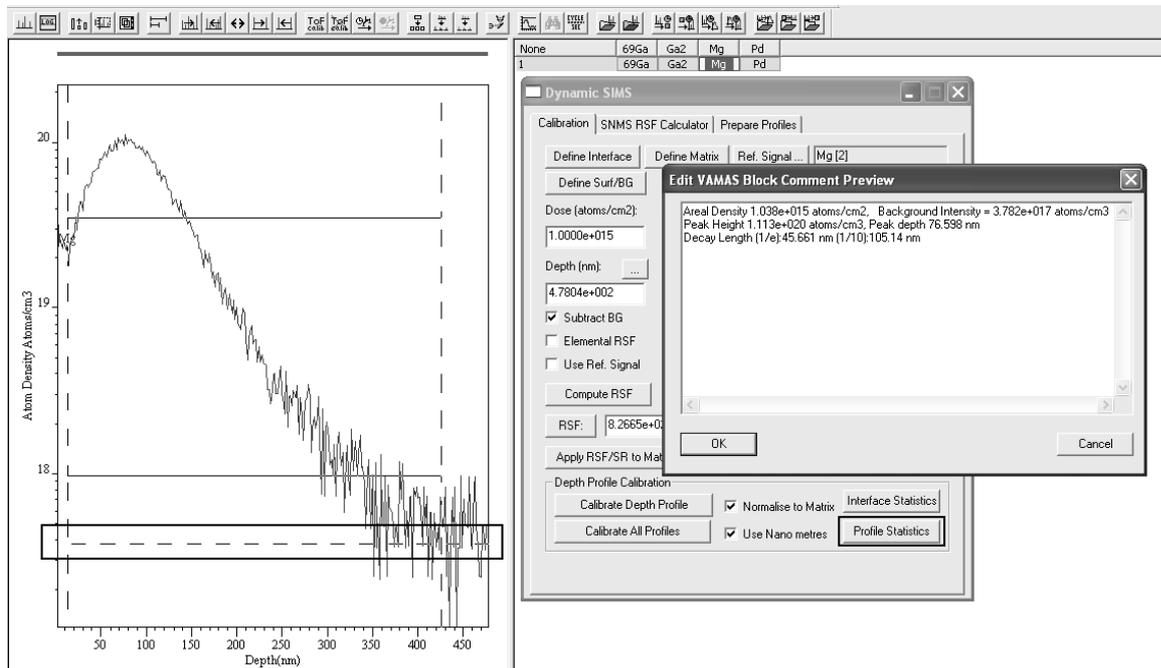
Enter the dose in atoms per cm<sup>2</sup> on the Calibration property page and press the button labelled **Compute RSF**. If the elemental RSF is required, the tick-box just above the Compute RSF button should be ticked.

### ***Step 5: Calibrate the Mg Profile***

Once the RSF is computed and the sputter rate updated, the values for each cycle corresponding to the Mg profile (currently displayed in the active tile) must be updated. In this example, the assignment for the matrix is sufficient to target the cycles for which RSF and sputter rates must be applied. Simply select any cycle using the Matrix Index column in the table and press the **Apply RSF/SR to Matrix** button. Since all the cycles are defined to have the same matrix, the table for the Mg profile will contain values for the RSF and sputter rate throughout. To calibrate the profile, press the button labelled **Calibrate Profile**.



Note that the Profile Statistics button has been used to create a VAMAS block comment showing the Areal Density and Decay Length for the Mg profile. Also note how the profiles for which no RSF is specified are scaled to allow their visualization within the same scale as the calibrated Mg profile.

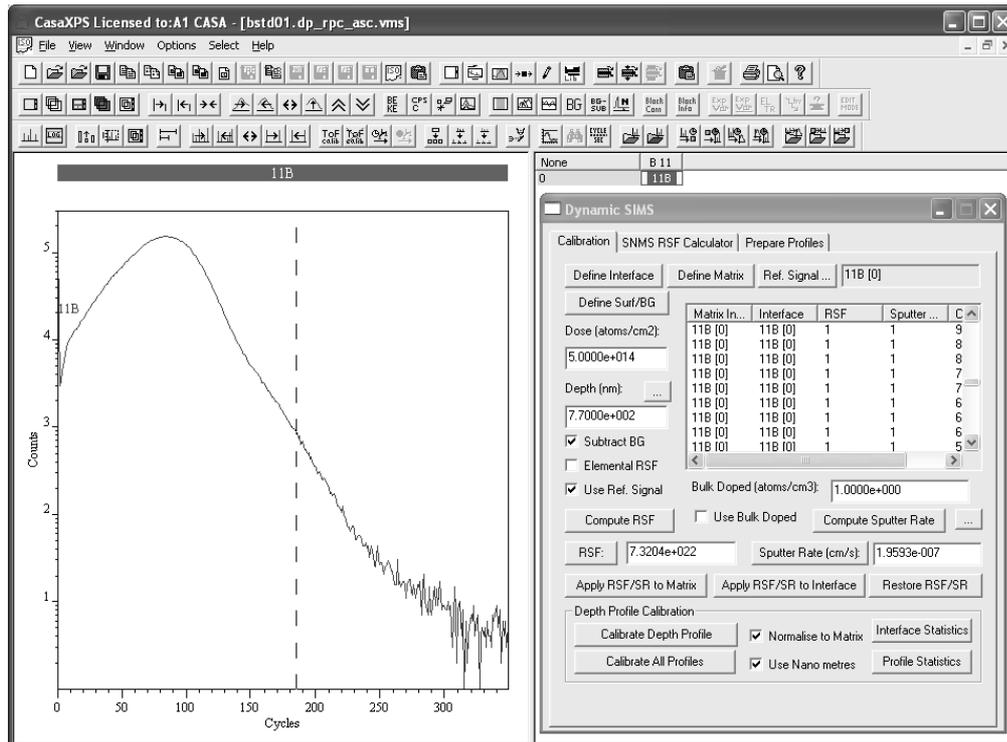


### Computing RSFs where the Matrix Signal is Measured following the Completion of the Implant Profile

Cameca dynamic SIMS instruments permit experiments in which only the implant is profiled. The inclusion of the matrix intensity in the computed RSF is achieved by measuring the matrix signal after the implant signal attenuates

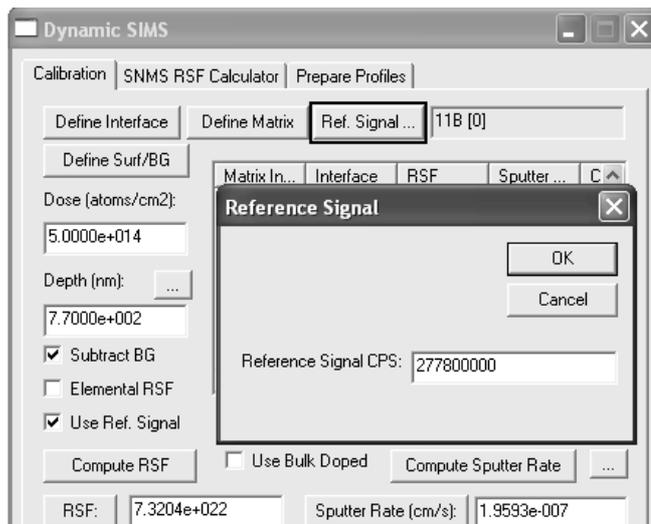
to background levels. The assumption is therefore that the matrix count rate is constant during the acquisition of the dopant profile. While in principle the Cameca files contain the experimental parameters for the profile, there are occasions where the matrix reference signal must be inspected and manually entered. To calculate the RSF for a standard material based on an implant profile only, the following features are employed.

The VAMAS file for a single boron implant in silicon consists of a single VAMAS block.



Following the measurement of the boron profile, the Cameca monitors the matrix signal, and records the counts per second for the matrix in the data file. It should be noted that the crater depth measured following such an experiment includes the depth etched during the matrix measurement which occurs after the boron profile is completed.

Calculation of the RSf for  $^{11}\text{B}$  implanted in silicon is computed identically to previous examples with the exception that the user inputs the matrix signal in counts per second via the Ref Signal button on the Calibration property page. The VAMAS block containing the boron profile is updated with the intensity of the matrix signal via the Reference Signal dialog window invoked by the Ref Signal button.



Computing the RSF is performed as follows:

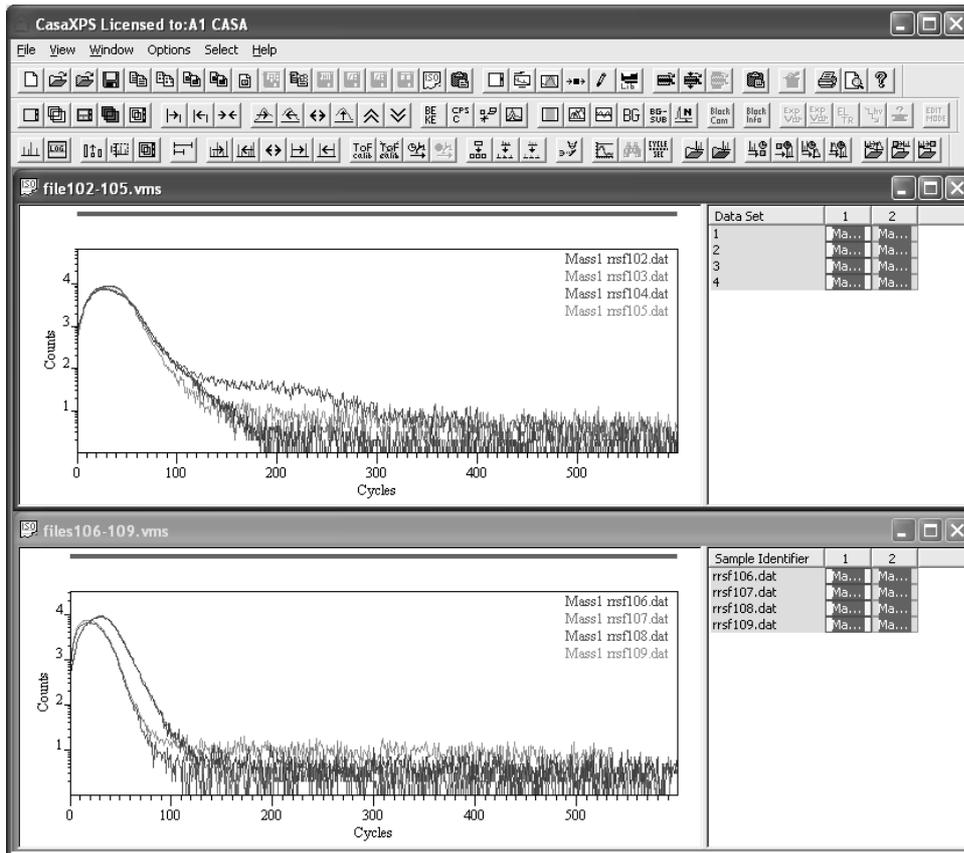
1. Enter the crater depth (770 nm) and press the Compute Sputter Rate button.
2. Enter the dose ( $5 \times 10^{14}$  atoms per  $\text{cm}^2$ ).
3. Check that the reference signal is correctly assigned and enter the correct value by pressing the Ref Signal button.
4. Press the Compute RSF button.

## ***Gathering Profile Data for Display and Calibration Purposes***

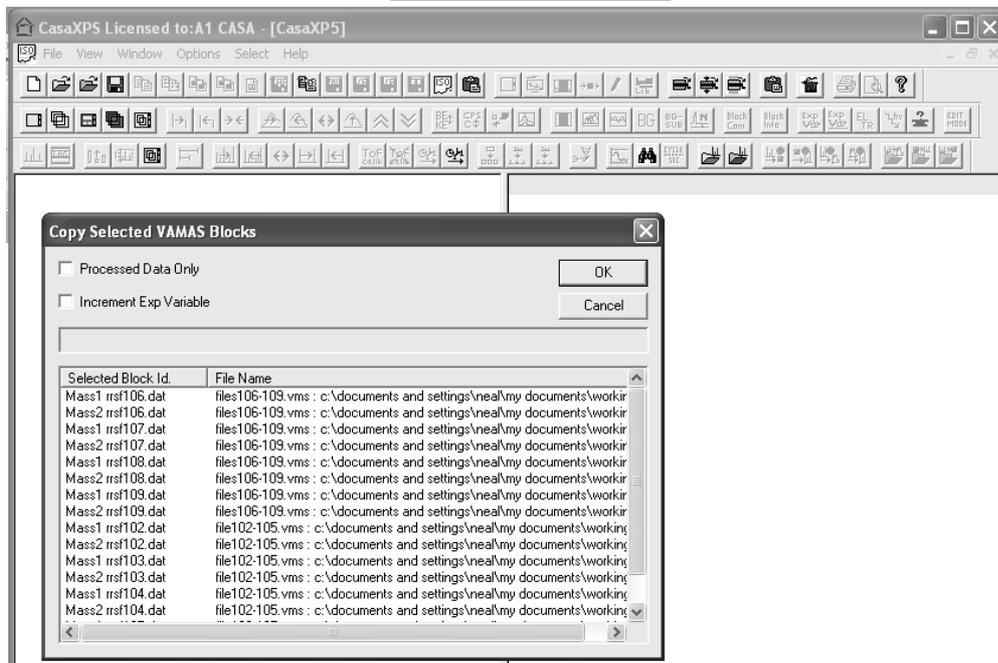
Profile data typically is stored as individual VAMAS files. There are however reasons why merging these files into a single experiment frame is desirable. For example, data can only be overlaid for display purposes for data located in the same experiment frame. A further reason for moving profiles into a single experiment frame is that Calibration of a dynamic SIMS profile is performed on the Calibration property page and the button for calibrating multiple profiles only acts on data within a given experiment frame. Copying profiles into a single experiment frame permits many profiles to be calibrated in one action.

By way of example, consider merging two VAMAS files containing profile data for which a display of the data in overlay format is required.

1. Open each of the two data files in CasaXPS.
2. Using the Window menu, tile the two experiment frames so that both right-hand panes are visible such that the VAMAS blocks are easily selected.

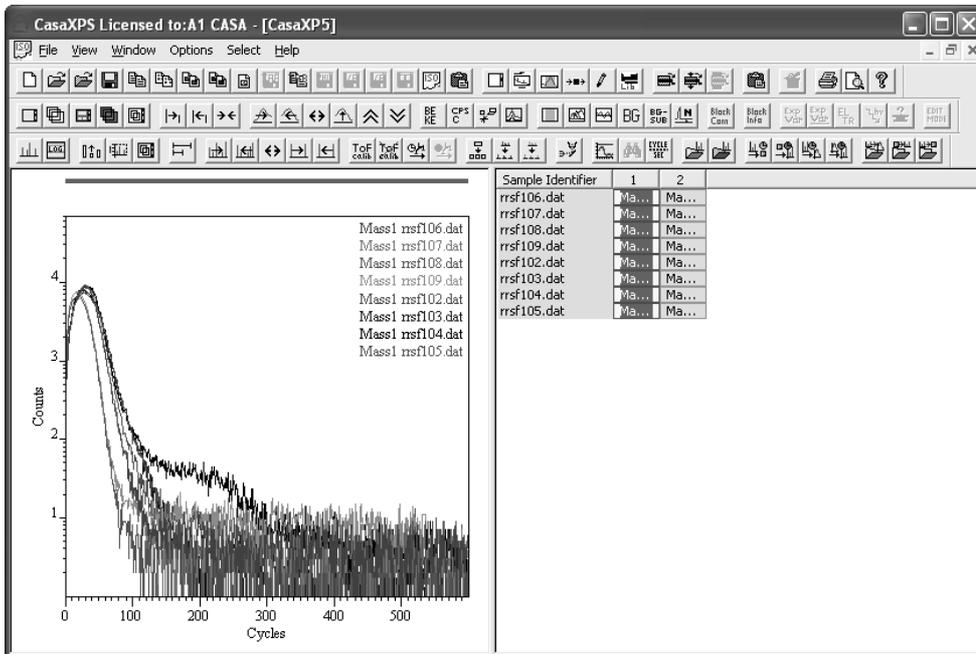


3. Create a new experiment frame  and press the Copy/Paste VAMAS blocks toolbar button.



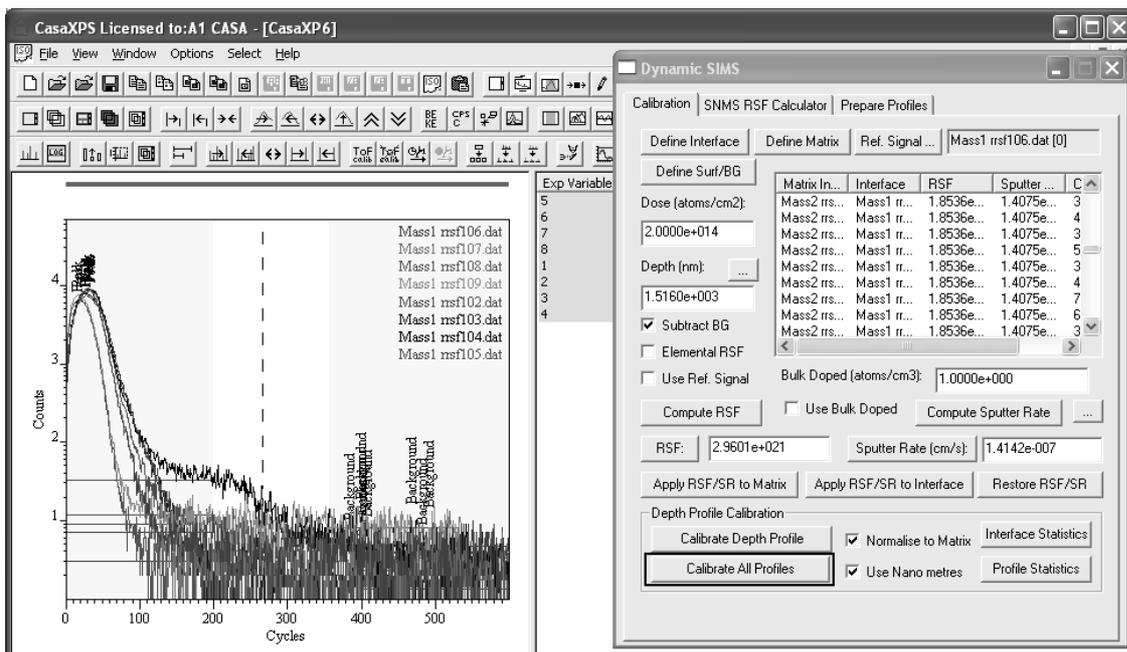
4. Check that the VAMAS blocks listed on the Copy Selection dialog window match those selected in the two files and press the OK button.

The selected VAMAS blocks now appear in the new experiment frame. Note that the selected VAMAS blocks are transferred to the experiment frame with focus. In the event that the experiment frame with focus already contains VAMAS blocks the selected VAMAS blocks are appended to the existing blocks. The target experiment frame for this example was initially empty therefore only the selected blocks appear in the experiment frame.

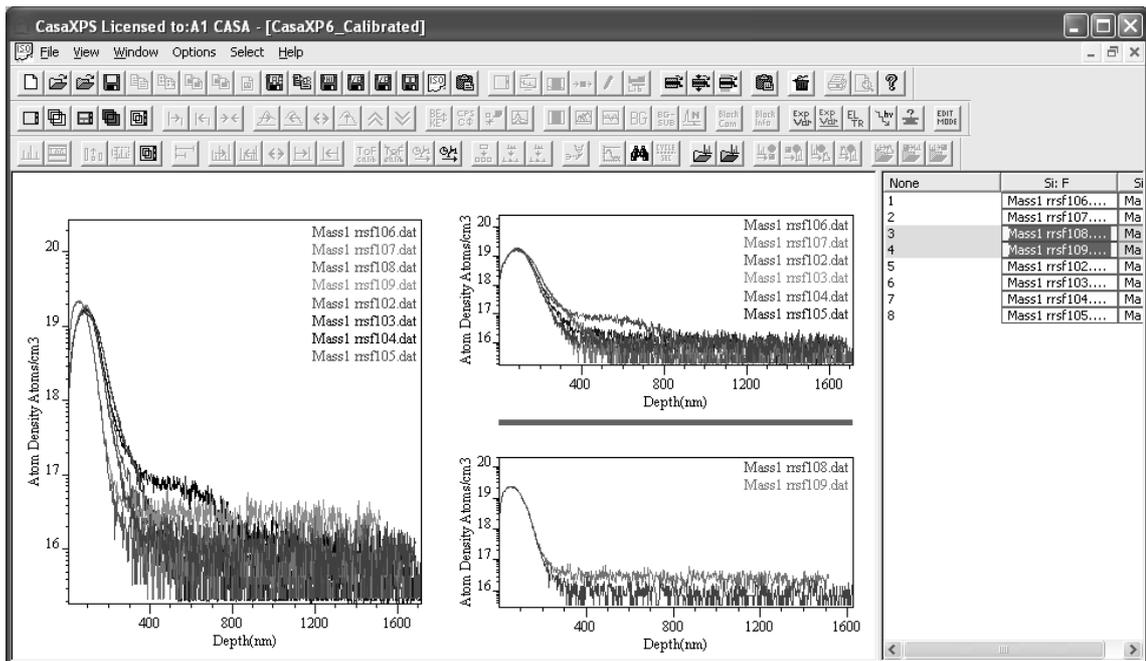


5. Save the new experiment frame to disk.

After preparing the profiles with appropriate RSFs and sputter rates the entire set of profiles is calibrated by overlaying the implant VAMAS blocks in the active tile and pressing the Calibration All Profile button.



A new experiment frame appears contain the quantified profiles.

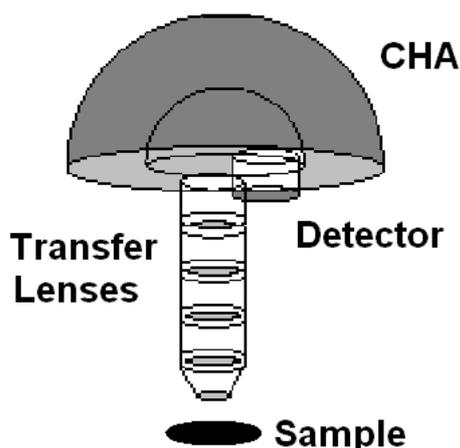


# XPS Instrument Transmission Correction

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## Electron Spectroscopy

X-rays illuminate an area of a sample causing electrons to be ejected with a range of energies and directions. The electron optics, possibly a combination of electrostatic and/or magnetic lens units, collects a proportion of these emitted electrons. Not all electrons emitted from the sample are transferred through the apertures and focused onto the analyser entrance slit. Electrostatic fields within the concentric hemispherical analyser (CHA or HSA) are established to only allow electrons of a given energy, the so called Pass Energy (PE), to arrive at the detector slits and onto the detectors. The efficiency with which electrons are collected as counts at the detector varies



as a function of the kinetic energy imparted to the electrons by the photoionisation process. Therefore, knowledge of these transmission characteristics is fundamental to proper quantification of XPS data.

A hemispherical analyser and transfer lenses are typically operated in the two most common modes, namely, Fixed Analyser Transmission (FAT), also known as Constant Analyser Energy (CAE), or Fix Retard Ratio (FRR) also known as Constant Retard Ratio (CRR). In FAT mode, the pass energy of the analyser is held at a constant value and it is entirely the job of the transfer lens system to retard the given kinetic energy channel to the range accepted by the analyser. Most XPS spectra are acquired using FAT. The alternative mode, FRR, scans the lens system but also adjusts the analyser pass energy to maintain a constant value for the quantity “initial electron energy” / “analyser PE”. This mode is typically used for Auger spectra since the energy interval accepted by the detection system (i.e. resolution) increases with kinetic energy and recovers weak peaks at high kinetic energies while

restricting the intense low energy background that could damage the detection system.

Electrons of a specific initial kinetic energy are measured by setting voltages for the lens system that both focus onto the entrance slit the electrons of the required initial energy and retards their velocity so the kinetic energy after passing through the transfer lenses matches the pass energy of the hemispherical analyser. To record a spectrum over a range of initial excitation energies it is necessary to scan the voltages applied to these transfer lenses; the prescription for a lens voltage is known as a lens function. Each operating mode for an instrument requires a lens function for each lens and these lens functions are typically stored in some configuration file used by the acquisition system. The efficiency with which electrons are sampled by a spectrometer is very dependent on these lens functions and without properly tuned lens functions the performance of an instrument can be severely impaired. Even with a well-tuned system the collection efficiency varies across the many operating modes and it is necessary to characterize an instrument using a corresponding transmission function for each of the lens modes, energy resolutions, aperture settings and spot-sizes of the x-ray source.

