

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 of -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).

While the infrastructure for adjusting the RSFs for angular distribution is in place for the JEOL software, the current JEOL system sets the asymmetry β 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° between the x-ray source and the analyser, and an energy

exponent of -0.2, numerically equivalent RSF values are reproduced in CasaXPS. Table 1 is a quantification table calculated in CasaXPS for the same data for which the JEOL system reports RSFs shown in Figure 1. The small differences between the total RSFs reported by CasaXPS and those in Figure 1 are due to different peak positions between the two systems, probably due to slight differences in the background definition.

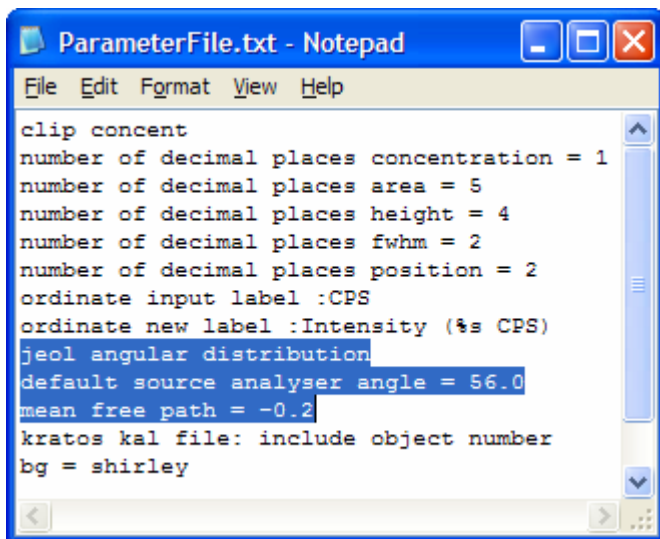
Name	Position	Library RSF	Total RSF	Raw Area	%At Conc
C 1s	284.7	1.01548	4.19415	6367.69	58.1
N 1s	401.2	1.82786	7.39709	78.6979	0.4
O 1s	532.4	2.97535	11.7345	2740.05	8.9
F 1s	688.6	4.49857	17.1189	3212.83	7.2
Si 2p	100.4	0.829645	3.5258	2337.71	25.4

Table 1: Quantification table generated in CasaXPS

Element	State	Sensitivity
C	1s	4.2586
N	1s	7.5129
O	1s	11.9144
F	1s	17.3911
Si	2p3/2	3.5270

Figure 1: JEOL RSF values for the transitions in Table 1.

In order to obtain the quantification table in Table 1, it is necessary to add lines to the ParameterFile.txt file in the CasaXPS.DEF directory as shown in Figure 2.



```

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
  
```

Figure 2: ParameterFile.txt file in the CasaXPS.DEF directory used in version 2.3.15 of CasaXPS.

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 in Figure 2 shows the method for specifying the require angle for the JEOL instrument, which is 56°. 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 column in Table 1 headed **Total RSF** is calculated 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.



Quantification Examples

The follow examples illustrate how to quantify data from the JEOL JPS-9200 instruments at University of Wageningen, The Netherlands.



Quantification of a Survey Spectrum

Survey spectra are typically used to measure elemental concentrations and therefore quantification regions are usually the tool of choice to measure the peak areas. A low resolution acquisition mode enhances the signal-to-noise in a survey spectrum, but broadens the peaks in the data making these peaks less appropriate for chemical state analysis by peak modelling, hence the use of regions only. The first example describes how to quantify a survey spectrum using quantification regions.

The Quantification Parameters dialog window is available from the Options menu on the CasaXPS main window or via the top toolbar button . Quantification Regions are edited on the Regions property page on the Quantification Parameters dialog window, where the limits of integration, background type and RSF parameters are set. For successful quantification of a sample using a survey spectrum, a set of Regions must be created with the appropriate RSFs for the transitions identified. To ensure the correct RSF is extracted from the element library, the best means of creating regions for survey spectra is to use the Element Library dialog window  to create the regions. Buttons labelled **Create Regions** are on both the Element Table property page (Figure 3) and the Periodic Table property page. These **Create Regions** buttons use the set of element marks currently defined on the survey spectrum to initialise a set of regions on the data. Figure 4 shows a survey

spectrum displaying element marks for oxygen, carbon and silicon in preparation for creating regions using the **Create Region** button.

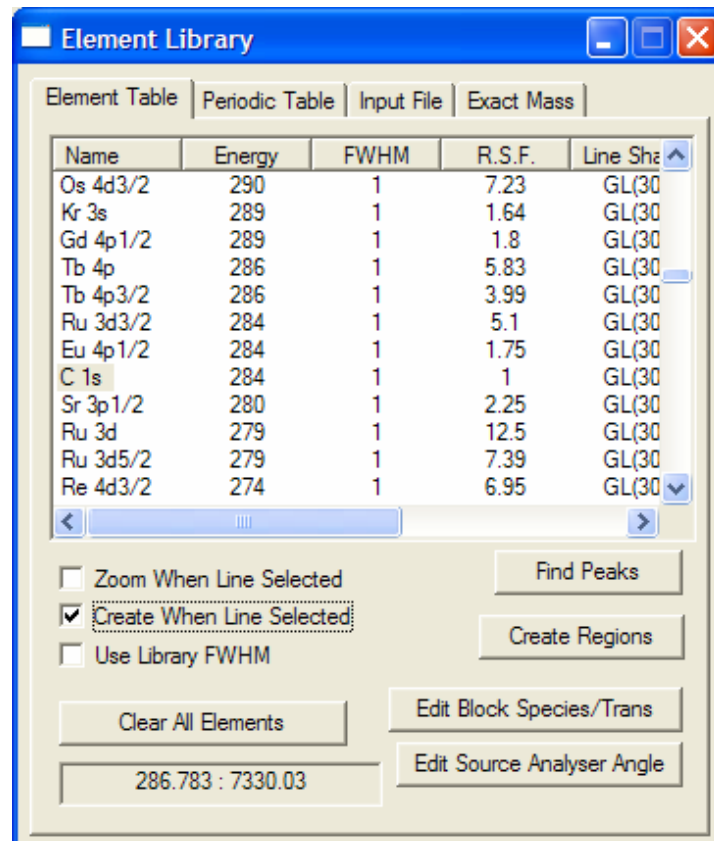


Figure 3: Element Library Dialog Window

Once the element marks are defined for the data, simply pressing one of the **Create Region** buttons on the Element Library dialog window will create a set of quantification regions for the spectrum. If a peak can be identified corresponding to the transitions with the largest RSF for each element, a region is created. If no peak can be detected, but it is desired to include a region for a “missing peak”, then a further mechanism to force the inclusion of a region is provided via the **Create When Line Selected** tick box on the Element Table property page. When ticked and the Region property page on the Quantification Parameter dialog window is the top most page on the dialog window, selecting a transition from the Element Table causes a quantification region to be created based on the library entry just selected coupled with the current display window in the active tile. It is therefore advisable to zoom into the energy interval over which the new region must cover before clicking on the Name field in the Element Table.

A further consequence of creating regions using the **Create Regions** button on the Element Library dialog window is the creation of an annotation table offering a quantification report which is displayed over the data as shown in Figure 5. While the automatic creation of the quantification regions and report is convenient, it is also advisable to check the limits for the quantification regions to ensure the backgrounds are defined appropriately for the data.