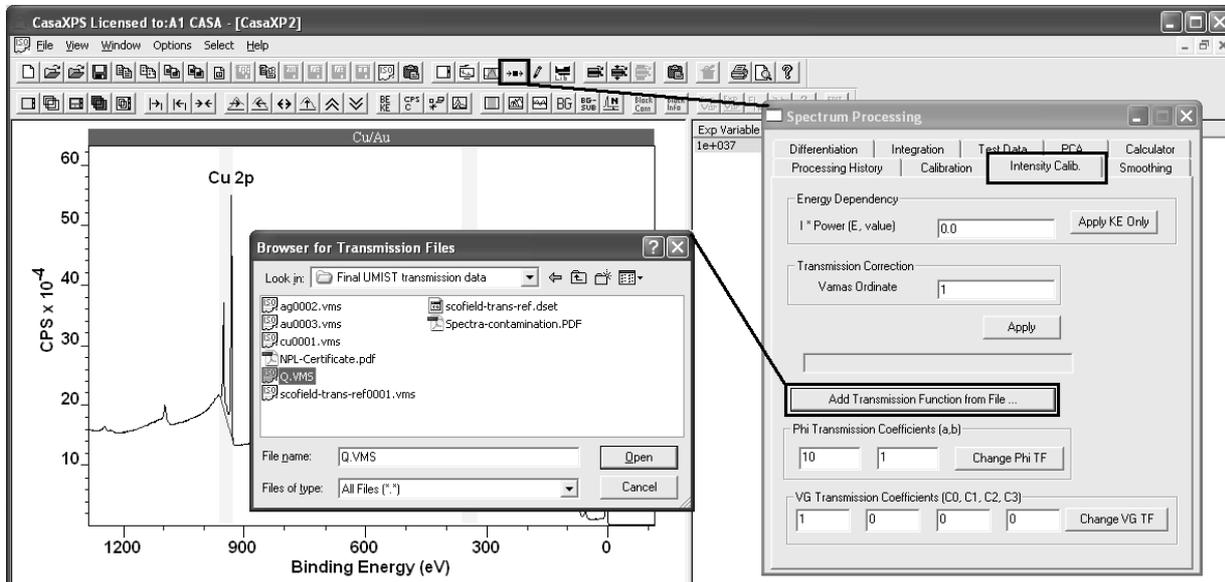
Transmission correction is central to quantitative XPS. Without proper transmission correction, a comparison of results measured from the same sample using different operating modes for an instrument would show significant variations in atomic concentrations. Thus, following any changes to the lens functions, aperture positions and even changes due to detector aging require the calibration of the intensity scale, which involves computing the transmission functions for any operating mode used in practice.

### ***Quantification of Spectra using Transmission Correction***

A transmission function, when available, is included with the spectral data in a VAMAS block as a second corresponding variable. Transmission functions are either:

1. Added to the data by the acquisition system e.g. SpecsLab 2 and Kratos Vision 2 VAMAS files.
2. Added to the data when converted through CasaXPS to the ISO 14976 format e.g. PHI Multipak, Thermo Advantage ASCII, Kratos KAL ASCII and SPECSLAB 1.

3. If the transmission function is available in certain formats, added to the data using options on the Intensity Calib property page on the Spectrum Processing dialog window e.g. instruments calibrated with the NPL intensity calibration system.



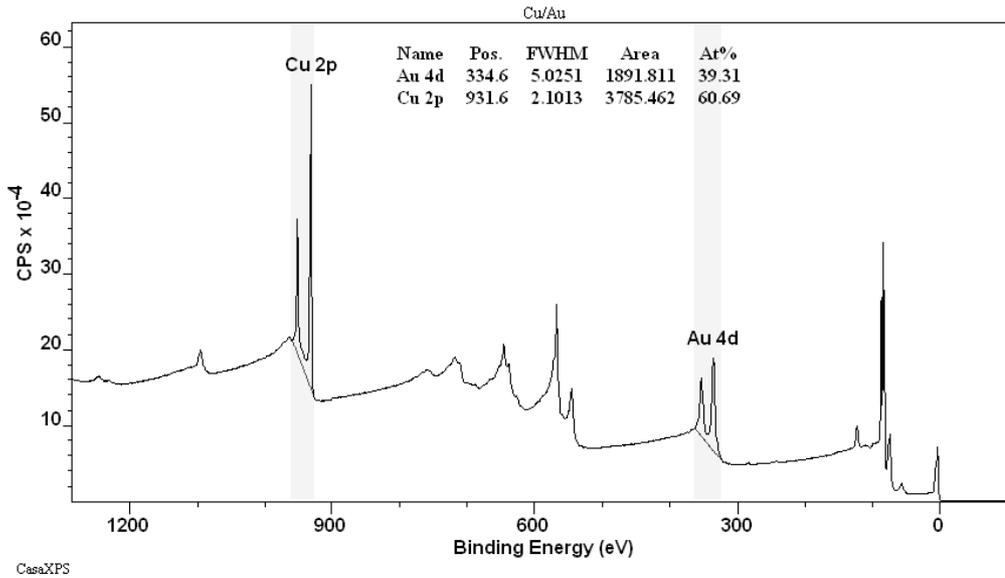
Provided a transmission function is included in the ISO 14976 (VAMAS) file, CasaXPS by default applies the transmission correction to the intensity values used to compute the atomic concentration displayed in quantification reports. Spectra displayed in the active tile appear as uncorrected intensities; however quantification tables, either displayed as annotation over the spectra or in the form of a text report include the transmission correction as part of the atomic concentration calculation. The percentage atomic concentration  $X_i$  is computed using the formula:

$$X_i = 100 \frac{A_i}{\sum_{i=1}^m A_i}$$

where the adjusted intensities  $A_i$  are determined from the measured intensity  $I_i$ , the transmission function  $T$  evaluated for electrons of recorded energy  $E$ , the relative sensitivity factor  $R_i$  for the transition  $i$  and the escape depth compensation exponent  $n$ :

$$A_i = \frac{I_i}{T(E)E^n R_i}$$

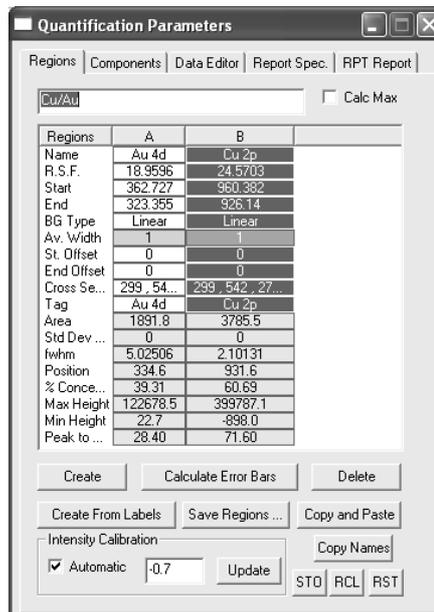
The column headed Area in the quantification report:



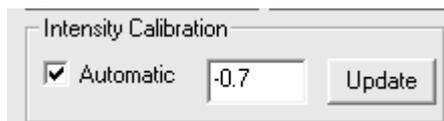
is corrected for transmission and escape depth, but does not include the relative sensitivity factor. If desired, all terms used in the quantification calculation, such as raw intensity in CPSeV or the transmission function value at the peak maximum, can be output in a Standard Report on the Report Spec property page. Obtaining the itemized quantification report involves using the configuration files described elsewhere.

Block Id	Name	Position	Raw Area	Library RSF	Transmission	%At Conc
Cu/Au	Au 4d	334.6	1.29E+06	18.9596	701.806	39.31
Cu/Au	Cu 2p	931.6	1.85E+06	24.5703	841.33	60.69

The quantification table is computed using the parameters defined in the table of quantification regions.

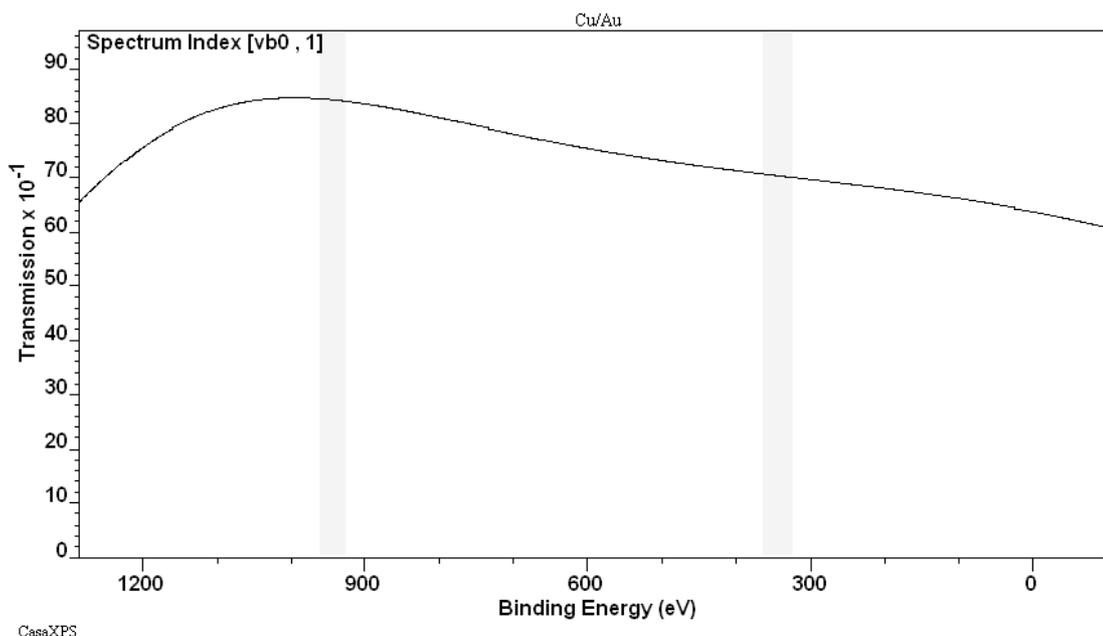


These parameters include the background type, the range of energies over which the background subtracted data is integrated to obtain the value for  $I_i$  in counts per second eV and the relative sensitivity factor (RSF). In principle, the RSF corrects the raw intensity for sample and transition specific intensity variations, in contrast to the transmission and escape depth correction terms, which are in general fixed for all samples and correct the measured intensity for instrumental influences. These instrumental corrections are controlled by the settings in the Intensity Calibration section on the Regions property page.



By way of example, the escape depth correction is assigned a value of -0.7, a value commonly used by SSI instruments. Note the exponent is given a negative value. This is because CasaXPS, for historical reasons, makes the correction to the intensity using the expression  $I * E^n$  rather than  $I / E^n$ . The fact that the transmission correction is active is indicated by the tick box labelled *Automatic*. For the data in the current example, a transmission function is included in the VAMAS block, therefore by default the *Automatic* tick box is ticked when the file is loaded into CasaXPS. The consequence of the *Automatic* tick box being ticked is the area reported in the quantification report over the spectrum is adjusted for transmission and escape depth.

A transmission function is added to a spectrum by including an additional corresponding variable in the VAMAS block containing the data. As stated above, the ticked state of the *Automatic* tick-box is an indicator that a transmission function is present in a data block. Visual inspection of the transmission function can be made by holding the Control key down and pressing the Page Up keyboard key. To return to the spectrum, use the Control key together with the Page Down key to step back to the display of the corresponding variable containing the spectral data. The transmission for the Au/Cu spectrum when displayed in the active tile using the Control + Page Up keyboard keys is as follows:



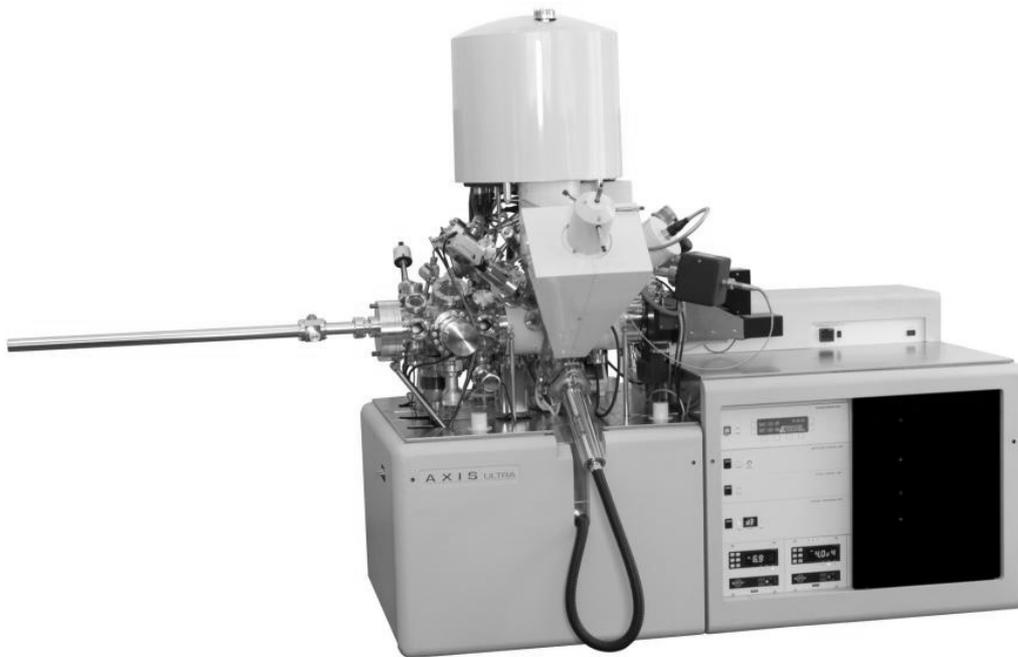
The correction to the intensity for transmission and escape depth is made by evaluating the functions at the position of the peak maximum before any energy calibration is performed to the peak positions.

### ***Practical Solutions to Transmission Correction***

Certain file formats include as part of the description of the data a transmission function. For example, the PHI Multipak files include a correction function of the form:

$$T(E) = PE \left[ \frac{a^2}{a^2 + \left(\frac{E}{PE}\right)^2} \right]^b$$

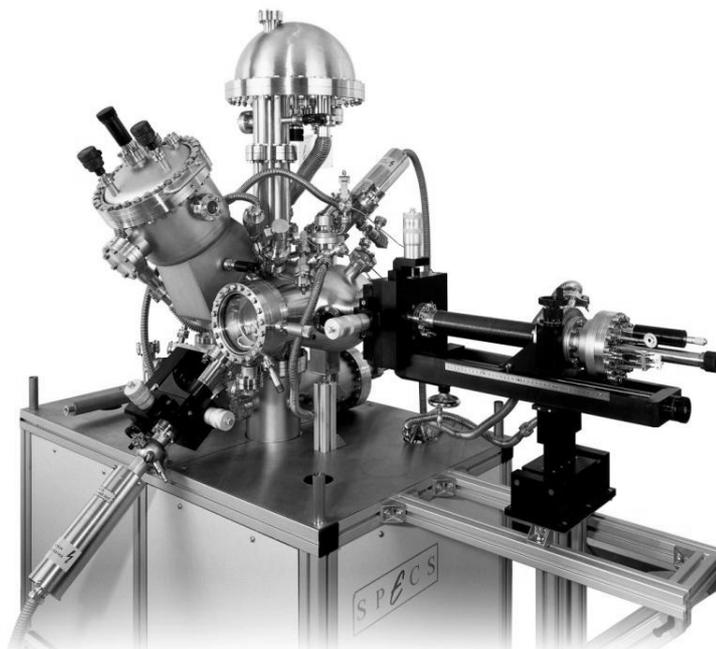
The PHI transmission function represents a scaling function for moving between pass energies within a lens mode. The objective of such a correction is to allow the comparison of intensities measured using different pass energies, where the parameters **a** and **b** are determined in a relative sense from a set of calibration spectra. PHI and Thermo offer intensity calibration functional forms, both of which are included in the VAMAS block created by CasaXPS when the data is converted from either file format to the ISO format used in CasaXPS. Kratos and SPECS SpecsLab2 also offer relative transmission correction; these transmission functions are written into the VAMAS files exported from the Vision Processing and SpecsLab2 systems.



The National Physical Laboratory UK offers an alternative solution to calibrating an XPS instrument. A transmission function is calculated using spectral background information, such that the intensity calibrated spectra can be quantified using a theoretically determined RSF library, namely Schofield cross-sections. The Schofield cross-sections may need modifying for angular distribution variations resulting from an angle between the x-ray source and the axis of the analyser differing from the magic angle ( $54^{\circ} 44'$ ). If calibrated using the NPL system, the possibility of all laboratories, regardless of instrument, using the same basic RSF library producing equivalent quantifications is conceivable. The transmission curve presented above was created using the NPL calibration software for a Kratos Axis Ultra at University of Manchester.

### ***Adding a Transmission Function to SPECS SpecsLab1 Data***

A transmission function file can be added to the CasaXPS file system which is read each time a SpecsLab1 data file is converted to the ISO 14976 format.



The ASCII file CasaXPS.trf, located in the same directory as the CasaXPS.exe executable file, is searched each time a SpecsLab1 exp file is converted through CasaXPS. The CasaXPS.trf file contains a set of transmission function definitions identified by the string used to specify an aperture. The exact set of parameters and functional form is determined from the entry in the CasaXPS.trf file. The following table shows an entry from an exp file where the aperture and the set of aperture strings are marked to illustrate the strings of importance to the transmission function file.

```

EnergyAnalyser: phoiboss
{
ea_mode = esca_c_ep;
ea_serial = 0;
ea_vers = 0;
ea_const = 50;
ea_ampl_fact = 0;
ea_particle_polarity = -1;
ea_detector_U = 2300;
ea_conversion_U = 0;
ea_aperture = 3;
ea_is_small_spot = 0;
ea_nchannels = 5;
ea_addinfo = "";
ea_apertures = "[Area 4x10:7x20:40mm][Area 3x10:7x20:40mm][Area
2x6:7x20:30mm][Area 1x3:7x20:30mm][Area 0.5dia:7dia:20mm][Area
0.1dia:1dia:10mm][UPS:7dia:20mm][ISS:7x20:50mm][AES:7x20:50mm][BAES:7x20:50mm]";
}

```

A file which included the aperture list and aperture parameter (an index starting at zero) as specified in the table would cause the second function defining in the table below to be loaded into a newly converted ISO file.

```
[Area 3.0:MM:7x20:40mm PE* ?]
functiontype5 2 -0.5

[Area 1x3:7x20:30mm PE* ?]
functiontype6
Response Function Parameter a0 +2.260820
Response Function Parameter a1 -19.874343
Response Function Parameter a2 +43.977369
Response Function Parameter a3 +39.042814
Response Function Parameter a4 -27.316750
Response Function Parameter b1 -8.950412
Response Function Parameter b2 +20.326906
Response Function Parameter b3 +15.764882
Response Function Parameter b4 -10.226651
```

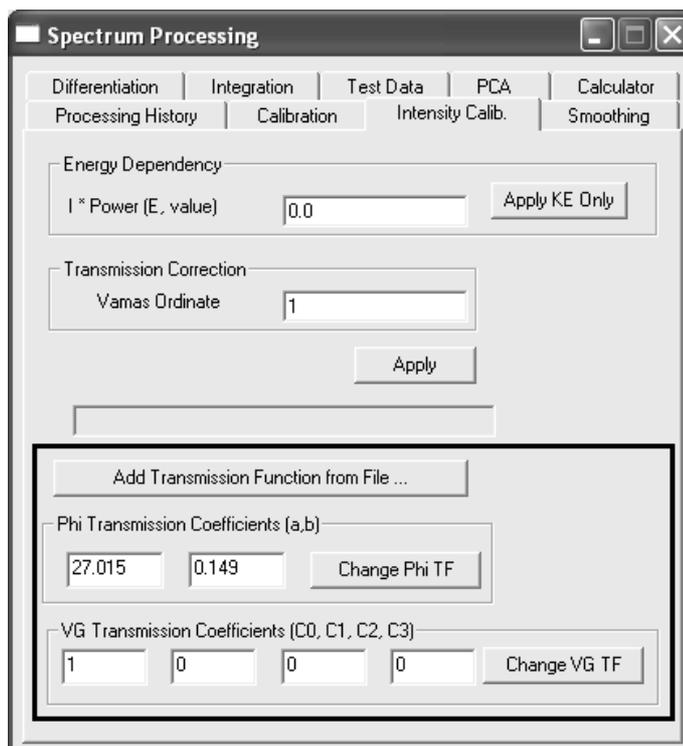
An entry in the CasaXPS.trf file consists of a header string delimited by a pair of square brackets, followed on the next line by a function-type string, which determines the meaning of the parameters that follow. The two entries are examples of *functiontype5* the standard SPECS prescription for the analyser transmission:  $T(E)=aE^b$  and *functiontype6* the set of parameters determined by the NPL calibration system:

$$T(E)=(a_0+a_1y+a_2y^2+a_3y^3+a_4y^4)/(1+b_1y+b_2y^2+b_3y^3+b_4y^4)$$

where  $y = (E-1000.0)/1000.0$ . The parameter list below the string *functiontype6* can be copied and pasted into the CasaXPS.trf file directly from the Q.vms file output from the NPL calibration system. The *functiontype6* NPL transmission function format appears in CasaXPS version 2.3.13 and above.

### **Adding a Transmission Function to Data Blocks**

Adding or replacing a transmission function to a set of VAMAS blocks is achieved via the Intensity Calib property page on the Spectrum Processing dialog window.



Three options are available for modifying an existing transmission function:

1. The **Add Transmission Function from File** button is pressed. A file containing the transmission function information is read and added to any blocks selected in the right-hand pane of the experiment frame.
2. PHI coefficients are entered in the text-fields adjacent to the **Change Phi TF** button. Again, the transmission function is added to the selected blocks in the right-hand pane of the experiment frame.
3. Similar to option 2 but the Thermo VG coefficients are used to compute the transmission function rather than the PHI.

### Add Transmission Function from File

There are three file formats accepted by the Add Transmission Function from File button:

1. A simple ASCII format where the first line is an integer format number, which must be 1. The next line is a positive integer specifying the number of energy, transmission function pairs which follow, one pair per line. The values for the energy and transmission function values must be separated by a space or a TAB.
2. A Q.vms file generated by the NPL Calibration system. The Q.vms file provides a VAMAS description of the transmission function, followed by the parameters and the results of the calibration process. When the

Q.vms file is read into CasaXPS, it is the parameter set which is used to compute the transmission function, the VAMAS fields are ignored.

3. A CasaXPS.trf formatted file. When a SpecsLab1 exp is converted, two strings are added to the VAMAS block comment tagged with the prefix "TRF STRING1:" and "TRF STRING2:". These strings are taken from the aperture list in the exp file and are used to extract a transmission function, on a block by block basis, from the CasaXPS.trf formatted file.

Transmission functions read from file are added to all data blocks selected in the right-hand pane of the experiment frame prior to pressing the button.

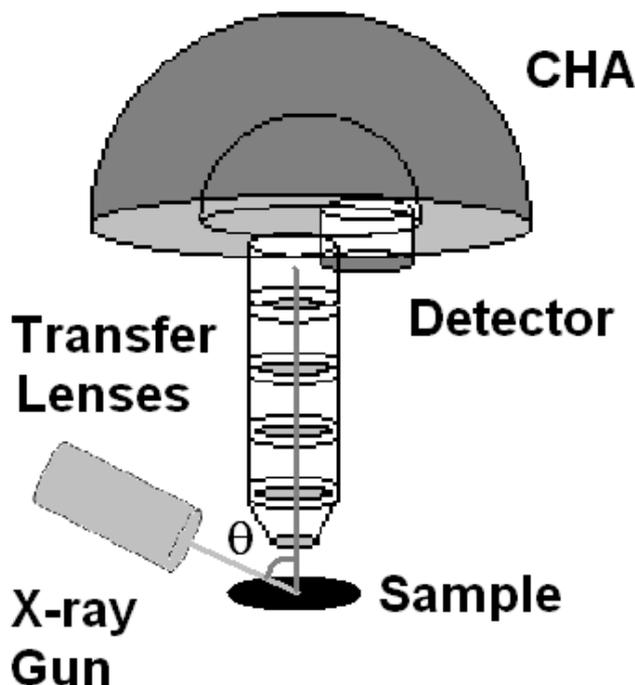
## Relative Sensitivity Factors and Instrument Geometry

In an ideal world, if a sample were analysed using a range of different instruments, the results presented as atomic concentrations would be entirely consistent regardless of type of XPS instrument used to make the measurements. The consistency of these measurements represents the *precision* with which these measurements can be made by the instrumentation in use. The *accuracy* obtained for the atomic concentrations is determined by the relative sensitivity factors (RSFs) used to scale the measured intensities for the different elements. Again, in an ideal world, a single set of RSFs offering the relative intensity of photoelectric lines for each *nI*-electron observed for a given x-ray anode would exist and could be applied to all samples. The goal of absolute accuracy based on a single set of RSFs for all samples is unattainable for many reasons; however the concept of relative accuracy is the accepted goal for many analysts using XPS. That is, assuming all instruments were calibrated for intensity variations due to transmission, then one would like to use a common RSF library to ensure the same quantification is reported irrespective of which instrument made the analysis. Scofield (J. Electron Spectrosc. Relat. Phenom. 8, 129 (1976)) compiled a set of photo-ionisation cross-sections for aluminium and magnesium x-ray sources. In principle these describe the relative intensities for the various photoelectric lines observed in the energy spectra. In practice, the principle of this statement is only true provided the x-ray source and energy analyser are at the, so called, magic angle of  $54^{\circ} 44'$ . For all other angles between these two mechanical components the relative sensitivity for the different transitions changes due to the angular distribution of photoelectrons ionized

by un-polarized light impinging on an  $n$ -shell electron. The equation describing the angular distribution is given by (Reilman et al, J. Electron Spectrosc. Relat. Phenom. 8, 389 (1976)):

$$\frac{d\sigma_{nl}(\varepsilon)}{d\Omega} = \frac{\sigma_{nl}(\varepsilon)}{4\pi} \left[ 1 - \frac{\beta_{nl}(\varepsilon)}{2} P_2(\cos \theta) \right]$$

where  $\varepsilon$  is the photoelectron energy,  $\sigma_{nl}(\varepsilon)$  is the cross-section for photo-ionizing an  $n$  electron (Scofield),  $\theta$  is the angle between the photon and the photoelectron direction:



and  $P_2(x) = (3x^2 - 1)/2$ .

$\beta_{nl}(\varepsilon)$ , the asymmetry parameter, like  $\sigma_{nl}(\varepsilon)$  also depends on the wave function. The complexity of the intensity variation with transition is removed for instruments such that  $P_2(\cos \theta) = 0$  or  $\theta = 54^\circ 44'$ , for which the term involving  $\beta_{nl}(\varepsilon)$  drops out of the equation above. For instruments where the angle  $\theta$  differs from the magic angle, the Scofield cross-sections must be corrected to account for the non-zero term involving  $\beta_{nl}(\varepsilon)$ . Sadly, most instruments to date do not use the magic angle between the analyser and x-ray source and therefore tables of asymmetry parameters are required to modify the RSF tables containing values appropriate for the magic angle configuration.

## PHI Multipak Data

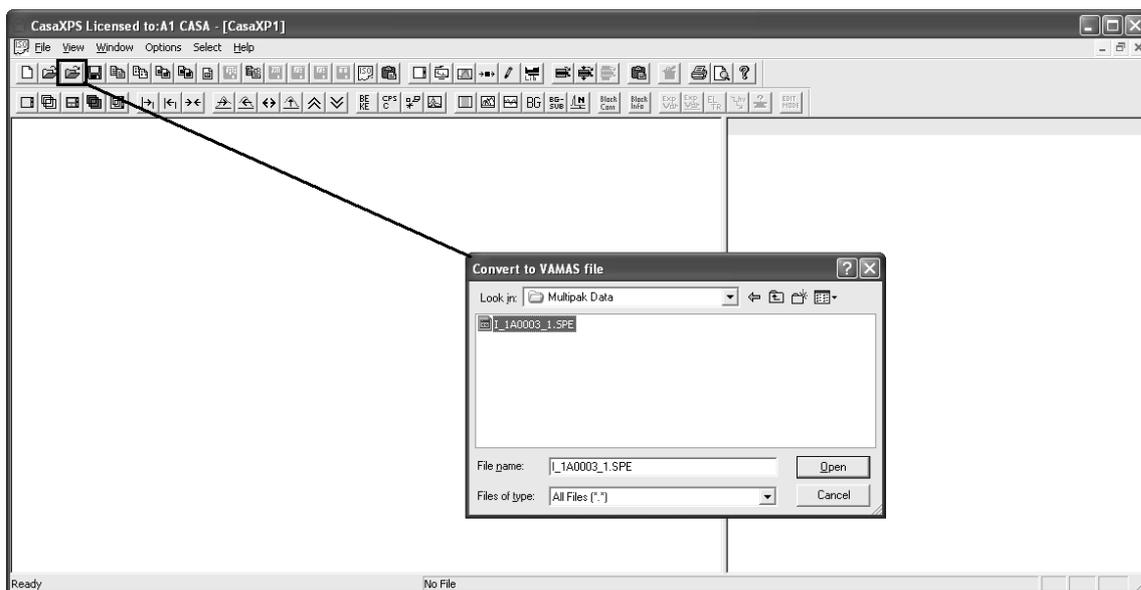
Data from a range of PHI instruments saved in PHI Multipak file formats may be converted to VAMAS format through CasaXPS.



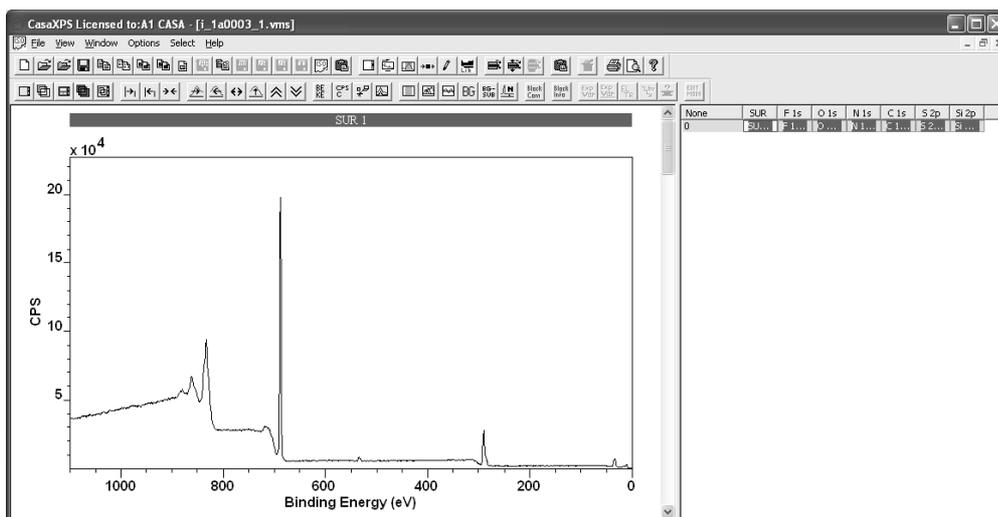
### PHI 5000 Versa Probe

To convert a file in Multipak format:

1. Select the Convert option on the File menu or via the top toolbar of CasaXPS.
2. Move to the directory containing the Multipak file.
3. Selecting the file into the File name text-field on the File dialog window.



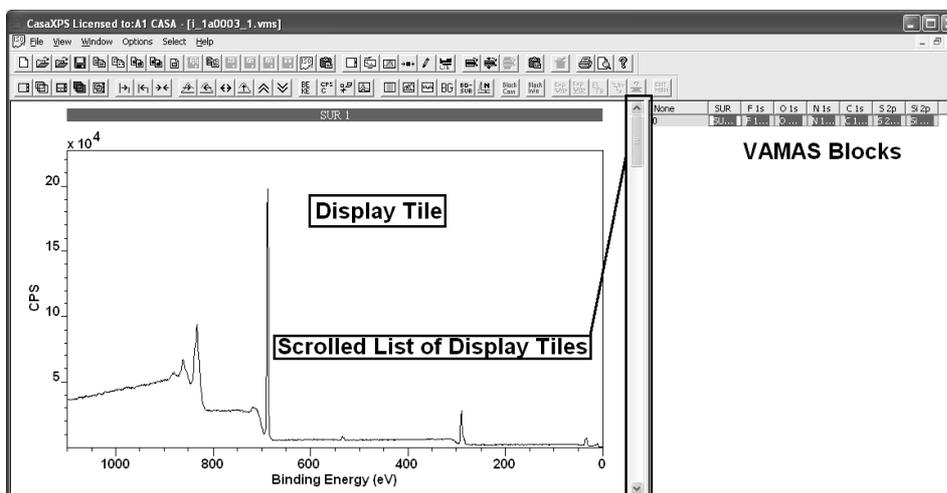
4. Press the Open button on the File dialog window.



The data within the Multipak file is converted from the binary format to the ISO 14976 VAMAS ASCII file format. Each acquisition region in the original Multipak format appears as a VAMAS block in the right-hand pane of the CasaXPS experiment frame.

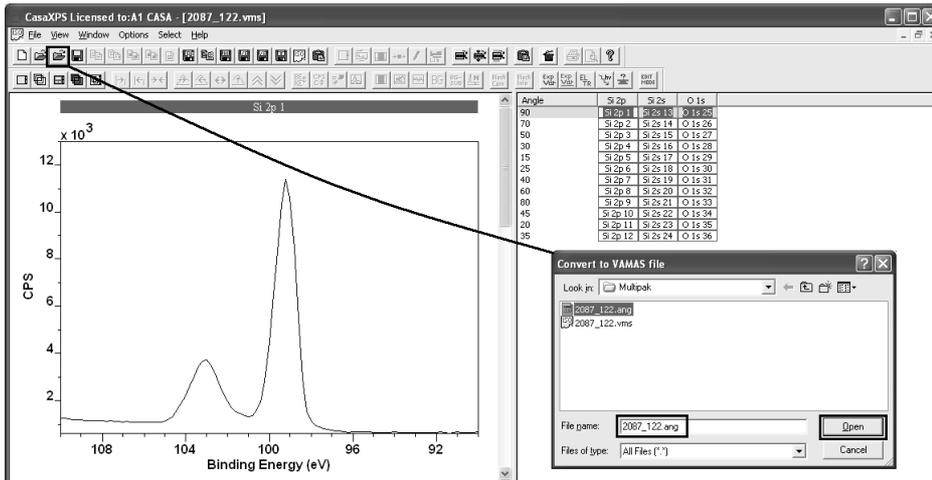
None	SUR	F 1s	O 1s	N 1s	C 1s	S 2p	Si 2p
0	SU...	F 1...	O ...	N 1...	C 1...	S 2...	Si ...

The data from the first row of VAMAS blocks are displayed in the left-hand pane using a scrolled list of display tiles.



Multipak saves data in files with a range of file extensions depending on the nature of the data within the file. A set of spectra measured at the same position on a sample under the same conditions is saved in a file with extension spe as illustrated above. The following illustrates other file formats used by Multipak.

Angle Resolver XPS (ARXPS) are saved with file extension ang:



The tilt angle used to acquire the data appears as an experimental variable in the VAMAS file. Each row of VAMAS blocks represents data acquired using the same angle.

Sputter depth profile data are assigned the file extension pro:

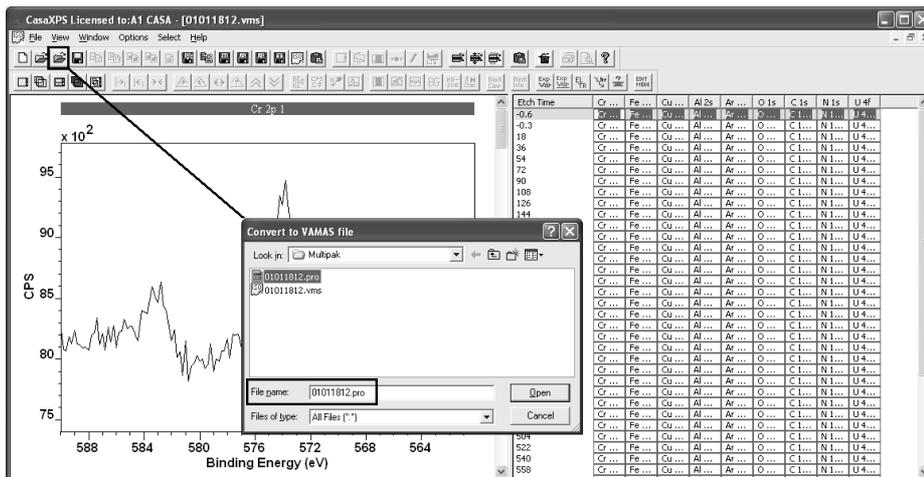


Image files are saved with various file extensions: map, sem, sxi:

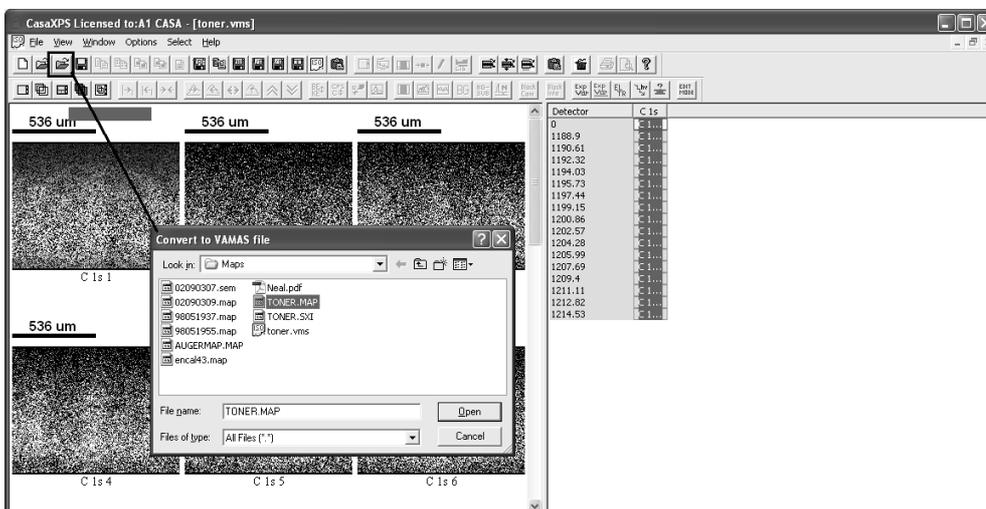
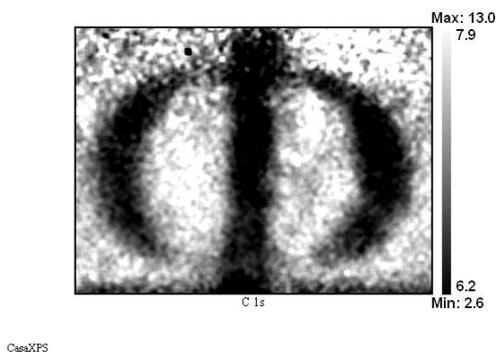


Image files with the file extension map include an image per detector available to the instrument. Processing of these energy-separated images can offer a significant improvement in the image information.



## ***Quantification of PHI Spectra***

The key steps to quantification of PHI data in CasaXPS are:

1. Converting the MultiPak binary files through CasaXPS to obtain VAMAS files which include the PHI transmission function correction.
2. Prepare an element library in CasaXPS format containing the PHI sensitivity factors.
3. Configure CasaXPS to make the angular distribution adjustments to the PHI sensitivity factors appropriate for the PHI instrument from which the data derives.

The Convert to VAMAS option in CasaXPS accepts files of many formats and converts the data into an equivalent ISO 14976 (VAMAS) format. In the case of PHI data, MultiPak binary files include information about the transmission function and also the angle between the analyser and the x-ray source. When the spectra are converted through CasaXPS, these data are also included in the VAMAS file and provide the means for adjusting the intensities of the spectra for transmission variation with kinetic energy of the recorded electrons, and the adjustments to the library sensitivity factors for the instrument geometry used to acquire the spectra.

While the transmission function is automatically applied by CasaXPS to the intensities used to calculate atomic concentrations, the sensitivity factors in the PHI library must be entered into a CasaXPS formatted library file; these sensitivity factors are corrected by CasaXPS at time of use. Provided the appropriate configuration entries are included in the CasaXPS.DEF/ParameterFile.txt file, whenever a sensitivity factor is extracted

from the element library, the appropriate adjustments for angular distribution are applied to the library sensitivity factor. The approach of maintaining a library of magic angle sensitivity factors which are corrected for a given piece of data is consistent with the approach adopted by PHI. By adjusting the sensitivity factors for the given data, data from different PHI instruments can be accommodated using the same library. The PHI Quantum series of instruments, including the Versa Probe, use an angle of 45° between the analyser and the x-ray source, while a 5600 instrument uses an angle of 90°; data from both instrument geometries are quantified under the PHI regime using the same element library adjusted for angular distribution.

## Creating a PHI Library

The CasaXPS library file is a simple ASCII file containing TAB separated rows of information for each transition. The default CasaXPS library contains Scofield cross-sections, which appear, if loaded into a spreadsheet program such as Excel, in the ninth column.

A	B	C	D	E	F	G	H	I	J	K	L
97	Si	2s	Si 2s	0.00E+00	BE	1.49E+02	1.00E+00	GL(30)	9.55E-01	AI	
98	P	2s	P 2s	0.00E+00	BE	1.89E+02	1.00E+00	GL(30)	1.18E+00	AI	
99	S	2s	S 2s	0.00E+00	BE	2.29E+02	1.00E+00	GL(30)	1.43E+00	AI	
100	Cl	2s	Cl 2s	0.00E+00	BE	2.70E+02	1.00E+00	GL(30)	1.69E+00	AI	
101	Ar	2s	Ar 2s	0.00E+00	BE	3.20E+02	1.00E+00	GL(30)	1.97E+00	AI	
102	K	2s	K 2s	0.00E+00	BE	3.77E+02	1.00E+00	GL(30)	2.27E+00	AI	
103	Ca	2s	Ca 2s	0.00E+00	BE	4.38E+02	1.00E+00	GL(30)	2.59E+00	AI	
104	Sc	2s	Sc 2s	0.00E+00	BE	5.00E+02	1.00E+00	GL(30)	2.91E+00	AI	
105	Ti	2s	Ti 2s	0.00E+00	BE	5.64E+02	1.00E+00	GL(30)	3.24E+00	AI	
106	V	2s	V 2s	0.00E+00	BE	6.28E+02	1.00E+00	GL(30)	3.57E+00	AI	
107	Cr	2s	Cr 2s	0.00E+00	BE	6.95E+02	1.00E+00	GL(30)	3.91E+00	AI	
108	Mn	2s	Mn 2s	0.00E+00	BE	7.69E+02	1.00E+00	GL(30)	4.23E+00	AI	
109	Fe	2s	Fe 2s	0.00E+00	BE	8.46E+02	1.00E+00	GL(30)	4.57E+00	AI	
110	Co	2s	Co 2s	0.00E+00	BE	9.26E+02	1.00E+00	GL(30)	4.88E+00	AI	
111	Ni	2s	Ni 2s	0.00E+00	BE	1.01E+03	1.00E+00	GL(30)	5.16E+00	AI	
112	Cu	2s	Cu 2s	0.00E+00	BE	1.10E+03	1.00E+00	GL(30)	5.46E+00	AI	

The simplest strategy for populating an element library with sensitivity factors is to load the CasaXPS library file into Excel and set all the values in the RSF column to zero before entering those sensitivity factors most commonly used. Once a basic library file is established, in the future, each time a new sensitivity factor is required, the value can be entered using the mechanism in CasaXPS for adding or changing an entry in the CasaXPS library.

## Editing an Element Library Entry

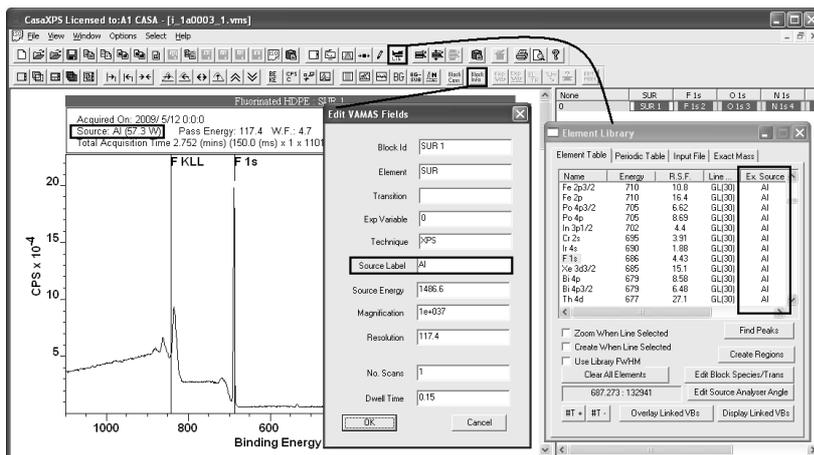
The default CasaXPS library is loaded at the time CasaXPS execution begins. As CasaXPS starts, the CasaXPS.exe executable file loads a file named CasaXPS.lib located in the same directory as the CasaXPS.exe file.

The format for a library file includes a standard set of ten fields per transition.

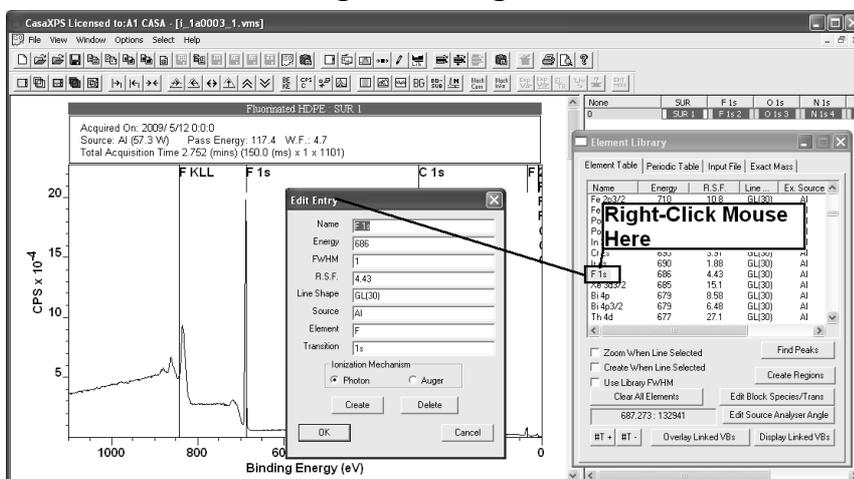
1. Element
2. Transition
3. Label/Name
4. Mass (Daltons)
5. Energy Type (BE or KE)
6. Energy (eV)
7. F.W.H.M.
8. Line shape (e.g. GL(30))
9. Relative Sensitivity Factor
10. Excitation source string

The photoionisation cross-section for electrons ejected by scattering with incident photons is dependent on the energy of the photon source. For this reason the element library may contain the same transition repeated for all possible x-ray gun anode materials. The two most commonly used anode materials are magnesium and aluminium, however silver and chromium are also used on occasion. The default CasaXPS library contains entries for Mg and Al anodes specified via field 10, namely, Excitation Source string, where different Scofield cross-sections for photon energies 1253.6 eV and 1486.6 eV are entered in field 9, Relative Sensitivity Factor (RSF). The library mechanism is designed to display the appropriate transitions and RSFs for the data in the active tile.

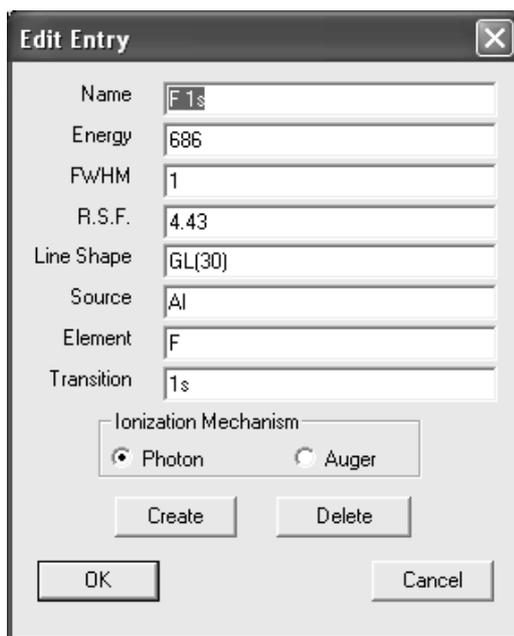
The excitation source string in the element library is used to select the appropriate transitions for the data displayed in the active tile. By default, when a Multipak file is converted through CasaXPS the VAMAS block field for the source label is assigned the string either Mg or Al, based on the information in the original file. A spectrum converted from a Multipak file specifying an aluminium anode, when displayed in the active tile, causes the Element Table property page of the Element Library dialog window to offer those library entries with excitation source Al. Auger transitions with excitation source label ANY will also appear in the element table.