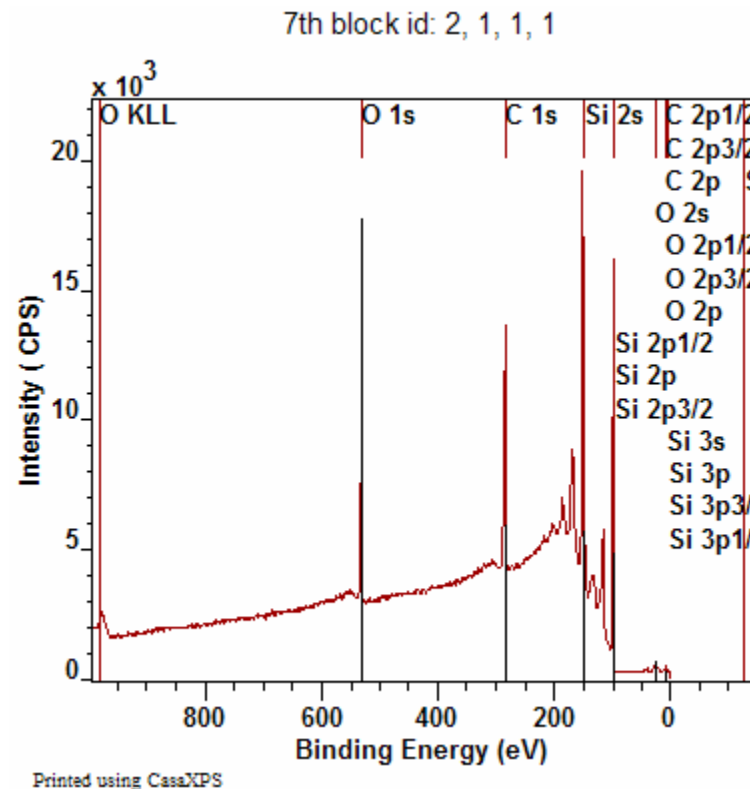




Figure 4: Element markers defined using the Element Library dialog window in preparation for creating quantification regions.

An easy way to investigate the region definitions is to press the Reset button  on the second toolbar and then sequentially press the Zoom Out button . The action of pressing the Reset button is that of loading the limits for each region

defined on the spectrum in the active tile onto the current zoom list. Each time the Zoom Out toolbar button is pressed, the regions, one-by-one, are displayed in the active tile. If the Regions property page is the top most property page on the Quantification Parameters dialog window, then the region limits can be adjusted using the left mouse-button to drag a vertical cursor marking the start or end energies for the region. Once each region has been visited, the final press of the Zoom Out toolbar button will display the full spectrum.

The Regions property page in Figure 6 corresponds to the data in Figure 5. Note how the RSFs in Figure 6 are adjusted using the configuration parameters in Figure 2 for the angular distribution correction, while the energy dependency exponent defined in Figure 2 appears on the Regions property page in Figure 6, but is not included in the RSFs reported on the Regions property page. Although the RSFs in Figure 6 differ from the underlying Scofield cross-sections, the ratios of these RSFs to the C 1s value are still in the relative proportions of the Scofield cross-sections and therefore simply using the Scofield cross-sections with the energy dependency exponent of -0.2 is sufficient to obtain the SpecSurf quantification.