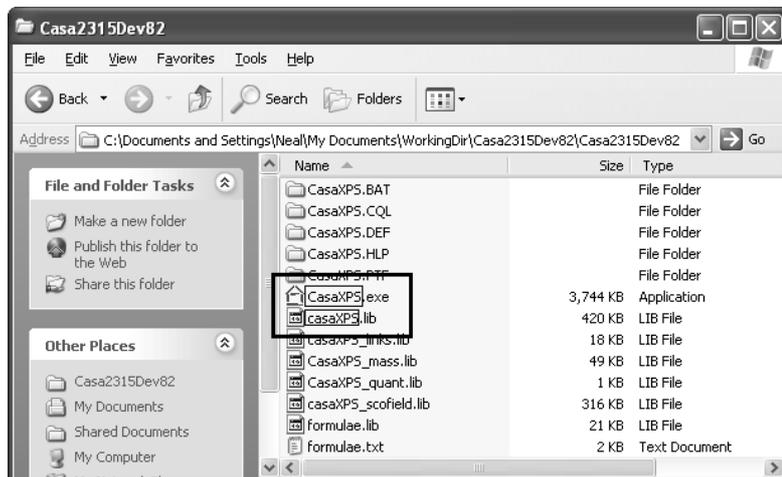
Modifying an entry displayed in the element table is achieved by placing the cursor over the name field and right-clicking the mouse.



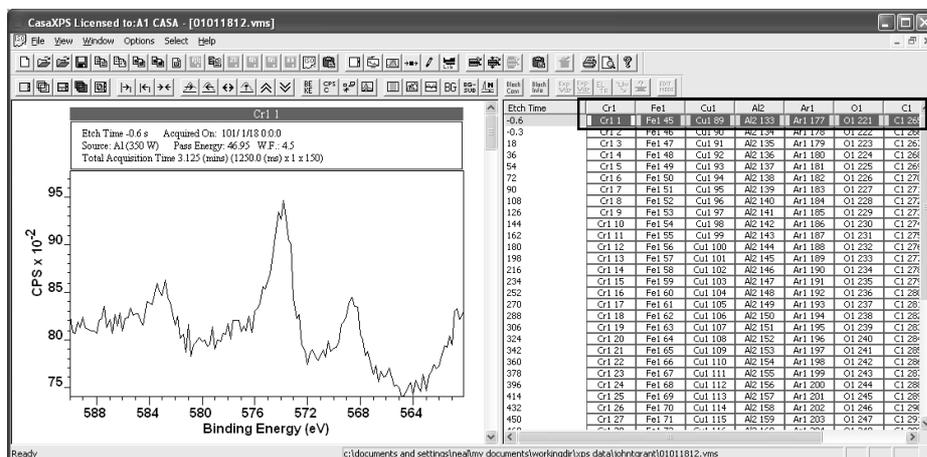
The dialog window invoked by the mouse action allows entries to be modified or a new library entry created depending on the button pressed to exit the dialog window.



The modified element library is written back to file only on exit from the CasaXPS main program. A file dialog offers a means of specifying the directory and name for the modified element library file. To make the modified element library file the default element library, move the file to the directory containing the CasaXPS executable and ensure the base name of the library file matches the base name of the executable.



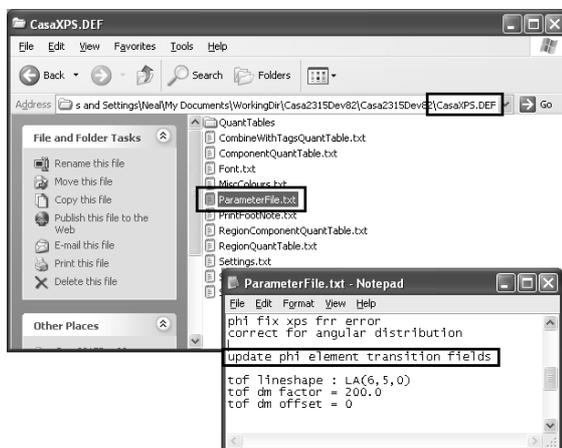
When preparing entries in the CasaXPS element library suitable for use with PHI data, it is important to ensure the name field in the CasaXPS library entry matches the region string used by the PHI acquisition software. The RSF entered into a newly created region or component will be extracted from the element library by matching the element/transition fields in the VAMAS blocks to the name-fields in the element library. For modern version of the PHI acquisition system, the acquisition names for the spectral regions typically match the default names used in the CasaXPS library. Older PHI systems tend to use a naming convention not so informative and so it may be necessary to adjust these strings to conform to the name-strings in the CasaXPS library or adjust the name strings in the CasaXPS library to match those used in the PHI data files.



Examples of the older PHI conventions are Fe1 meaning Fe 2p and Cr1 meaning Cr 2p. An alternative to manually adjusting these strings to match the element library name-fields is to configure an automatic assignment for the data converted from the PHI data files.

### ***Automatic Adjustment of Acquisition Names***

Version 2.3.15 of CasaXPS includes an option for automatically adjusting the names used by older version of the PHI acquisition system to match the name-fields in the element library. A configuration line added to the CasaXPS.DEF/ParameterFile.txt file instructs CasaXPS to examine the acquisition parameters associated with the regions defined in the Multipak files to determine the appropriate element library entry for the data.

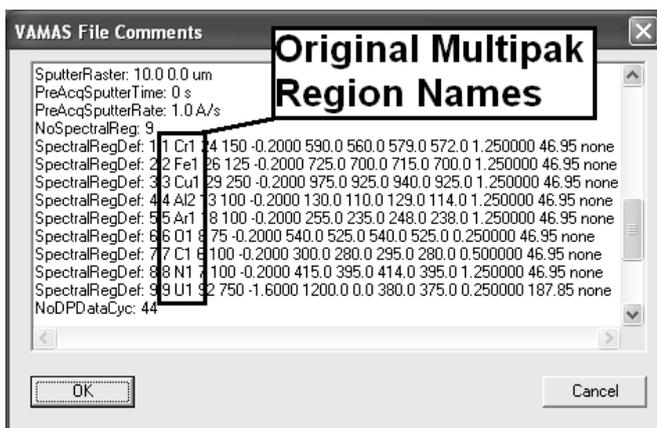


To enable this option, the text string:

***update phi element transition fields***

must be added to the ParameterFile.txt file in the CasaXPS.DEF directory. Once CasaXPS is restarted, each PHI Multipak file when converted through CasaXPS will be labelled using the most appropriate element library entry for the data.

The configuration option transforms the original names for the acquisition regions:



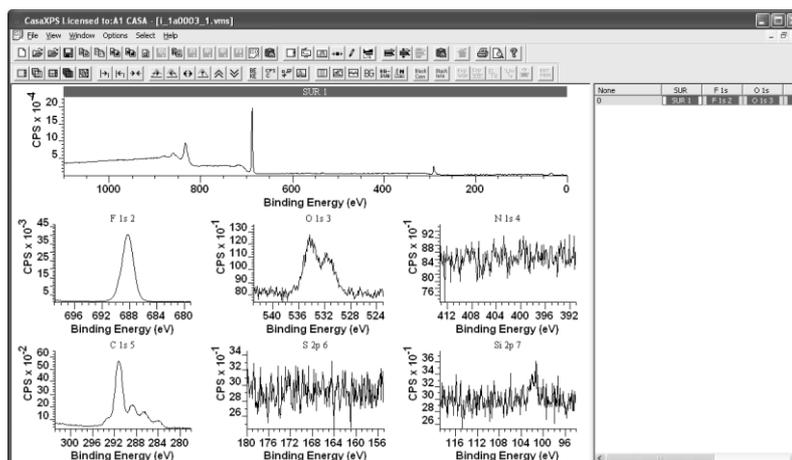
To element/transitions strings matching the element library entries:

Etch Time	Cr 2p	Fe 2p	Cu 2p	Al 2s	Ar 2p	O 1s	C 1s	N 1s	U 4f
-0.6	Cr 2p 1	Fe 2p 45	Cu 2p 89	Al 2s 133	Ar 2p 177	O 1s 221	C 1s 265	N 1s 309	U 4f 353
-0.3	Cr 2p 2	Fe 2p 46	Cu 2p 90	Al 2s 134	Ar 2p 178	O 1s 222	C 1s 266	N 1s 310	U 4f 354
18	Cr 2p 3	Fe 2p 47	Cu 2p 91	Al 2s 135	Ar 2p 179	O 1s 223	C 1s 267	N 1s 311	U 4f 355
36	Cr 2p 4	Fe 2p 48	Cu 2p 92	Al 2s 136	Ar 2p 180	O 1s 224	C 1s 268	N 1s 312	U 4f 356

### Creating Quantification Regions

A typical multiplex Multipak data file includes a survey spectrum together with a set of high resolution narrow scan spectra. To create a quantification table from these data, the simplest approach is based on quantification regions. Quantification regions specify how to compute the intensity for a particular transition and therefore form the basis for measuring the elemental composition of a sample. Often the energy resolution used to measure a survey spectrum is sufficient for obtaining an elemental quantification for a sample.

Quantification for a polymer sample measured on a PHI 5000 Versa Probe will be used to illustrate the features in CasaXPS.

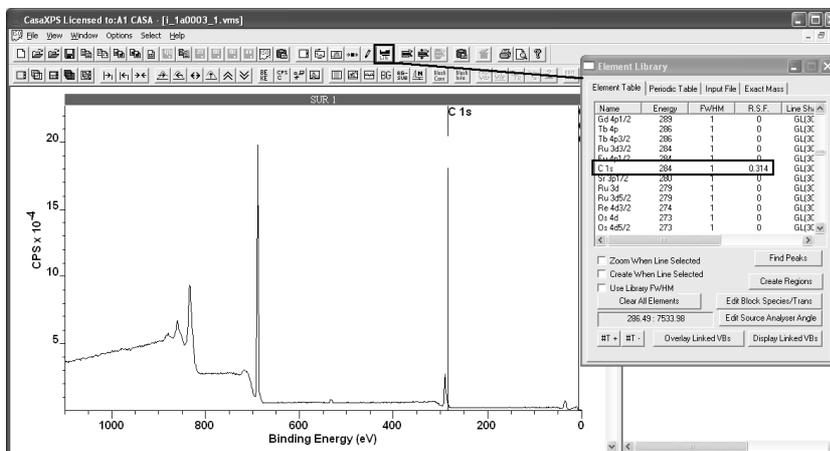


### Quantification of a Survey Spectrum

The polymer sample is a fluorinated HDPE material. The survey spectrum shows significant evidence of fluorine, oxygen and carbon. The bare minimum requirement in terms of relative sensitivity factors is therefore RSFs for the transitions F 1s, O 1s and C 1s. The default CasaXPS library can be made to form the skeleton for a library suitable for Multipak data by changing the RSFs previously assigned Scofield cross-sections to have zero values. The transitions for which RSFs are required are added to the skeletal file using a spreadsheet program and saved as a TAB delimited ASCII file.

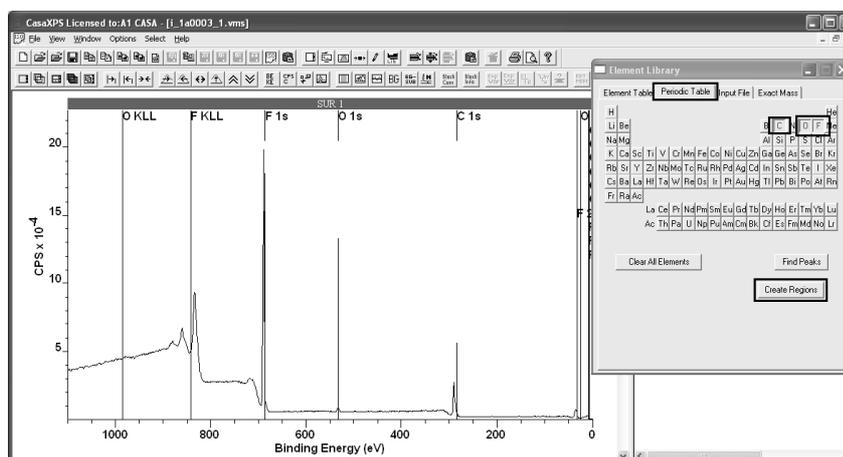
	A	B	C	D	E	F	G	H	I	J	K	L
80	H	1s	H 1s	0.00E+00	BE	1.40E+01	1.00E+00	GL(30)	0.00E+00	AI		
81	He	1s	He 1s	0.00E+00	BE	2.50E+01	1.00E+00	GL(30)	0.00E+00	AI		
82	Li	1s	Li 1s	0.00E+00	BE	5.50E+01	1.00E+00	GL(30)	0.00E+00	AI		
83	Be	1s	Be 1s	0.00E+00	BE	1.11E+02	1.00E+00	GL(30)	0.00E+00	AI		
84	B	1s	B 1s	0.00E+00	BE	1.88E+02	1.00E+00	GL(30)	0.00E+00	AI		
85	C	1s	C 1s	0.00E+00	BE	2.84E+02	1.00E+00	GL(30)	3.14E-01	AI		
86	N	1s	N 1s	0.00E+00	BE	3.99E+02	1.00E+00	GL(30)	0.00E+00	AI		
87	O	1s	O 1s	0.00E+00	BE	5.32E+02	1.00E+00	GL(30)	7.33E-01	AI		
88	F	1s	F 1s	0.00E+00	BE	6.86E+02	1.00E+00	GL(30)	1.00E+00	AI		
89	Ne	1s	Ne 1s	0.00E+00	BE	8.67E+02	1.00E+00	GL(30)	0.00E+00	AI		

When loaded into CasaXPS, the new library file offers only three non-zero RSFs for F 1s, O 1s and C 1s.

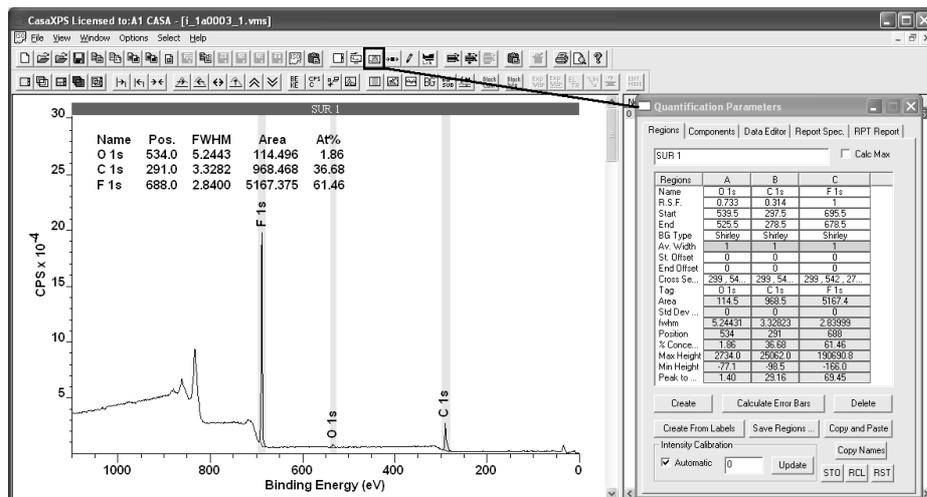


Creating quantification regions is performed explicitly using the Quantification Parameters dialog window, however for survey spectra the Element Table property page or the Periodic Table property page on the Element library dialog window provide a quick means of creating regions directly from the element library information. To create a set of regions:

1. Using the Element Table or the Periodic Table property pages, place peak markers on the survey spectrum.



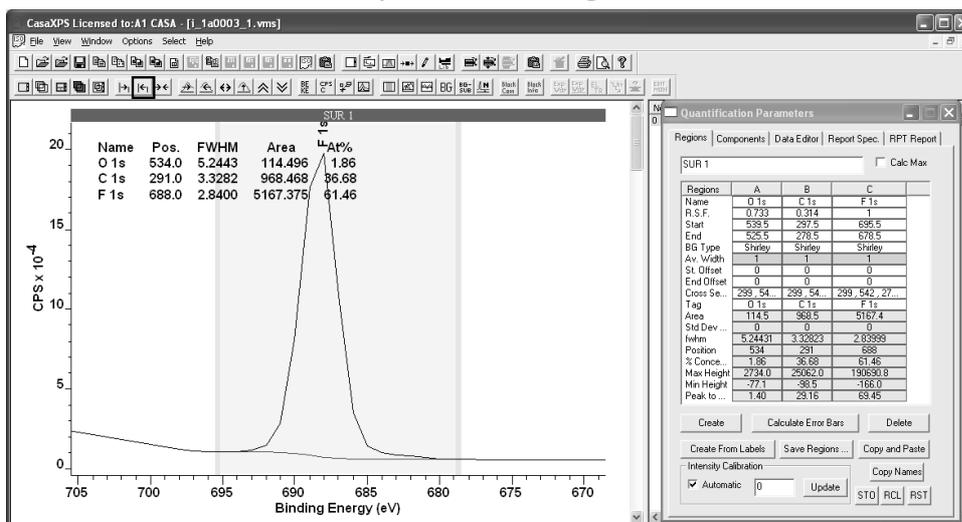
## 2. Press the Create Regions button.



Quantification regions created using the Element Library dialog window ensure RSFs are extracted from the element library appropriate for the name used to label the region. The user is still responsible for ensuring the named region spans the appropriate peak or, in the case of the double pairs, peaks. A simple mechanism based on the zoom-list maintained for the active tile permits the region limits and suitability of the background for the peaks selected for quantification to be assessed and adjusted. After the regions are created, pressing the Reset toolbar button loads the set of regions onto the zoom-list.



Subsequently, each time the zoom out toolbar button is pressed, the display in the active tile offers a close-up view of a region.

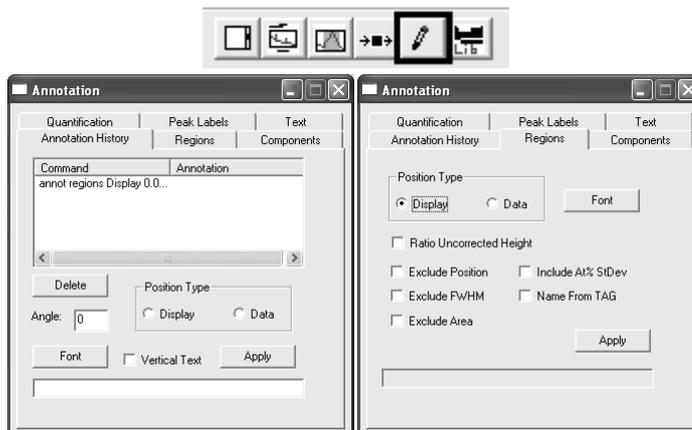


If the Region property page is top-most on the Quantification Parameters dialog window, adjustments to the region limits can be made using the mouse or directly via the text-fields on the property page.

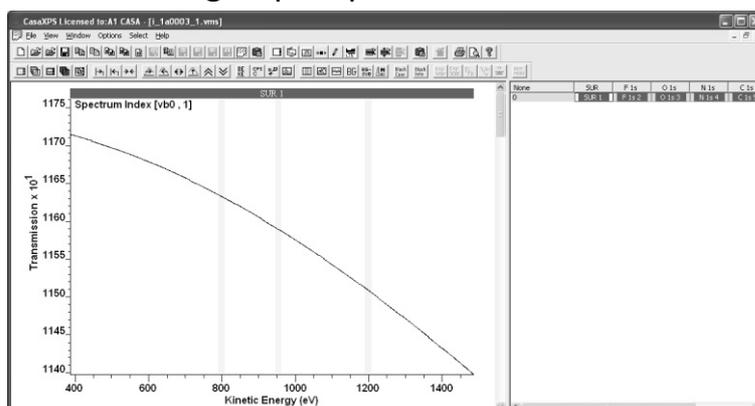
Use of the Create Regions buttons on the Element Library dialog window also causes the creation of an annotation table.

SUR_1					
	Name	Pos.	FWHM	Area	At%
30	O 1s	534.0	5.2443	114.496	1.86
	C 1s	291.0	3.3282	968.468	36.68
25	F 1s	688.0	2.8400	5167.375	61.46

The format and position of the annotation table are altered via the Annotation dialog window.



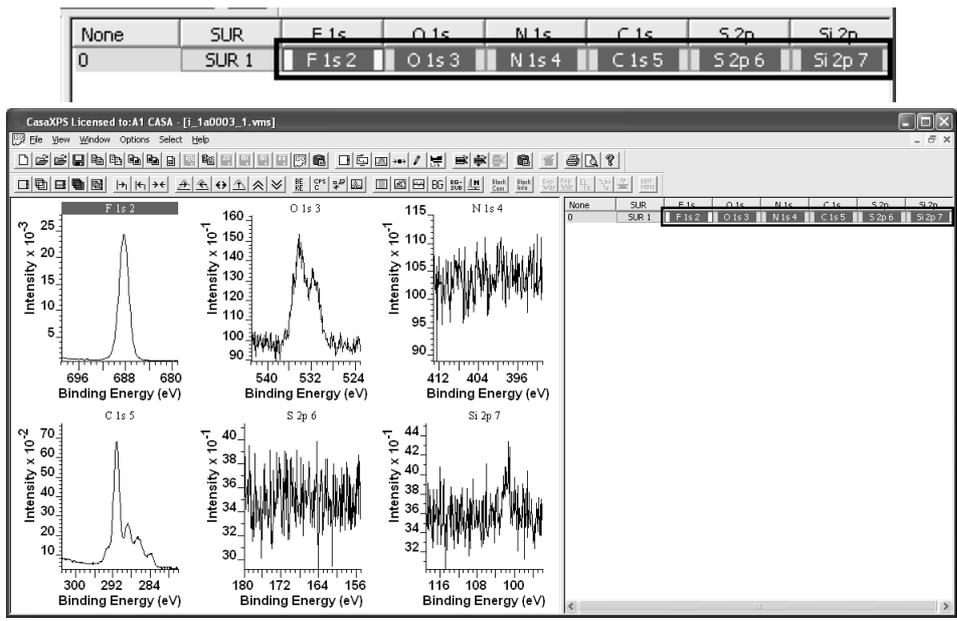
Quantification of the survey spectrum requires the correct sensitivity factors corresponding to the transmission correction for the instrument recording the spectrum. Multipak data files include the information about the transmission function in the header section of the file. When the Multipak file is converted by CasaXPS, the transmission function is added to the VAMAS file and automatically included in the calculation of the atomic concentrations reported for the spectrum. The transmission function is added as a second corresponding variable to each VAMAS block; the first corresponding variable contains the spectral data. To view the transmission function the keyboard key sequence Control + Page Up steps upwards through the corresponding variables, while Control + Page Down causes the reversal of the Control + Page Up step.