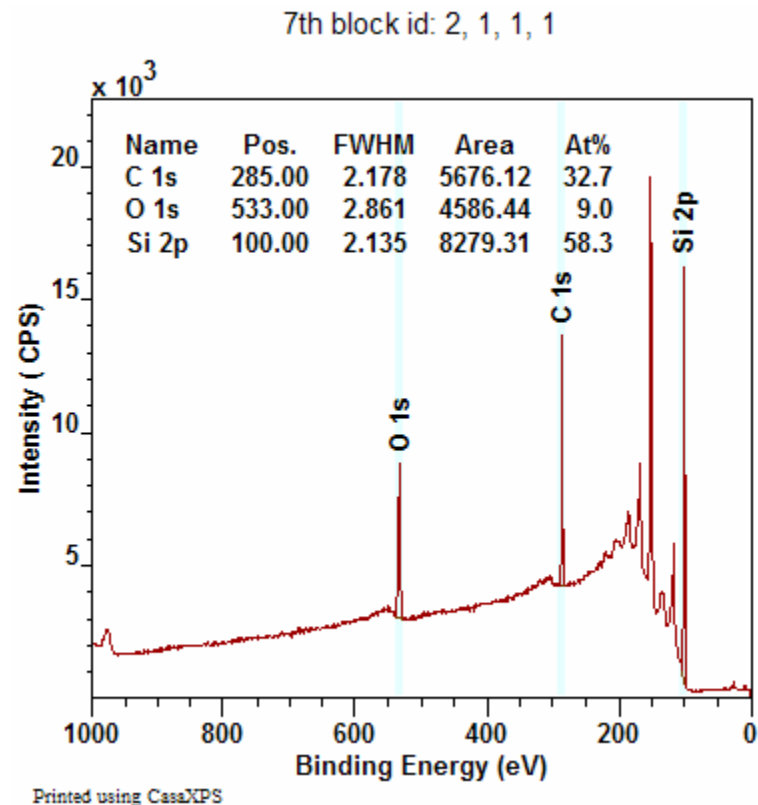


Figure 5: Quantification regions created using the Create Regions button on the Element Table property page.

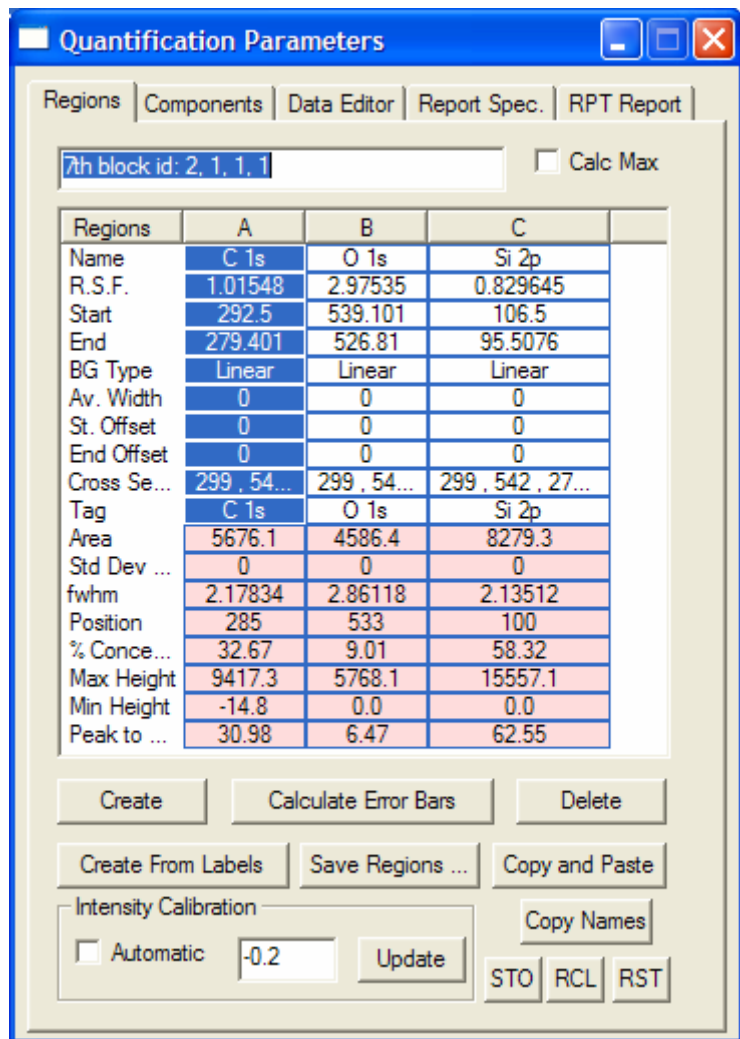


Figure 6: Regions property page showing the parameters used to create the table over the spectrum in Figure 5.

Quantification of Similar Data

The survey spectrum in Figure 5 is one of four spectra acquired from different positions on a sample. The sequence of experiments appear in CasaXPS as shown in Figure 7, where in addition to the survey spectra, high resolutions spectra are recorded at each of the four sample positions.