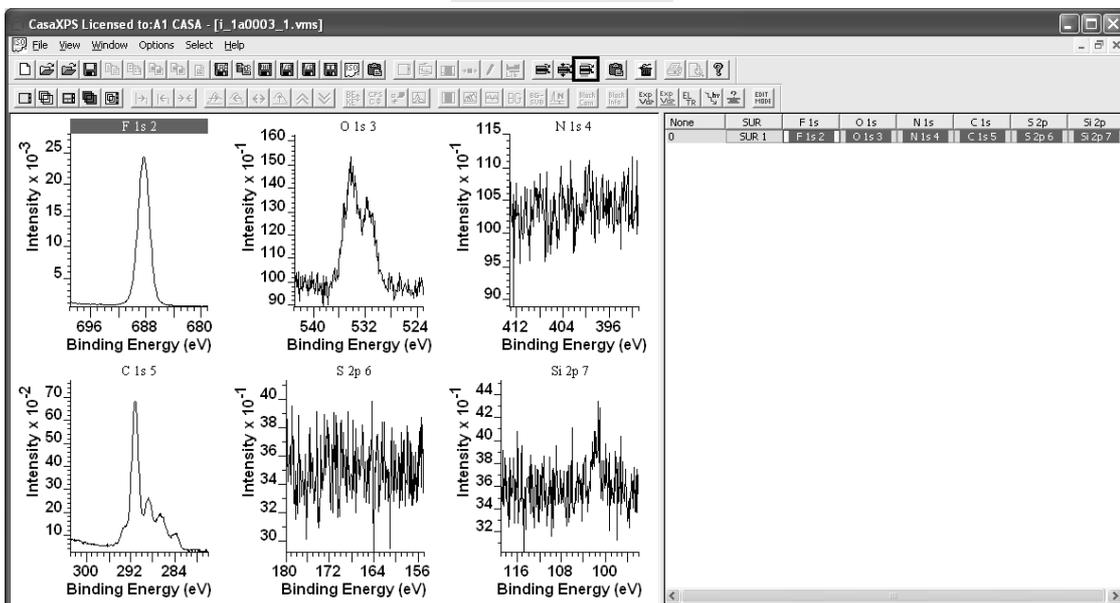
While the Multiplex data include these transmission functions, PHI recommend good practice dictates that quantification is performed based on data recorded using the same lens mode and pass energy; a recommendation endorsed here and appropriate for all XPS data regardless of instrument origin.

### Quantification based on Narrow Scan Spectra

Multiplex data appear in an experiment frame as a row of VAMAS blocks.

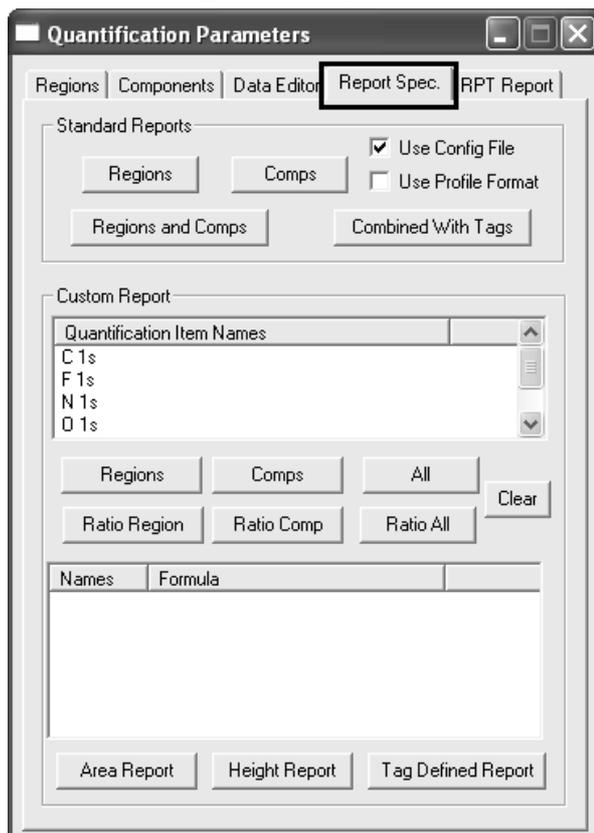


The simplest way to add regions to a set of multiplex data is to select the VAMAS blocks corresponding to the narrow scan spectra in the right-hand pane of the experiment frame before pressing the Add Regions toolbar button.



One region is added to each narrow scan spectrum for which the VAMAS block is selected in the right-hand pane. The RSF and name for each region created by this means is determined from the element/transition VAMAS block fields. It is therefore important to ensure these are correctly assigned prior to pressing the toolbar button.

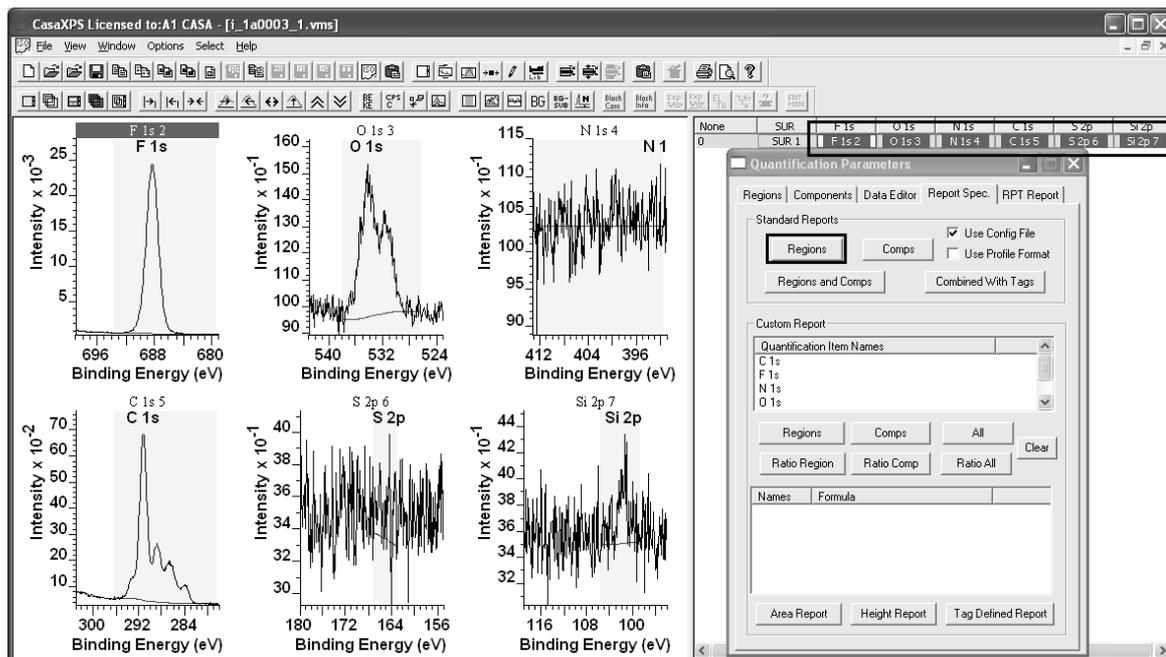
Quantification reports generated from the Report Spec property page of the Quantification Parameters dialog window require the VAMAS blocks to appear in the same row in the right-hand pane.



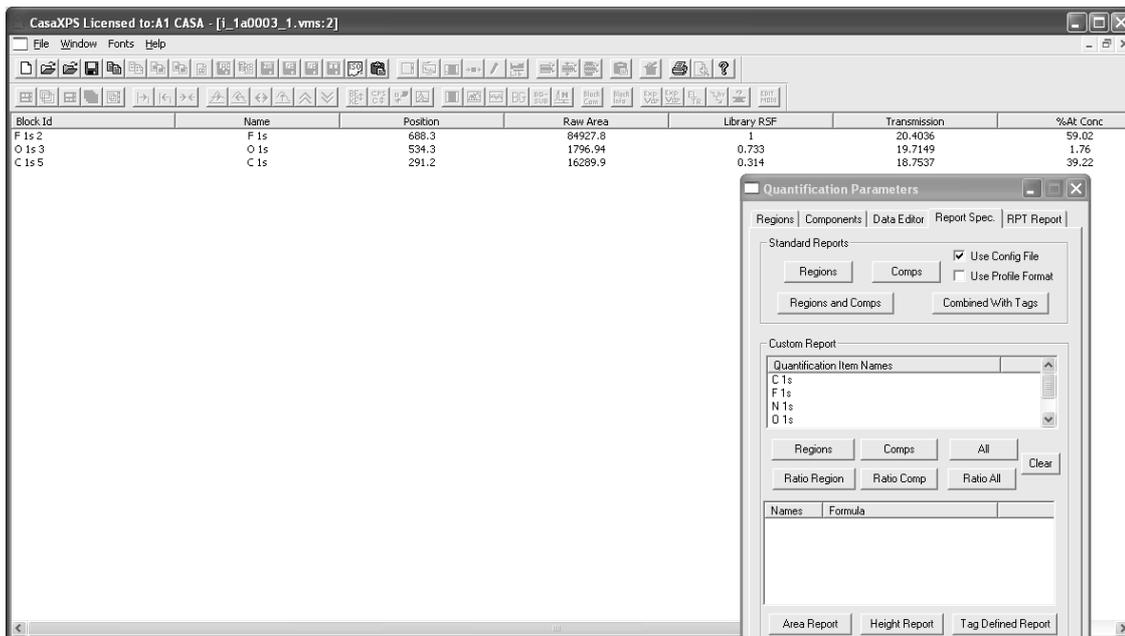
A text-based report is generated from the Standard Report section on the Report Spec property page. The contents of the report are determined by a configuration file and appear within CasaXPS as an additional window. To generate a report from a set of VAMAS blocks:

1. Select a row of VAMAS blocks for which quantification regions are defined.
2. For a report generated from quantification regions, press the button labelled Regions in the Standard Report section of the Report Spec property page.

State of the selection before pressing the Regions button:



State of the display after pressing the Regions button:



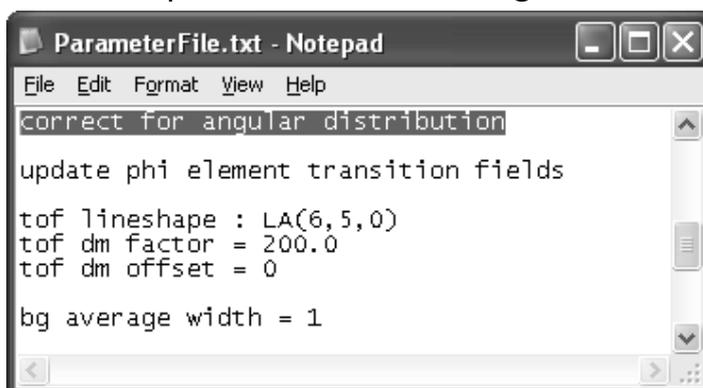
The quantification report contains the results for only three of the six spectra selected in the right-hand pane even though all the spectra have regions defined. The reason only three of the intended six regions are included in the report is because the skeletal element library only contained non-zero RSFs for O 1s, C 1s and F 1s. The N 1s, S 2p and Si 2p RSFs are all zero in the library; therefore the quantification regions for these data were assigned zero RSFs too. Any region with a zero RSF is excluded from any quantification report. To remedy the problem, the regions must be updated with the appropriate non-zero RSFs.

The N 1s data can be updated using the value for the RSF listed in the PHI Manual; however the S 2p and Si 2p regions differ from the manual entries for the RSFs due to angular distribution intensity variations; since the 45° angle between the x-ray source and the analyser of the Versa Probe used to collect the spectra differs from the magic angle, the RSF value becomes instrument dependent and must be calculated from the library RSF. To make the modification to the PHI Manual RSF value for a p-orbital, the manual RSF should be entered into the CasaXPS library and the quantification region RSF updated in turn from the value stored in the CasaXPS element library.

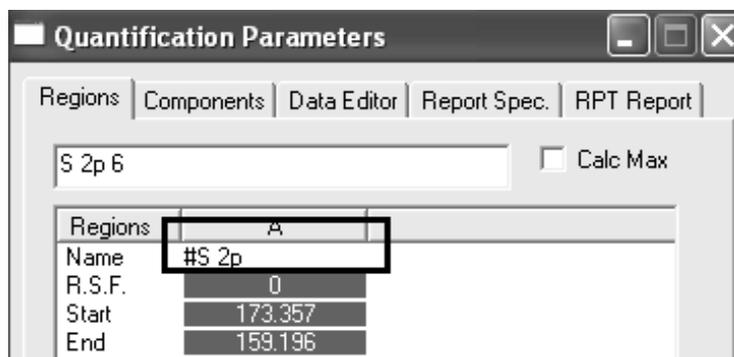
To enable the modification of RSFs based on the instrument geometry, a configuration entry must be added to the file named ParameterFile.txt located in the CasaXPS.DEF directory. The string:

*correct for angular distribution*

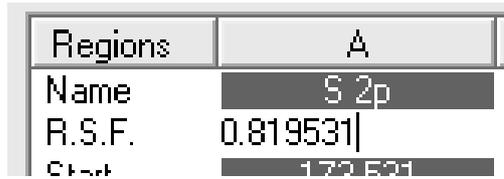
must be entered onto a separate line of the configuration file:



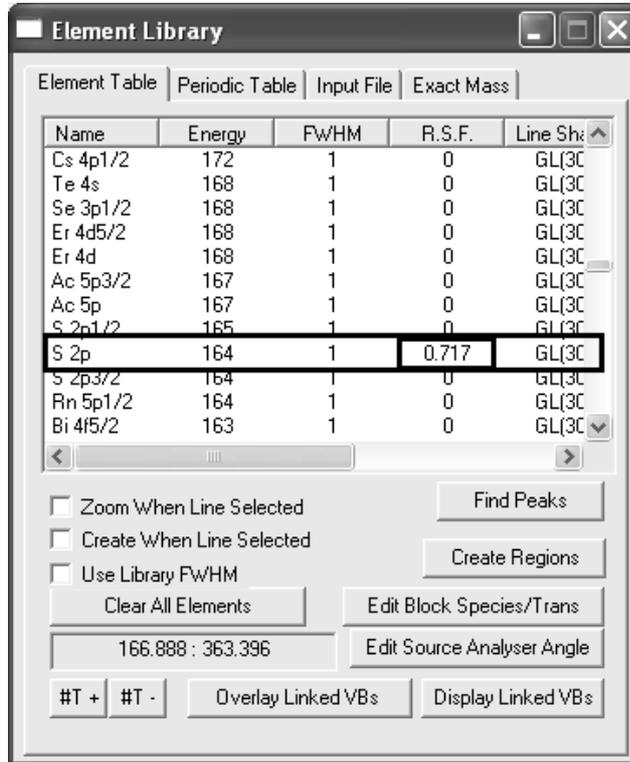
The element library entries for N 1s, S 2p and Si 2p can be updated as described above. Once entered into the CasaXPS library, the values for the RSF fields in the quantification regions are also updated using the name field for the region. Enter the name used in the element library for the name field in the region and add the # character as a prefix.



After the Enter keyboard key is pressed, the name field is entered into the region without the # character and the RSF is updated with the corrected RSF value.



The retrieved RSF is modified appropriately from the value for the S 2p entered into the CasaXPS library:



After repeating the process of updating the RSFs for each of the Si 2p and N 1s regions, the quantification report generated using identical steps to those above produces the report containing results for all six spectra.

Block Id	Name	Position	Raw Area	Library RSF	Transmission	%At. Conc
F 1s 2	F 1s	688.3	84927.8	1	20.4036	58.73
O 1s 3	O 1s	534.3	1796.94	0.733	19.7149	1.75
N 1s 4	N 1s	392.1	149.945	0.499	19.1342	0.22
C 1s 5	C 1s	291.2	16289.9	0.314	18.7537	39.03
S 2p 6	S 2p	164.3	51.3283	0.819531	18.3099	0.05
Si 2p 7	Si 2p	101.4	117.655	0.42872	18.1032	0.21

## Quantification of Thermo Scientific Data

The last ten years have seen the XPS technique develop from a technique used predominantly by experts of XPS to a tool used by application oriented scientists. The emergence of instruments such as the Thermo Scientific K-Alpha shows that there is a place for an instrument with a high performance to cost ratio and lower cost of ownership. Instruments with these characteristics offer a route for the XPS technique into application areas previous limited by the constraints of expensive high performance technology. There will always be a place for high performance systems run by experts, but these new low cost XPS systems can only be good for surface science.



The data from the Thermo Scientific K-Alpha is supported in version 2.3.15 of CasaXPS, where a number of enhancements are included to streamline the conversion and processing of the new ASCII files. The ASCII files exported from the K-Alpha include a new flag to indicate whether or not the intensities are corrected for transmission. Version 2.3.15 of CasaXPS detects the new flag and converts the ASCII file to the ISO 14796 format using the counts-per-bin computed from the transmission corrected data. The necessity of returning the data to counts-per-bin lies in the assumption that the noise in the data is governed by Poisson statistics, which is required when measuring the goodness-of-fit and when performing Monte Carlo error analysis on peak models. The ISO file written by CasaXPS includes both the counts-per-bin and also the transmission functions from the ASCII file, therefore quantification of

the spectra in CasaXPS proceeds exactly the same way as for other data acquired using the Thermo Avantage data system.

An attractive feature of the K-Alpha is the possibility of combining a new resource with existing high performance instruments, either in-house or available from external laboratories. To accommodate the use of more than one instrument, data converted from a K-Alpha have a unique source label assigned to each VAMAS block and hence entries specific to the K-Alpha can be added to the CasaXPS element library. This feature permits the default CasaXPS library to offer the appropriate RSFs for data from different instruments.



A new toolbar button provides a further means of creating quantification regions for a set of VAMAS blocks based on the element/transition fields in the VAMAS blocks. When converted from the Avantage ASCII files, the spectra are assigned the element/transition fields based on the name assigned to the data. For example, a carbon 1s transition might appear in the Avantage data file with the name “C 1s Scan” or “C 1s Snap”, depending on the acquisition mode. On conversion to ISO format through CasaXPS, these strings are used to extract the element “C” and transition “1s”. Armed with these strings, the new toolbar button identifies the entry corresponding to the photoelectric line in the element library and uses the element library information to create regions for each selected VAMAS block correctly assigned in terms of element/transition.

## Converting Avantage Data

Data from the K-Alpha are exported from the Avantage system as ASCII files. These ASCII files can be converted as follows.

```

Survey.avg - Notepad
File Edit Format View Help
=====
; Dump of DataSpace 'f:\snap_test\snap-survey\X-RayQ10 400um - PG OFF\platten\Survey.Vgd'
; on 13/5/2008 at 10:17:23
=====
; [Note that this file can be reloaded only if certain syntax rules are NOT broken]
$FORMAT=3

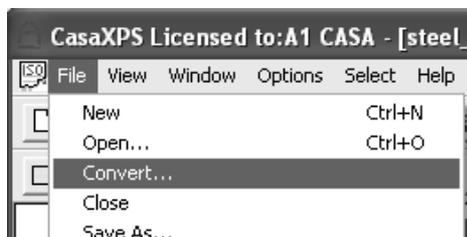
; Summary Properties present:
$PROPERTIES=SUM
DS_EXT_SUPROPID_TITLE      : VT_BSTR = 'Survey'
DS_EXT_SUPROPID_SUBJECT   : VT_BSTR = 'Vg scientific acquisition datafile'
DS_EXT_SUPROPID_AUTHOR    : VT_BSTR = 'yengineer'
DS_EXT_SUPROPID_COMMENTS  : VT_BSTR = ''
DS_EXT_SUPROPID_CREATED   : VT_DATE  = 12/5/2008  17:05:17
DS_EXT_SUPROPID_SAVED     : VT_DATE  = 12/5/2008  17:07:56

; Standard Properties present:
$PROPERTIES=STD
DS_GEPROPID_INSTRUMENT    : VT_BSTR = 'Alpha'
DS_GEPROPID_SOURCE_TYPE  : VT_I4   = 1
DS_GEPROPID_GUID         : VT_BSTR = '{B33AAC0E-1008-4617-AA24-A2A2506ABF1E}'
DS_GEPROPID_SOURCE_GUID  : VT_BSTR = '{B33AAC0E-1008-4617-AA24-A2A2506ABF1E}'
DS_GEPROPID_EXPT_RUN_GUID: VT_BSTR = '{5C4C37CB-861D-4F03-837A-F3AFE7E49C43}'
DS_GEPROPID_VALUE_TYPE   : VT_I4   = 11
DS_GEPROPID_VALUE_LABEL  : VT_BSTR = 'Counts'
DS_GEPROPID_VALUE_SYMBOL : VT_BSTR = 'C'
DS_GEPROPID_VALUE_UNIT   : VT_BSTR = ''
DS_DATASTORAGEID_DATA_STORAGE_METHOD : VT_I4 = 0
DS_SOPROPID_STYPE        : VT_I4   = 10
DS_SOPROPID_MNOX        : VT_BOOL  = True
DS_SOPROPID_ENERGY       : VT_R4    = 1486.680054
DS_SOPROPID_VOLTAGE      : VT_R4    = 12000.000000
DS_SOPROPID_CURRENT      : VT_R4    = 0.000500
DS_SOPROPID_WIDTH        : VT_R4    = 400.000000
DS_SOPROPID_LENGTH       : VT_R4    = 400.000000
DS_SOPROPID_GUN          : VT_I2    = 9
  
```

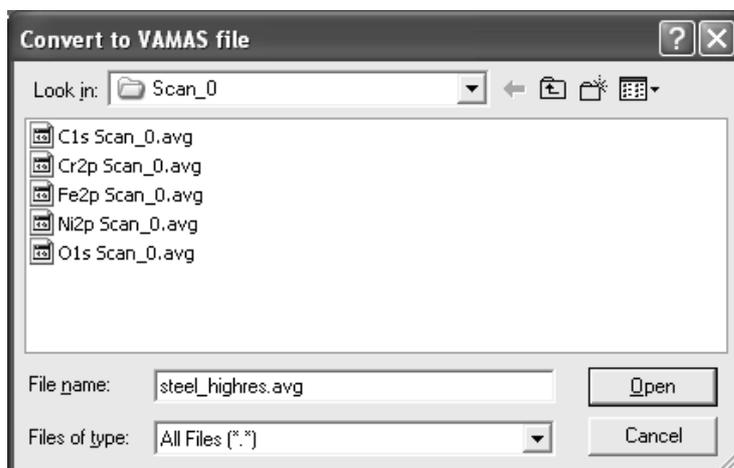
## Thermo Scientific Avantage Files

The Avantage binary files must be converted via an Avantage utility program (DataSpace\_BatchDump.exe) to ASCII equivalent files. These ASCII files are created with the file extension .avg and can be converted to ISO 14976 (VAMAS) format using the Convert to VAMAS dialog window available from the File menu or the top toolbar of CasaXPS:

1. Using the Avantage utility program DataSpace\_BatchDump.exe, convert all the .vgd binary files for an experiment to .avg ASCII files.
2. Select the Convert to VAMAS dialog window in CasaXPS either using the toolbar button or via the Convert menu item on the File menu.



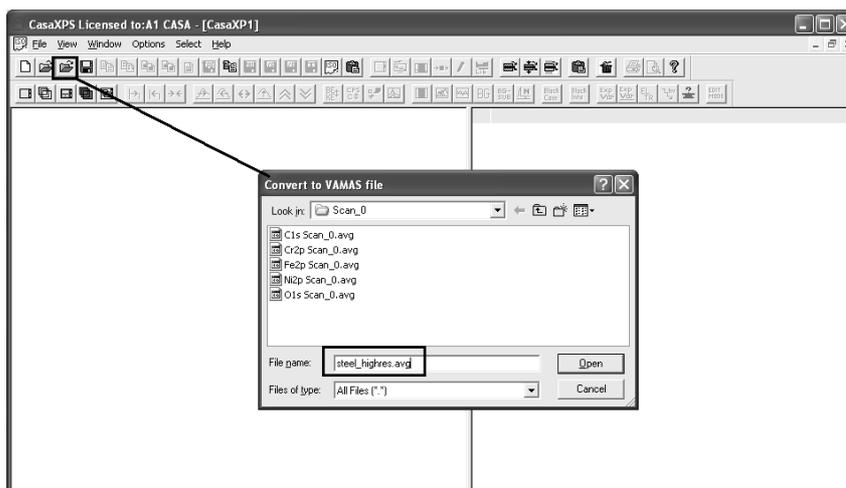
3. Move to the directory containing the .avg ASCII files; the DataSpace\_BatchDump.exe program offers the user the choice of where the ASCII files should be created.



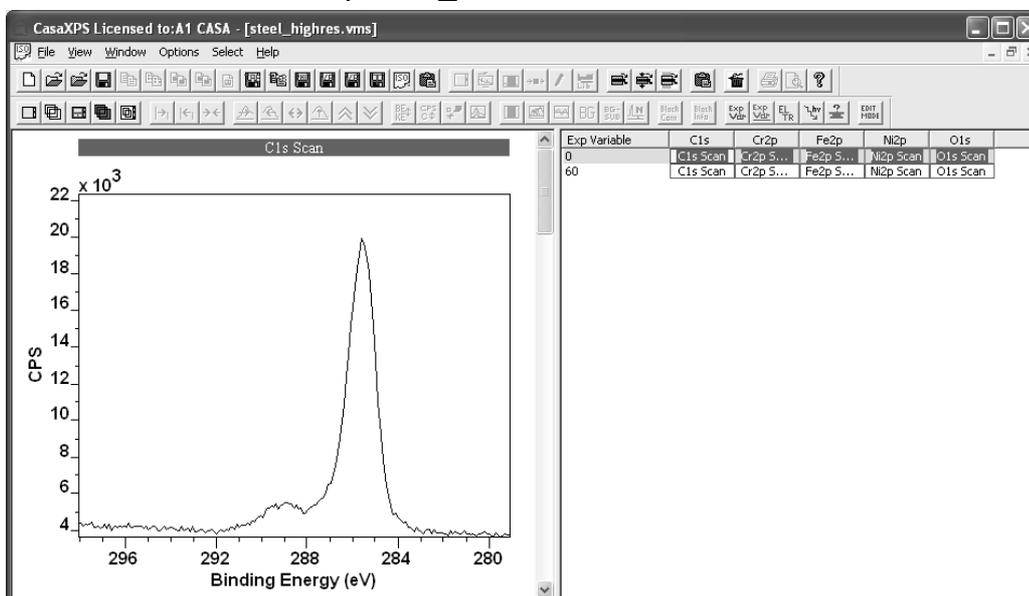
4. Enter a name for the new VAMAS file using the file extension .avg and press the Open button. For example, if you wish to call your new file sample001.vms, then you should enter **sample001.avg** into the file name field on the Convert to VAMAS file dialog window. Each .avg file found in the current directory will be read and entered into the new VAMAS file named sample001.vms.

A directory of ASCII files is converted to a single VAMAS file as follows.

Enter the name for the new VAMAS file followed by the file extension avg:



A new ISO file named `steel_highres.vms` will be created from the set of avg files in the current directory `Scan_0`.



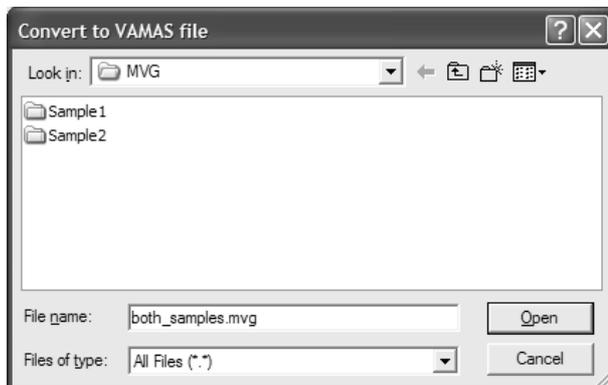
Note how the base-name for the ISO file is used together with the .avg conversion switch to instruct CasaXPS to read the set of .avg files in the directory and converted all the files in the directory to a single ISO format file. Each avg file in the directory contains two spectra per file, before and after etching the sample surface, hence the two rows of VAMAS blocks in the VAMAS file.

## ***Merging Sets of Experiments***

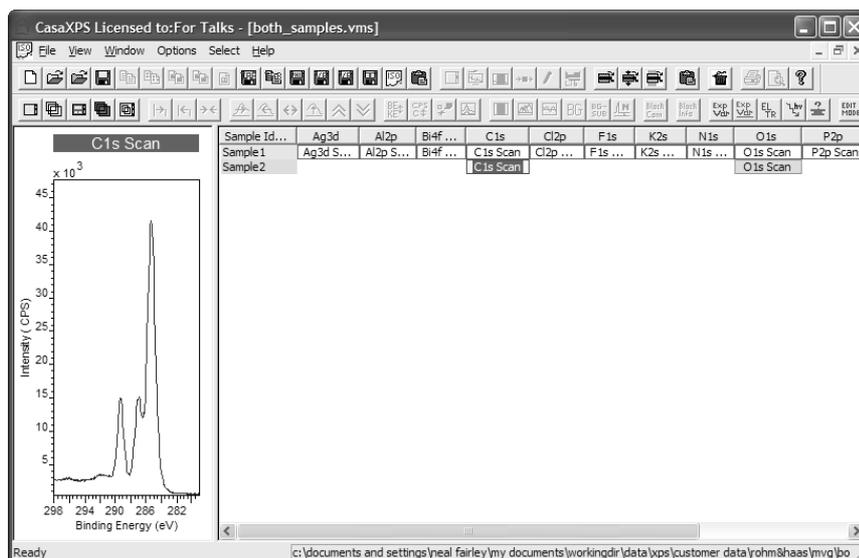
The acquisition regions for each experiment are exported into separate ASCII files with the .avg extension, thus an experiment is typically recorded, once exported, as a set of ASCII files in a directory. If an experiment is one in a sequence of experiments, all of which might reasonably be processed as a

unit, then a further import option allows a set of such data directories to be converted to a single ISO 14976 VAMAS file.

Given a set of directories each containing exported Avantage data, a new VAMAS file is created by moving to the directory using the Convert to VAMAS File Dialog containing these data sub-directories and entering the new filename with an extension of .mvg.



A VAMAS file with the extension .vms is created at the level of the directory containing the data sub-directories. The .avg files found in the sub-directories are converted and entered into the new VAMAS file with the experimental variable set to a Data Set index number. The index assigned to the experimental variable is dependent on the order of the sub-directories when read. In addition to the Data Set index, the rows are also assigned labels based on the names given to the sub-directories, which can be view using the Edit Mode toolbar button.

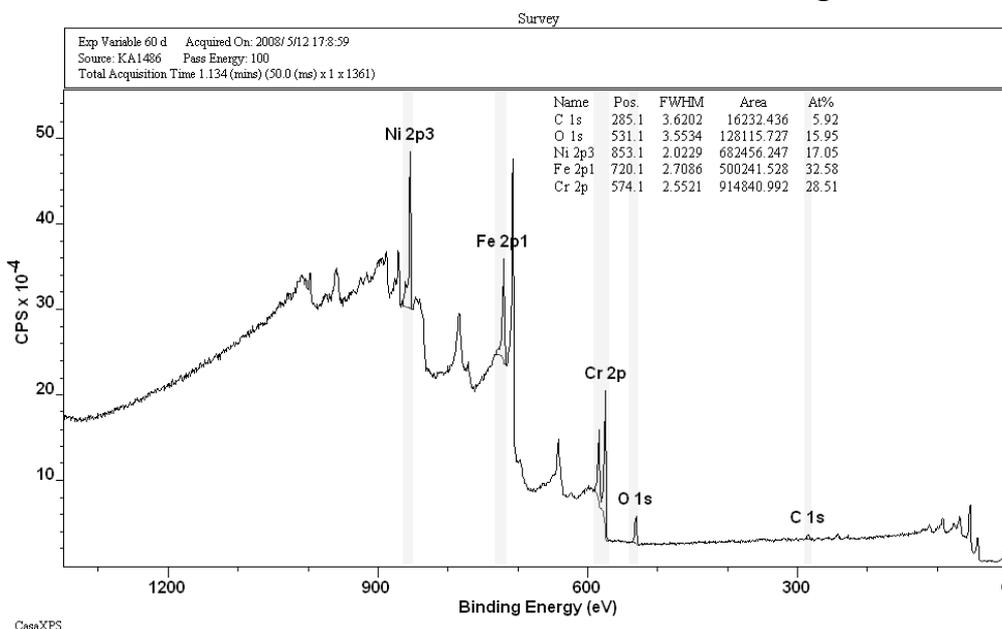


## Quantification

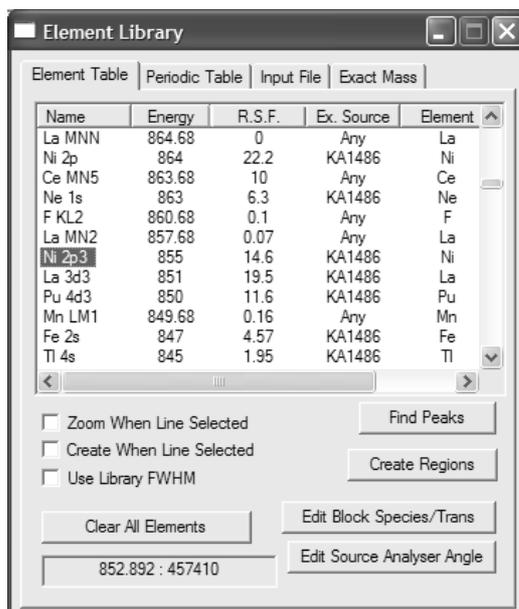
The principal features used to quantify data from the K-Alpha can be discussed using survey spectra:

## Element Library Excitation Source String

The following is a survey spectrum measured using a K-Alpha instrument, exported to ASCII format and converted to ISO format using CasaXPS.



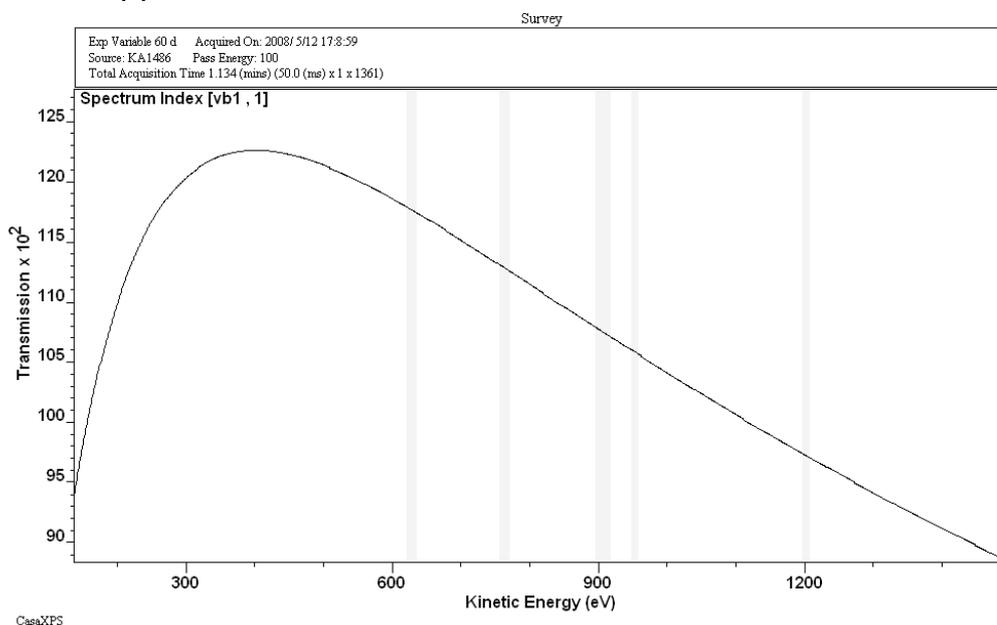
The header above the spectrum includes the source string assigned by CasaXPS for the aluminium anode, namely, **KA1486**. The significance of the unique source string assignment for the K-Alpha data is that the **KA1486** string allows a set of element library entries to be prepared for use with the K-Alpha data. When a spectrum is displayed in the active tile in CasaXPS, the element library entries visible on the Element Table property page are selected based on a match between the source string stored in the VAMAS block for the spectral data and the Excitation Source string located in the element library file.



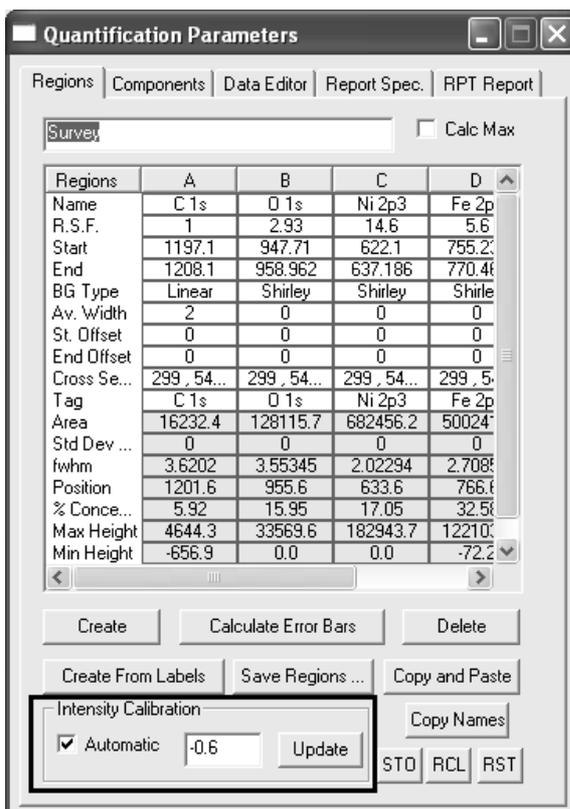
The element library file may contain entries for use with different instruments, and provided the excitation source strings are different for the different instruments, only those entries appropriate for a given instrument will be displayed in the element table. Thus, if a laboratory owned a PHI Quantum 2000, say, and also a Thermo Scientific K-Alpha, the element library entries for the PHI instrument could be populated with the excitation source strings **AI** while the K-Alpha will be assigned **KA1486**. On loading data from the PHI Quantum, CasaXPS will use and display only the entries with excitation source **AI**, while similarly K-Alpha data in CasaXPS cause the display of the K-Alpha sensitivity factors on the Element Table property page.

## Transmission Function

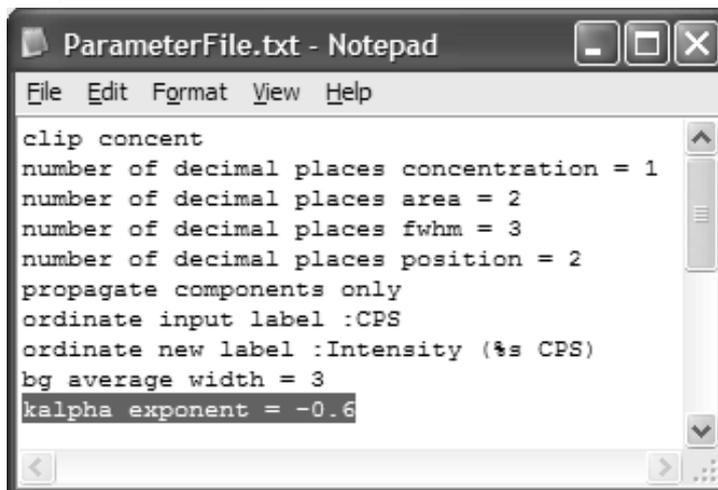
The transmission function for the K-Alpha is included in the ISO file created by CasaXPS. To view the transmission function in CasaXPS, hold down the Control key on the keyboard and press the PageUp or PageDown keys to switch between a display of the transmission curve or return to the spectral data. The transmission function for the survey spectrum above, when viewed in CasaXPS, appears as follows.



The quantification table annotating the spectrum computes the atomic concentrations using the raw area for each peak assigned a quantification region. CasaXPS divides the raw background subtracted area by the transmission function and the relative sensitivity factor, then applies the energy dependent correction calculated from the energy exponent (entered on the Regions property page) to the adjusted peak intensity.



The default energy dependent exponent for the K-Alpha used with the Scofield cross-sections is -0.6; the value used for the K-Alpha data is configured in the CasaXPS.DEF/ParameterFile.txt file, so other values for the exponent are possible. An example of the ParameterFile.txt file illustrates the configuration entry used to define the default value for the energy exponent.



The highlighted line specifies the energy exponent added to the data when converted from the Avantage ASCII files.

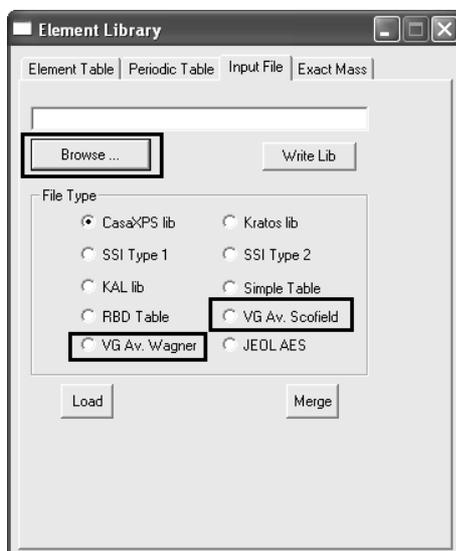
### ***Preparing an Element Library for use with the K-Alpha***

The Avantage element library information is stored in a Microsoft Access database file. **The libraries supplied with Avantage are covered by the**

**Avantage software license agreement and the original libraries or any converted formats must not be distributed. However, Thermo have made the library format available to enable individual users to obtain consistent results between Avantage and CasaXPS.**

Using Microsoft Access to open the .mdb file, select the Peaks table and copy the table into Excel. The Peaks table, viewed in Excel, can then be written to a Tab Delimited ASCII file for use in CasaXPS. Once the Tab Delimited ASCII file is available, the sensitivity factors from the Avantage system are loaded into CasaXPS using the Input File property page on the Element Library dialog window:

1. Use the Browse ... button on the Input File property page to identify the Peaks table file written from Excel.



2. Select the VG Av. Wagner or VG Av Scofield radio buttons on the same property page, depending of the sensitivity factors desired.
3. Press the Load button to replace the current CasaXPS library with the values from the Avantage Peak table file.
4. Exit CasaXPS, at which point CasaXPS will prompt for the filename used to save the modified element library. Save the element library to a new filename, e.g. CasaXPS\_AvScofield.lib.
5. Open the newly created library file in Excel and globally change the source label strings as follows. The newly created file will contain rows for each transition in the original Peaks table file which will include entries for both Al and Mg anodes. Globally change the Al anode string to KA1486 and the Mg anode string to KA1253.

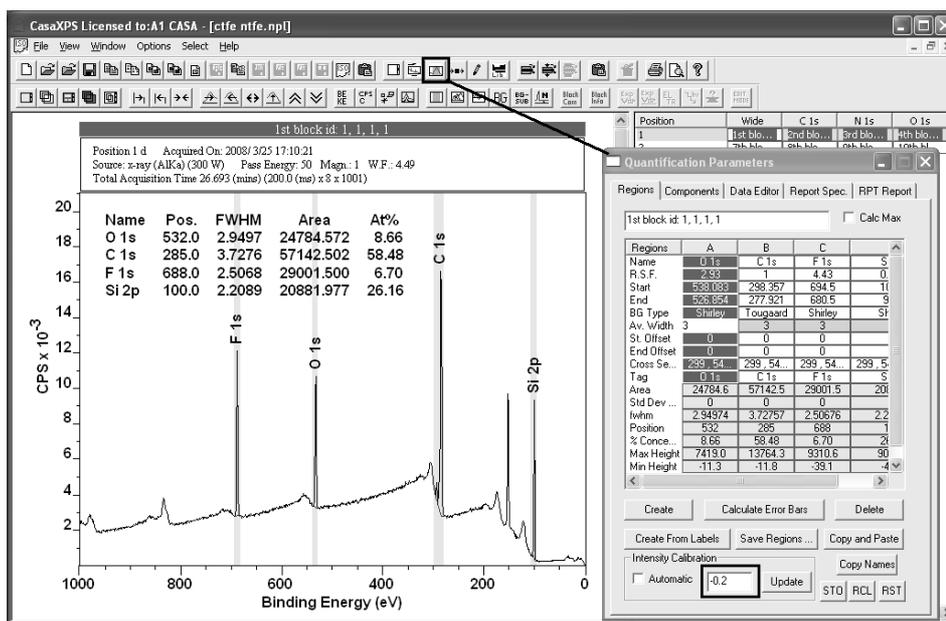
6. If another instrument using different RSFs is also in use, in Excel, open the current CasaXPS.lib file located in the CasaXPS directory containing the CasaXPS.exe executable file. Copy the entries from the newly created and source label adjusted CasaXPS formatted file corresponding to the K-Alpha library into the Excel file containing the current CasaXPS.lib file. The resulting spreadsheet should contain all the existing entries followed by all the entries from the Avantage file in CasaXPS format. After saving the resulting table of CasaXPS formatted entries to file, the combined file will need to replace the default CasaXPS library file called CasaXPS.lib in the directory containing the CasaXPS.exe executable file.

Once the new element library is prepared and in the correct location, CasaXPS will need to be restarted and data from each type of instrument examined. Load a spectrum from each of the instruments involved, open the Element Table property page and click on the tile displaying the spectra. Ensure the Ex. Source column displays the correct anode label for the data being viewed and also the RSF column is appropriate for the spectrum in the active tile.

Given an appropriate element library prepared as described above, data from either instrument will be quantified in exactly the same way. Each time a region or component is created using the element library, the appropriate RSF for the data will be retrieved from the combined element library.

## Quantification of JEOL XPS Spectra from SpecSurf

The quantification procedure used by the JEOL SpecSurf software involves modifying the Scofield cross-sections to account for both an energy dependency and also angular distribution corrections. However, to reproduce the quantification tables in CasaXPS produced by the JEOL SpecSurf software, it is sufficient to use an energy exponent equal to  $-0.2$ , entered on the Regions property page, and the unaltered Scofield cross-sections for the RSF values.



While the reported RSFs will not match in absolute terms, the relative RSFs are the same between the two systems and therefore the quantification tables will be identical (assuming the same calculated peak areas and positions for the peaks).

Although the infrastructure for adjusting the RSFs for angular distribution is in place for the JEOL software, the current JEOL system sets the asymmetry  $\beta$  parameter to unity and therefore the angular distribution function returns the same value for all transitions, hence the Scofield cross-sections are all scaled by the same factor. The only significant adjustment to the quantification values derive from the energy dependency. The actual modifications to the Scofield cross-sections applied by the JEOL system can be fully reproduced in CasaXPS version 2.3.15, where a set of configuration parameters defined in the ParameterFile.txt file in the CasaXPS.DEF directory control the calculated RSFs. When initialised using an angle of  $56^\circ$  between

the x-ray source and the analyser, and an energy exponent of -0.2, numerically equivalent RSF values are reproduced in CasaXPS. The following table are results from CasaXPS.

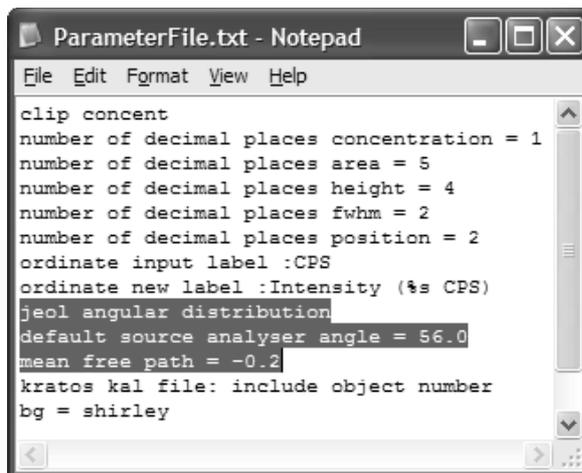
Name	Position	Library RSF	Total RSF	Raw Area	%At Conc
C 1s	284.7	1.01548	4.19415	6367.69	58.1
N 1s	401.2	1.82786	7.39709	78.6979	0.4
O 1s	532.4	2.97535	11.7345	2740.05	8.9
F 1s	688.6	4.49857	17.1189	3212.83	7.2
Si 2p	100.4	0.829645	3.5258	2337.71	25.4

The RSFs should be compared to the RSFs reported for the same data by the JEOL software:

Element	State	Sensitivity
C	1s	4.2586
N	1s	7.5129
O	1s	11.9144
F	1s	17.3911
Si	2p3/2	3.5270

The small differences between the total RSFs reported by CasaXPS and those from the JEOL software are due to different peak positions between the two systems, probably due to slight differences in the background definition.

In order to obtain quantification tables from CasaXPS consistent with the JEOL software, it is necessary to add lines to the ParameterFile.txt file in the CasaXPS.DEF directory as follows:



```

clip concent
number of decimal places concentration = 1
number of decimal places area = 5
number of decimal places height = 4
number of decimal places fwhm = 2
number of decimal places position = 2
ordinate input label :CPS
ordinate new label :Intensity (%s CPS)
jeol angular distribution
default source analyser angle = 56.0
mean free path = -0.2
kratos kal file: include object number
bg = shirley

```

The JEOL element library includes the asymmetry parameters and therefore, should these be implemented in future releases of the JEOL software the line in the ParameterFile.txt file “jeol angular distribution” would need to be changed to “correct for angular distribution”. With this adjustment, CasaXPS would extract RSFs from a Scofield library to include the full angular distribution correction.

The theory behind the use of angular distribution correction is discussed in detail elsewhere in the CasaXPS manual. An outline of the procedure will be given below.



The default CasaXPS library is populated with Scofield cross-sections. These Scofield cross-sections are computed from Hartree-Slater wave-functions and therefore are appropriate for an XPS instrument designed with the, so called, magic angle between the x-ray source and the analyser axis. Given the angle between the x-ray source and the analyser, a correction can be made to these magic angle RSFs appropriate for the given instrument. The configuration file method for specifying the require angle for the JEOL instrument, which is  $56^\circ$  is shown below.

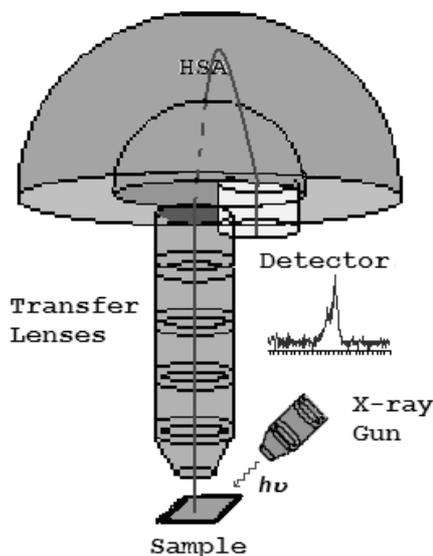
```
***** NEW LABEL *****  
jeol angular distribution  
default source analyser angle = 56.0  
mean free path = -0.2
```

Each time one or more files are opened in CasaXPS for which the angle has yet to be set, a dialog window prompts the user for the missing angle and offers the configured angle as the default.

Once a file is updated with an entry in the VAMAS file comment of the form “SourceAnalyserAngle: 56.000000 d”, the source to analyser angle is defined for that file. When coupled with the configuration entry, “jeol angular distribution”, the magic angle Scofield cross-sections from the element library will be adjusted each time an RSF is extracted from the element library for use with a Region or Component. The **Total RSF** in the table above calculated by CasaXPS is computed from the RSF in the Region or Component multiplied by the energy dependence defined by the value in the text-field on the Regions property page.

## XPS Spectra

The XPS technique is used to investigate the chemistry at the surface of a sample.



**Figure 47: Schematic of an XPS instrument.**

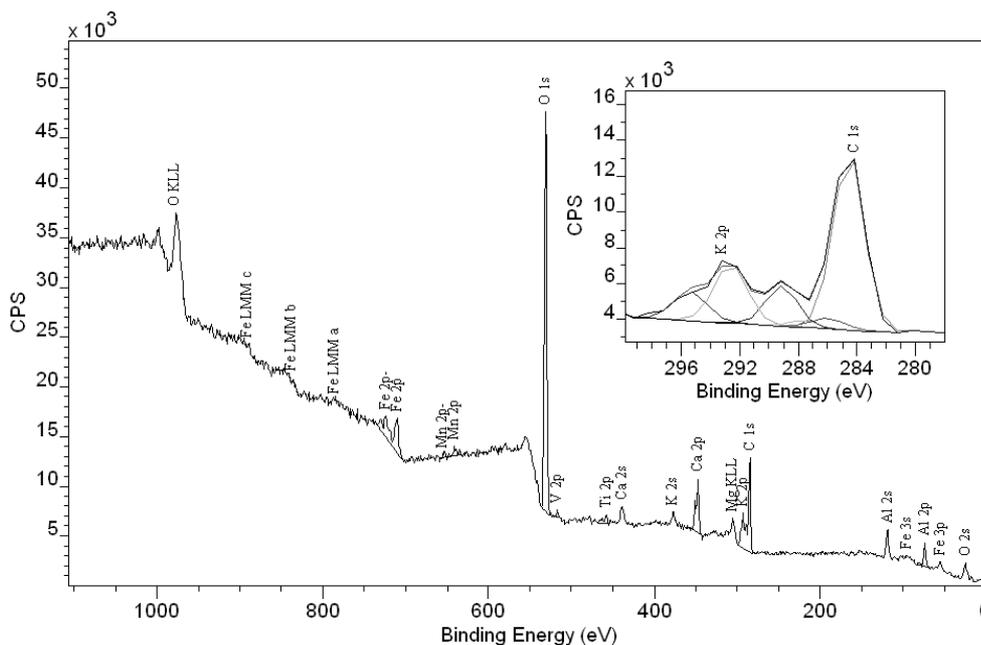
The basic mechanism behind an XPS instrument is illustrated in Figure 47. Photons of a specific energy are used to excite the electronic states of atoms below the surface of the sample. Electrons ejected from the surface are energy filtered via a hemispherical analyser (HSA) before the intensity for a defined energy is recorded by a detector. Since core level electrons in solid-state atoms are quantized, the resulting energy spectra exhibit resonance peaks characteristic of the electronic structure for atoms at the sample surface. While the x-rays may penetrate deep into the sample, the escape depth of the ejected electrons is limited. That is, for energies around 1400 eV, ejected electrons from depths greater than 10nm have a low probability of leaving the surface without undergoing an energy loss event, and therefore contribute to the background signal rather than well defined primary photoelectric peaks.

In principle, the energies of the photoelectric lines are well defined in terms of the binding energy of the electronic states of atoms. Further, the chemical environment of the atoms at the surface result in well defined energy shifts to the peak energies. In the case of conducting samples, for which the detected electron energies can be referenced to the Fermi energy of the spectrometer, an absolute energy scale can be established, thus aiding the

identification of species. However, for non-conducting samples the problem of energy calibration is significant. Electrons leaving the sample surface cause a potential difference to exist between the sample and the spectrometer resulting in a retarding field acting on the electrons escaping the surface. Without redress, the consequence can be peaks shifted in energy by as much as 150 eV. Charge compensation designed to replace the electrons emitted from the sample is used to reduce the influence of sample charging on insulating materials, but nevertheless identification of chemical state based on peak positions requires careful analysis.

XPS is a quantitative technique in the sense that the number of electrons recorded for a given transition is proportional to the number of atoms at the surface. In practice, however, to produce accurate atomic concentrations from XPS spectra is not straight forward. The precision of the intensities measured using XPS is not in doubt; that is intensities measured from similar samples are repeatable to good precision. What may be doubtful are results reporting to be atomic concentrations for the elements at the surface. An accuracy of 10% is typically quoted for routinely performed XPS atomic concentrations. For specific carefully performed and characterised measurements better accuracy is possible, but for quantification based on standard relative sensitivity factors, precision is achieved not accuracy. Since many problems involve monitoring changes in samples, the precision of XPS makes the technique very powerful.

The first issue involved with quantifying XPS spectra is identifying those electrons belonging to a given transition. The standard approach is to define an approximation to the background signal. The background in XPS is non-trivial in nature and results from all those electrons with initial energy greater than the measurement energy for which scattering events cause energy losses prior to emission from the sample. The zero-loss electrons constituting the photoelectric peak are considered to be the signal above the background approximation. A variety of background algorithms are used to measure the peak area; none of the practical algorithms are correct and therefore represent a source for uncertainty when computing the peak area. Peak areas computed from the background subtracted data form the basis for most elemental quantification results from XPS.

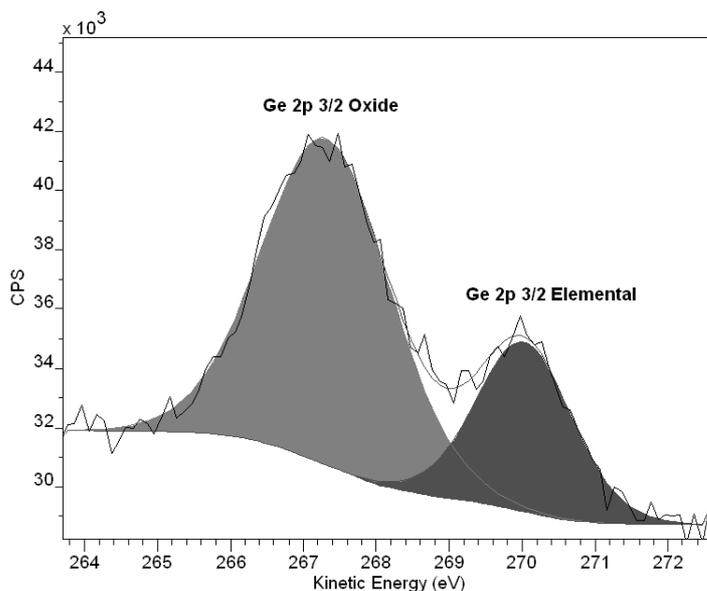


**Figure 48: An example of a typical XPS survey spectrum taken from a compound sample.**

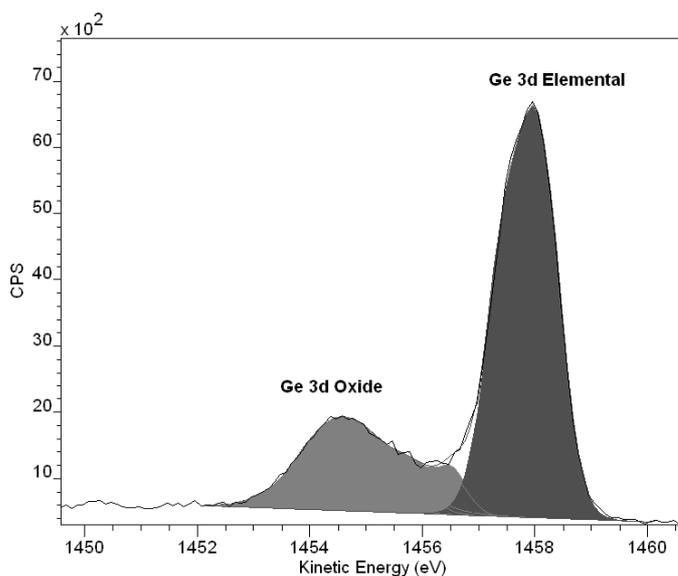
The data in Figure 48 illustrates an XPS spectrum measured from a typical sample encountered in practice. The inset tile within Figure 48 shows the range of energies associated with the C 1s and K 2p photoelectric lines. Since these two transitions include multiple overlapping peaks, there is a need to apportion the electrons to the C 1s or the K 2p transitions using a synthetic peak model fitted to the data. The degree of correlation between the peaks in the model influences the precision and therefore the accuracy of the peak area computation.

Relative sensitivity factors of photoelectric peaks are often tabulated and used routinely to scale the measured intensities as part of the atomic concentration calculation. These RSF tables can only be accurate for homogenous materials. If the sample varies in composition with depth, then the kinetic energy of the photoelectric line alters the depth from which electrons are sampled. It is not uncommon to see evidence of an element in the sample by considering a transition at high kinetic energy, but find little evidence for the presence of the same element when a lower kinetic energy transition is considered. Transitions of this nature might be Fe 2p compared to Fe 3p both visible in Figure 48, where the relative intensity of these peaks will depend on the depth of the iron with respect to the surface. Sample roughness and angle of the sample to the analyser also changes the relative

intensity of in-homogenous samples, thus sample preparation and mounting can influence quantification values.



**Figure 49: Germanium Oxide relative intensity to elemental germanium measured using photoelectrons with kinetic energy in the range 262 eV to 272 eV.**



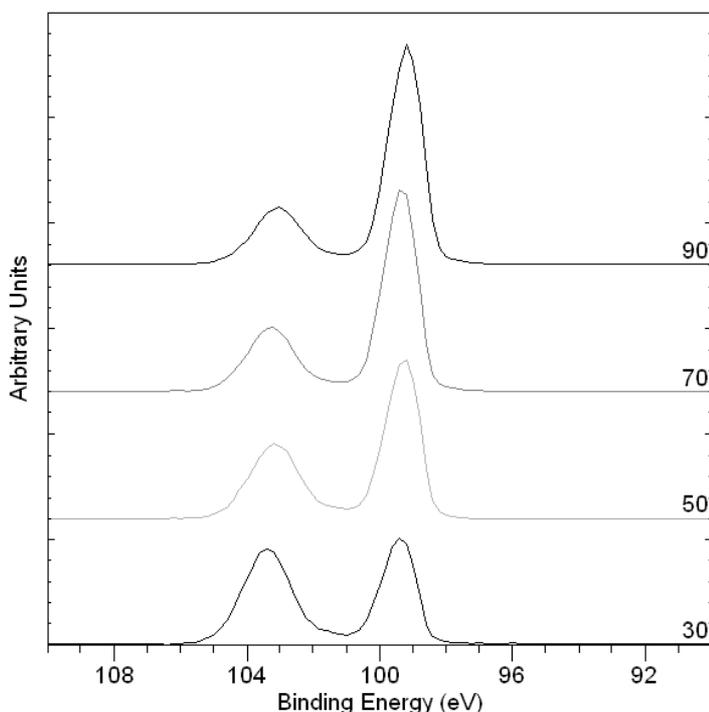
**Figure 50: Germanium Oxide relative intensity to elemental germanium measured using photoelectrons with kinetic energy in the range 1452 eV to 1460 eV.**

The chemical shifts seen in XPS data are a valuable source of information about the sample. The spectra in Figure 49 and Figure 50 illustrate the separation of elemental and oxide peaks of germanium due to chemical state. Both spectra were acquired from the same sample under the same conditions with the exception that the ejected electrons for the Ge 3d peaks are about 1200 eV more energetic than the Ge 2p electrons. The

consequence of choosing to quantify based on one of these transitions is that the proportion of oxide to elemental germanium differs significantly. The oxide represents an over layer covering of the elemental germanium and therefore the low energy photoelectrons from the Ge 2p line are attenuated resulting in a shallower sampling depth compared to the more energetic Ge 3d electrons. Hence the volume sampled by the Ge 2p transition favours the oxide signal, while the greater depth from which Ge 3d electrons can emerge without energy loss favours the elemental germanium. While these variations may seem a problem, such changes in the spectra are also a source for information about the sample.

Tilting the sample with respect to the axis of the analyser results in changing the sampling depth for a given transition and therefore data collected at different angles vary due to the differing composition with depth. Figure 51 is a sequence of Si 2p spectra measured from the same silicon sample at different angles. The angles associated with the spectra are with respect to the axis of the analyser and the sample surface. Data measured at 30° favours the top most oxide layers; while at 90° the elemental substrate becomes dominant in the spectrum.

Si2p Oxide and Elemental Peaks

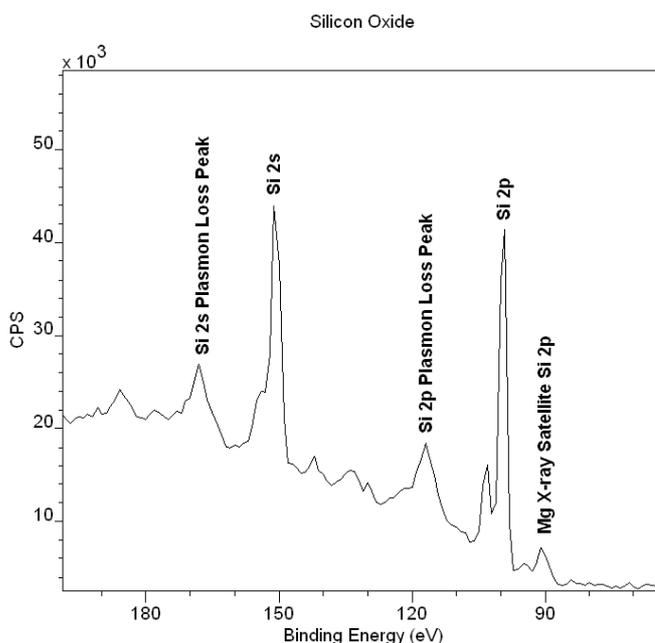


**Figure 51: Angle resolved Si 2p spectra showing the changes to the spectra resulting from tilting the sample with respect to the analyser axis.**

## Other Peaks in XPS Spectra

Not all peaks in XPS data are due to the ejection of an electron by a direct interaction with the incident photon. The most notable are the Auger peaks, which are explained in terms of the decay of a more energetic electron to fill the vacant hole created by the x-ray photon, combined with the emission of an electron with an energy characteristic of the difference between the states involved in the process. The spectrum in Figure 48 includes a sequence of peaks labelled O KLL. These peaks represent the energy of the electrons ejected from the atoms due to the filling of the O 1s state (K shell) by an electron from the L shell coupled with the ejection of an electron from an L shell.

Unlike the photoelectric peaks, the kinetic energy of the Auger lines is independent of the photon energy for the x-ray source. Since the kinetic energy of the photoelectrons are given in terms of: the photon energy  $h\nu$ , the binding energy for the ejected electron  $E_{be}$  and a work function  $\phi$  by the relationship  $E_{ke} = h\nu - E_{be} - \phi$ , altering the photon energy by changing the x-ray anode material causes the Auger lines and the photoelectric lines to move in energy relative to one another.



**Figure 52: Elemental Silicon loss peaks and also x-ray satellite peak.**

Less prominent than Auger lines are x-ray satellite peaks. Data acquired using a non-monochromatic x-ray source create satellite peaks offset from the

primary spectral lines by the difference in energy between the resonances in the x-ray spectrum of the anode material used in the x-ray gun and also in proportion to the peaks in the x-ray spectrum for the anode material. Figure 52 indicates an example of a satellite peak to the primary Si 2p peak due to the use of a magnesium anode in the x-ray source. Note that Auger line energies are independent of the photon energy and therefore do not have satellite peaks.

A further source for peaks in the background signal is due to resonant scattering of electrons by the surface materials. Plasmon peaks for elemental silicon are also labelled on Figure 52. The sharpness of these plasmon peaks in Figure 52 is due to the nature of the material through which the photoelectrons must pass. For silicon dioxide, the loss structures are much broader and follow the trend of a typical XPS background signal. The sharp loss structures in Figure 52 are characteristic of pure metallic-like materials.

## Basic Quantification of XPS Spectra

XPS counts electrons ejected from a sample surface when irradiated by x-rays. A spectrum representing the number of electrons recorded at a sequence of energies includes both a contribution from a background signal and also resonance peaks characteristic of the bound states of the electrons in the surface atoms. The resonance peaks above the background are the significant features in an XPS spectrum shown in Figure 53.

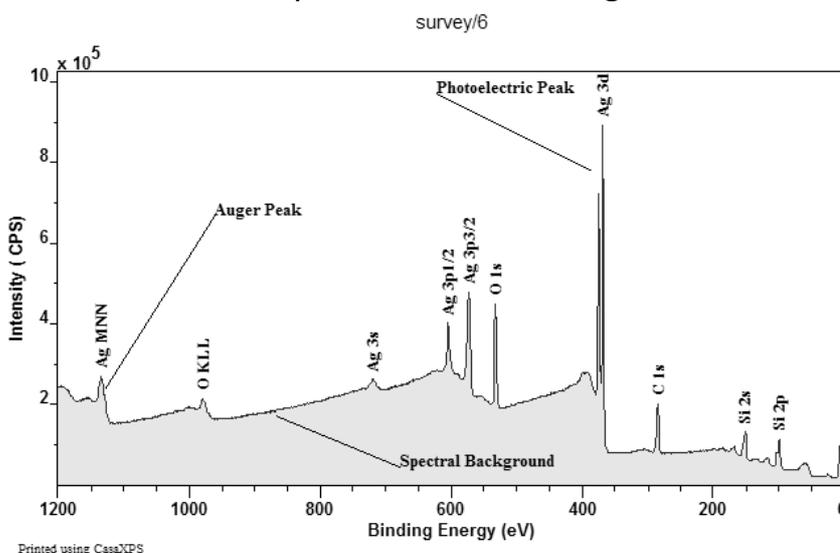
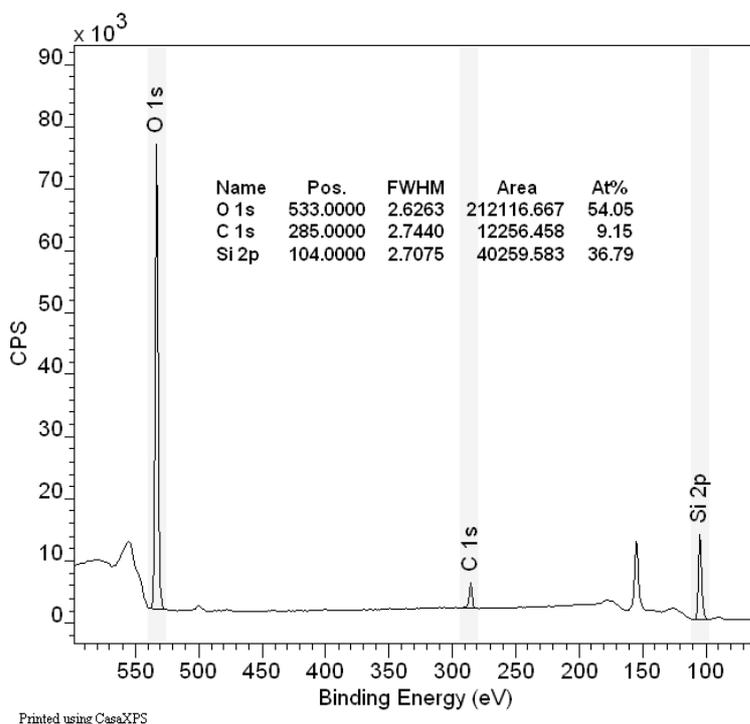


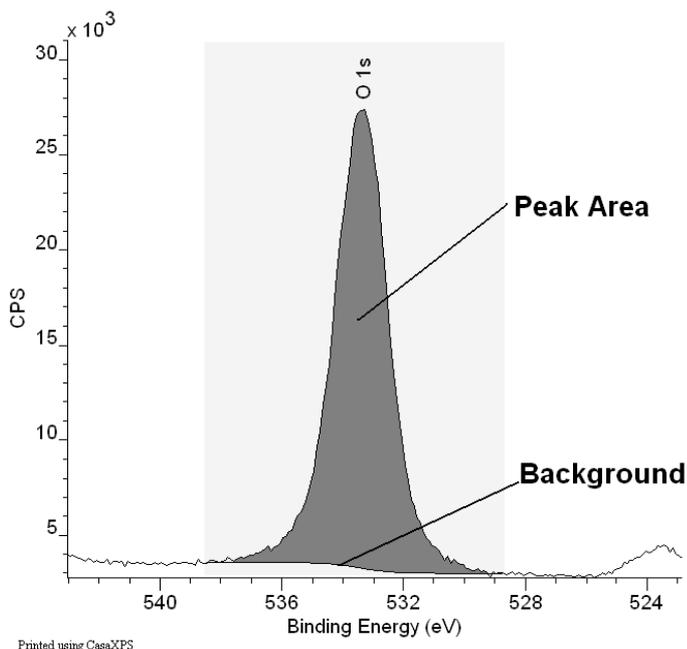
Figure 53: XPS and Auger peaks appear above a background of scattered electrons.

XPS spectra are, for the most part, quantified in terms of peak intensities and peak positions. The peak intensities measure how much of a material is at the surface, while the peak positions indicate the elemental and chemical composition. Other values, such as the full width at half maximum (FWHM) are useful indicators of chemical state changes and physical influences. That is, broadening of a peak may indicate: a change in the number of chemical bonds contributing to a peak shape, a change in the sample condition (x-ray damage) and/or differential charging of the surface (localised differences in the charge-state of the surface).



**Figure 54: Quantification regions**

The underlying assumption when quantifying XPS spectra is that the number of electrons recorded is proportional to the number of atoms in a given state. The basic tool for measuring the number of electrons recorded for an atomic state is the quantification region. Figure 54 illustrates a survey spectrum where the surface is characterised using a quantification table based upon values computed from regions. The primary objectives of the quantification region are to define the range of energies over which the signal can be attributed to the transition of interest and to specify the type of approximation appropriate for the removal of background signal not belonging to the peak.



**Figure 55: O 1s Region**

### How to Compare Samples

A direct comparison of peak areas is not a recommended means of comparing samples for the following reasons. An XPS spectrum is a combination of the number of electrons leaving the sample surface and the ability of the instrumentation to record these electrons; not all the electrons emitted from the sample are recorded by the instrument. Further, the efficiency with which emitted electrons are recorded depends on the kinetic energy of the electrons, which in turn depends on the operating mode of the instrument. As a result, the best way to compare XPS intensities is via, so called, percentage atomic concentrations. The key feature of these percentage atomic concentrations is the representation of the intensities as a percentage, that is, the ratio of the intensity to the total intensity of electrons in the measurement. Should the experimental conditions change in any way between measurements, for example the x-ray gun power output, then peak intensities would change in an absolute sense, but all else being equal, would remain constant in relative terms.

### Relative Intensity of Peaks in XPS

Each element has a range of electronic states open to excitation by the x-rays. For an element such as silicon, both the Si 2s and Si 2p transitions are of

suitable intensity for use in quantification. The rule for selecting a transition is to choose the transition for a given element for which the peak area, and therefore in principle the RSF, is the largest, subject to the peak being free from other interfering peaks.

Transitions from different electronic states from the same element vary in peak area. Therefore, the peak areas calculated from the data must be scaled to ensure the same quantity of silicon, say, is determined from either the Si 2s or the Si 2p transitions. More generally, the peak areas for transitions from different elements must be scaled too. A set of relative sensitivity factors are necessary for transitions within an element and also for all elements, where the sensitivity factors are designed to scale the measured areas so that meaningful atomic concentrations can be obtained, regardless of the peak chosen.

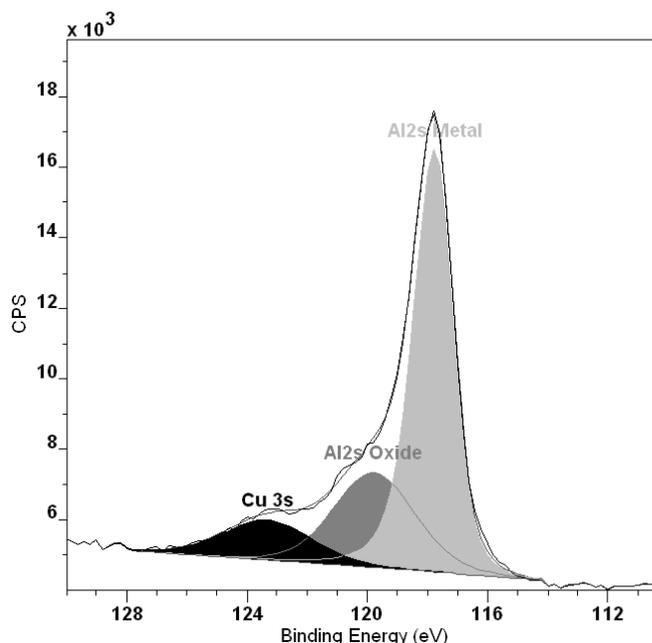
Regions	A	B	C	D
Name	Si 2p	C 1s	O 1s	N 1s
R.S.F.	0.817	1	2.93	1.8
Start	107.681	290.883	539.7	407.179
End	92.0543	279.378	522.516	389.065
BG Type	Shirley	Shirley	Shirley	Linear
Av. Width	0	0	0	2
St. Offset	0	0	0	0
End Offset	0	0	0	0
Cross Se...	299.54...	299.5...	299.5...	299.542...
Tag	Si 2p	C 1s	O 1s	N 1s
Area	9634.0	3124.3	15332.5	332.6
Std Dev ...	0	0	0	0
fwhm	2.61846	3.09819	2.73225	2.12241
Position	98.7091	284.709	531.709	396.709
% Conce...	57.99	15.37	25.73	0.91
Max Height	101708.5	29472.1	16005...	4107.5
Min Height	-268.6	0.0	0.0	-945.4
Peak to ...	58.95	13.92	25.80	1.33

**Figure 56: Regions Property Page.**

Quantification of the spectrum in Figure 54 requires the selection of one transition per element. Figure 55 illustrates the area targeted by the region defined for the O 1s transition; similar regions are defined for the C 1s, N 1s and Si 2p transitions leading to the quantification table displayed over the data in Figure 54. The Regions property page shown in Figure 56 provides the basic mechanism for creating and updating the region parameters influencing the computed peak area. Relative sensitivity factors are also entered on the Regions property page. The computed intensities are adjusted for instrument

transmission and escape depth corrections, resulting in the displayed quantification table in Figure 54.

Quantification regions are useful for isolated peaks. Unfortunately not all samples will offer clearly resolved peaks. A typical example of interfering peaks is any material containing both aluminium and copper. When using the standard magnesium or aluminium x-ray anodes, the only aluminium photoelectric peaks available for measuring the amount of aluminium in the sample are Al 2s and Al 2p. Both aluminium peaks appear at almost the same binding energy as the Cu 3s and Cu 3p transitions. Thus estimating the intensity of the aluminium in a sample containing these elements requires a means of modelling the data envelope resulting from the overlapping transitions illustrated in Figure 57.



**Figure 57: Aluminium and Copper both in evidence at the surface.**

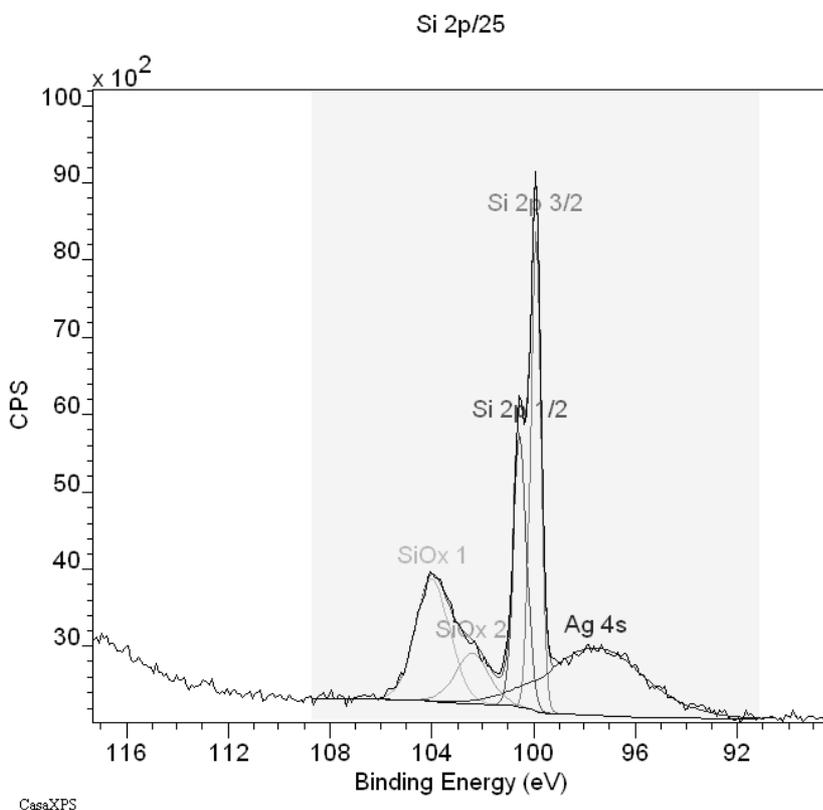
### Overlapping Peaks

Techniques for modelling data envelopes not only apply to separating elemental information, such as the copper and aluminium intensities in Figure 57, but also apply to chemical state information about the aluminium itself. Intensities for the aluminium oxide and metallic states in Figure 57 are measured using synthetic line-shapes or components. An XPS spectrum typically includes multiple transitions for each element; while useful to identify the composition of the sample, the abundance of transitions

frequently leads to interference between peaks and therefore introduces the need to construct peak models. Figure 58 illustrates a spectrum where a thin layer of silver on silicon (University of Iowa, Jukna, Baltrusaitis and Virzonis, 2007, unpublished work) introduces an interference with the Si 2p transition from the Ag 4s transition.

The subject of peak-fitting data is complex. A model is typically created from a set of Gaussian/Lorentzian line-shapes. Without careful model construction involving additional parameter constraints, the resulting fit, regardless of how accurate a representation of the data, may be of no significance from a physical perspective. The subject of peak fitting XPS spectra is dealt with in detail elsewhere.

Peak models are created using the Components property page on the Quantification Parameters dialog window shown in Figure 59. A range of line-shapes are available for constructing the peak models including both symmetric and asymmetric functional forms. The intensities modelled using these synthetic line-shapes are scaled using RSFs and quantification using both components and regions are offered on the Report Spec property page of CasaXPS.



**Figure 58: Elemental and oxide states of Silicon**

## Peak Positions

In principle, the peak positions in terms of binding energy provide information about the chemical state for a material. The data in Figure 48 provides evidence for at least three chemical states of silicon. Possible candidates for these silicon states might be  $\text{SiO}_2$ ,  $\text{Si}_2\text{O}_3$ ,  $\text{SiO}$ ,  $\text{Si}_2\text{O}$  or  $\text{Si}$ , however an assignment based purely on the measured binding energies for the synthetic line-shapes relies on an accurate calibration for the energy scale. Further, the ability to calibrate the energy scale is dependent on the success of the charge compensation for the sample and the availability of a peak at known binding energy to provide a reference for shifting the energy scale.

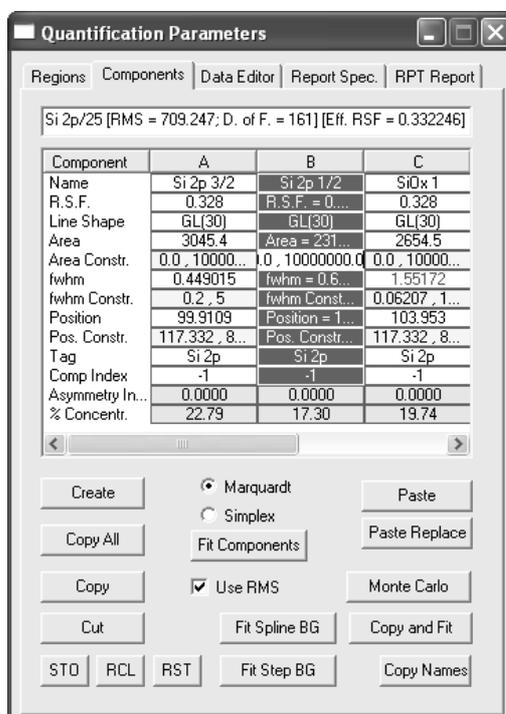


Figure 59: Components property page on the Quantification Parameters dialog window.

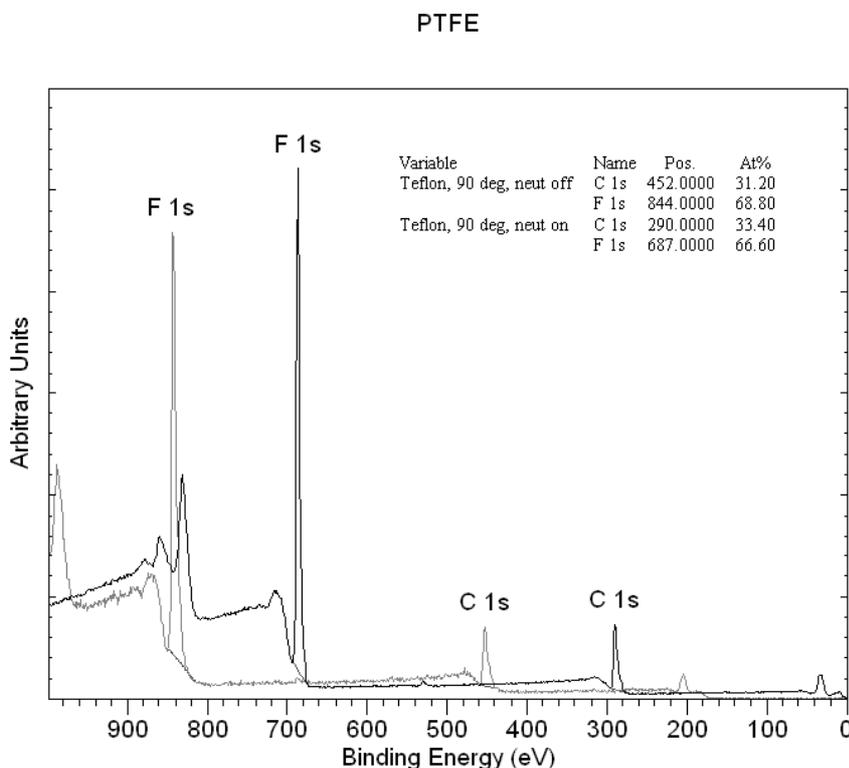
## Charge Compensation

The XPS technique relies on electrons leaving the sample. Unless these emitted electrons are replaced, the sample will charge relative to the instrument causing a retarding electric field at the sample surface. For conducting samples electrically connected to the instrument, the charge balance is easily restored; however, for insulating materials electrons must be replaced via an external source. Insulating samples are normally electrically isolated from the instrument and low energy electrons and/or

ions are introduced at the sample surface. The objective is to replace the photoelectrons to provide a steady state electrical environment from which the energy of the photoelectrons can be measured.

The data in Figure 60 shows spectra from PTFE (Teflon) acquired with and without charge compensation. The C 1s peaks are shifted by 162 eV between the two acquisition conditions, but even more importantly, the separation between the C 1s and the F 1s peaks differ between the two spectra by 5 eV. Without effective charge compensation, the measured energy for a photoelectric line may change as a function of kinetic energy of the electrons.

Charge compensation does not necessarily mean neutralization of the sample surface. The objective is to stabilize the sample surface to ensure the best peak shape, whilst also ensuring peak separation between transitions is independent of the energy at which the electrons are measured. Achieving a correct binding energy for a known transition is not necessarily the best indicator of good charge compensation. A properly charge compensated experiment typically requires shifting in binding energy using the Calibration property page, but the peak shapes are good and the relative peak positions are stable.



**Figure 60: Insulating sample before and after charge compensation.**

A nominally conducting material may need to be treated as an insulating sample. Oxide layers on metallic materials can transform a conducting material into an insulated surface. For example, aluminium metal oxidizes even in vacuum and a thin oxide layer behaves as an insulator.

Calibrating spectra in CasaXPS is performed using the Calibration property page on the Spectrum Processing dialog window.

## Depth Profiling using XPS

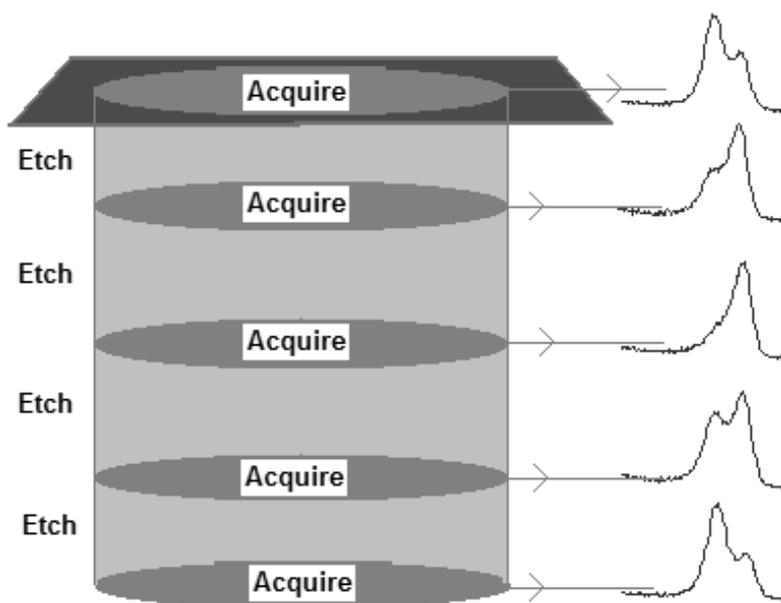
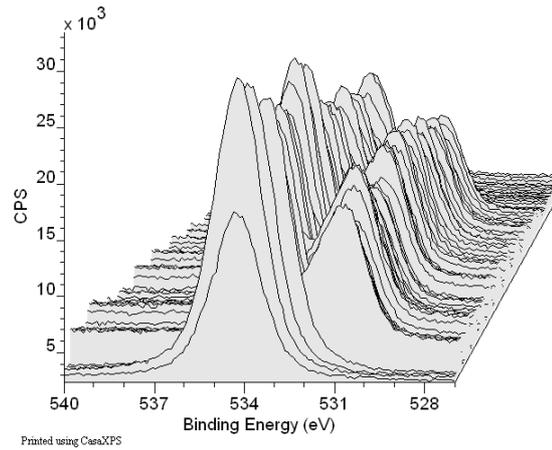


Figure 61: Segment of an XPS depth profile.

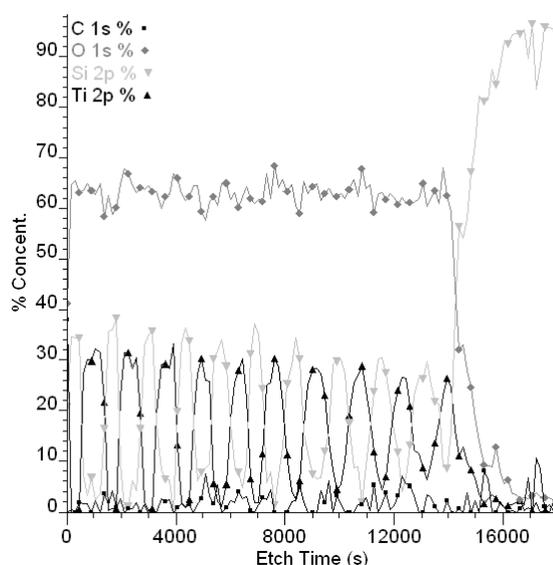
While XPS is a surface sensitive technique, a depth profile of the sample in terms of XPS quantities can be obtained by combining a sequence of ion gun etch cycles interleaved with XPS measurements from the current surface. An ion gun is used to etch the material for a period of time before being turned off whilst XPS spectra are acquired. Each ion gun etch cycle exposes a new surface and the XPS spectra provide the means of analysing the composition of these surfaces.

The set of XPS spectra corresponding to the oxygen 1s peaks from a depth profile experiment depicted logically in Figure 61 are displayed in Figure 62. The objective of these experiments is to plot the trend in the quantification values as a function of etch-time.



**Figure 62: The set of O 1s spectra measured during a depth profiling experiment.**

The actual depth for each XPS analysis is dependent on the etch-rate of the ion-gun, which in turn depends on the material being etched at any given depth. For example, the data in Figure 62 derives from a multilayer sample consisting of silicon oxide alternating with titanium oxide layers on top of a silicon substrate. The rate at which the material is removed by the ion gun may vary between the layers containing silicon oxide and those layers containing titanium oxide, with a further possible variation in etch-rate once the silicon substrate is encountered. The depth scale is therefore dependent on characterizing the ion-gun however each XPS measurement is typical of any other XPS measurement, with the understanding that the charge compensation steady state may change between layers.



**Figure 63: XPS Depth Profile of silicon oxide/titanium oxide multilayer sample profiled using a Kratos Amicus XPS instrument.**

Etch ...	Ti 2p	Si 2p	O 1s	C 1s
0	Ti 2p/2	Si 2p/3	O 1s/4	C 1s/5
150	Ti 2p/8	Si 2p/9	O 1s/10	C 1s/11
300	Ti 2p/14	Si 2p/15	O 1s/16	C 1s/17
450	Ti 2p/20	Si 2p/21	O 1s/22	C 1s/23
600	Ti 2p/26	Si 2p/27	O 1s/28	C 1s/29
750	Ti 2p/32	Si 2p/33	O 1s/34	C 1s/35
900	Ti 2p/38	Si 2p/39	O 1s/40	C 1s/41
1050	Ti 2p/44	Si 2p/45	O 1s/46	C 1s/47
1200	Ti 2p/50	Si 2p/51	O 1s/52	C 1s/53
1350	Ti 2p/56	Si 2p/57	O 1s/58	C 1s/59
1500	Ti 2p/62	Si 2p/63	O 1s/64	C 1s/65
1650	Ti 2p/68	Si 2p/69	O 1s/70	C 1s/71
1800	Ti 2p/74	Si 2p/75	O 1s/76	C 1s/77
1950	Ti 2p/80	Si 2p/81	O 1s/82	C 1s/83
2100	Ti 2p/86	Si 2p/87	O 1s/88	C 1s/89
2250	Ti 2p/92	Si 2p/93	O 1s/94	C 1s/95
2400	Ti 2p/98	Si 2p/99	O 1s/100	C 1s/101
2550	Ti 2p/104	Si 2p/105	O 1s/106	C 1s/107
2700	Ti 2p/110	Si 2p/111	O 1s/112	C 1s/113
2850	Ti 2p/116	Si 2p/117	O 1s/118	C 1s/119
3000	Ti 2p/122	Si 2p/123	O 1s/124	C 1s/125
3150	Ti 2p/128	Si 2p/129	O 1s/130	C 1s/131
3300	Ti 2p/134	Si 2p/135	O 1s/136	C 1s/137
3450	Ti 2p/140	Si 2p/141	O 1s/142	C 1s/143
3600	Ti 2p/146	Si 2p/147	O 1s/148	C 1s/149
3750	Ti 2p/152	Si 2p/153	O 1s/154	C 1s/155
3900	Ti 2p/158	Si 2p/159	O 1s/160	C 1s/161
4050	Ti 2p/164	Si 2p/165	O 1s/166	C 1s/167

**Figure 64: Logical structure of the VAMAS blocks in an XPS depth profile.**

The XPS depth profile in Figure 63 is computed from the VAMAS file data logically ordered in CasaXPS as shown in Figure 64. The O 1s spectra displayed in Figure 62 are highlighted in Figure 64. One point to notice about the profile in Figure 63 is that the atomic concentration calculation for the O 1s trace is relatively flat for the silicon oxide and titanium oxide layers, in contrast to the raw data in Figure 62, where the chemically shifted O 1s peaks would appear to be more intense for the silicon oxide layers compared to the titanium oxide layers. This observation is supported by the plot of adjusted peak areas in Figure 65, where again the O 1s trace is far from flat. The profile in Figure 63 is far more physically meaningful than the variations displayed in Figure 65. Normalization of the XPS intensities to the total signal measured on a layer by layer basis is important for understanding the sample. This example is a good illustration of why XPS spectra should be viewed in the context of the other elements measured from a surface.

The details of how to analyze a depth profile in CasaXPS are discussed at length in The Casa Cookbook and other manual pages available from the Help option on the Help menu.

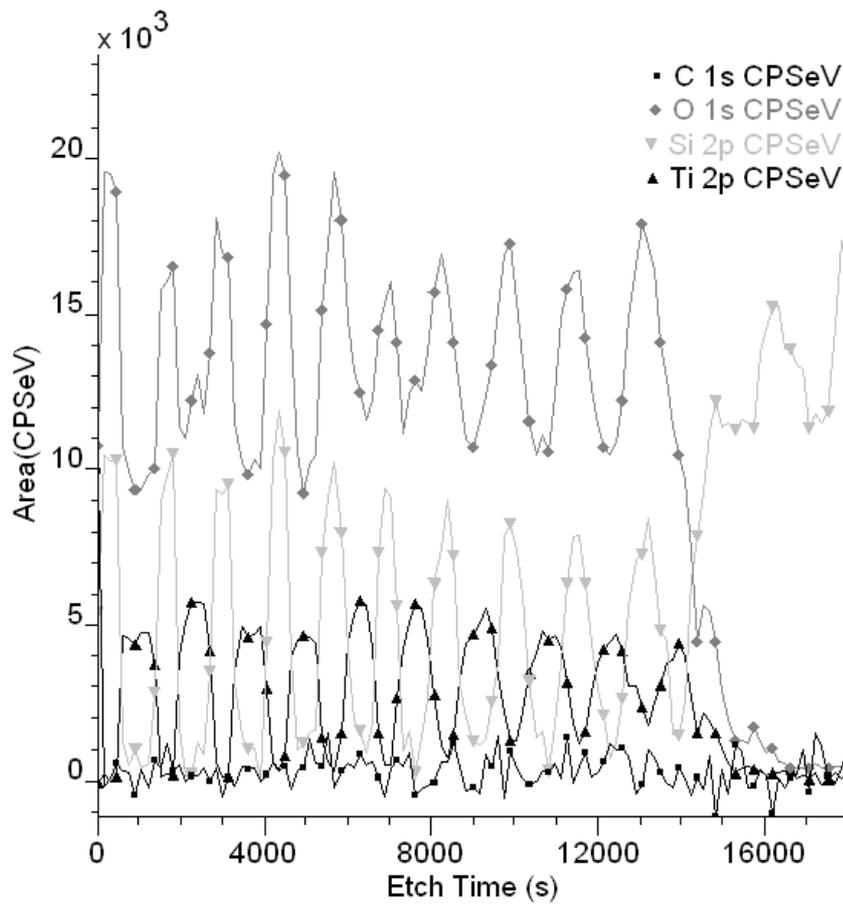


Figure 65: Peak areas scaled by RSF used to compute the atomic concentration plots in Figure 63.