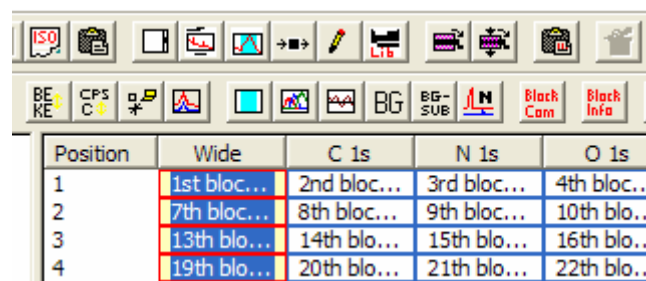


Figure 7: Right-hand-side of the Experiment Frame showing the set of spectra in a VAMAS file.

Given that the survey spectra are all similar in peak structure, elemental quantification for each of the four sample positions can be obtained by propagating the regions define on the spectrum in Figure 5 to the other three survey spectra in the file. To propagate regions from one spectrum to other spectra, display the spectrum for which the regions are already defined in the active display tile in the left-hand-side of the experiment frame and select the target VAMAS blocks in the right-hand-side, before right-clicking the mouse with the cursor over the active tile displaying the quantified spectrum. A dialog window appears as shown in Figure 8 in which the source VAMAS block is indicated and a list of target VAMAS blocks displays

both the block identifier string of the VAMAS blocks and the filename in which the VAMAS blocks are located. Propagation is not limited to the file containing the source VAMAS block, but any open VAMAS files for which VAMAS blocks are selected can be targeted by the propagation operation.

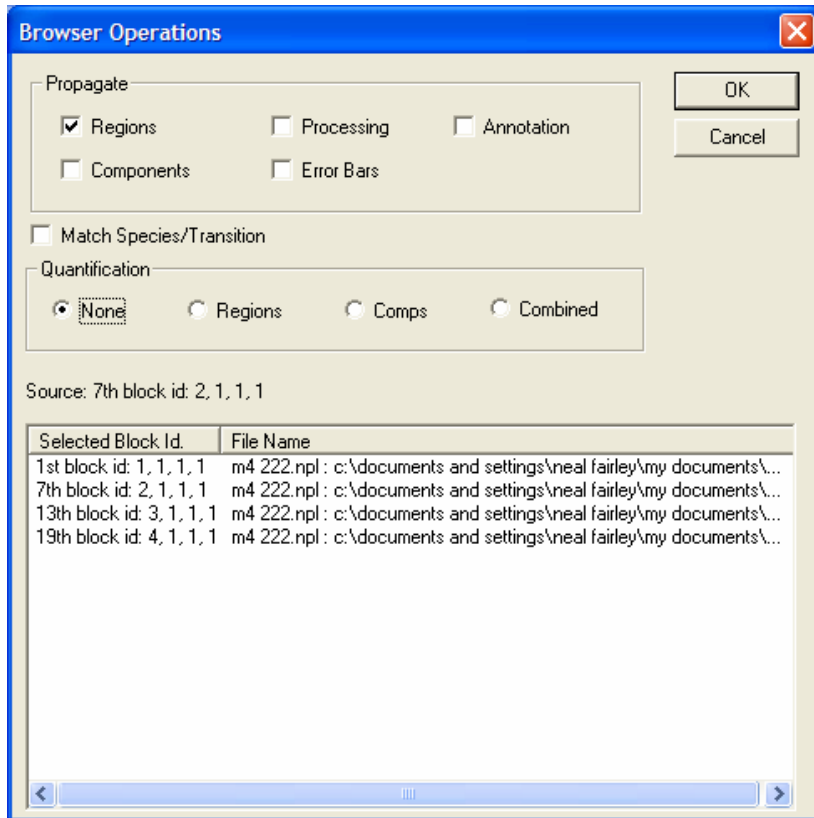


Figure 8: Browser Operations dialog window.

The actions taken on pressing the OK button on the dialog window in Figure 8 are determined by the tick-boxes in the Propagate section. The state of the Browser Operations in Figure 8 causes the regions from the survey spectrum measured from sample position 2 in Figure 7 and defined by Figure 6 to be transferred to the three other survey spectra.

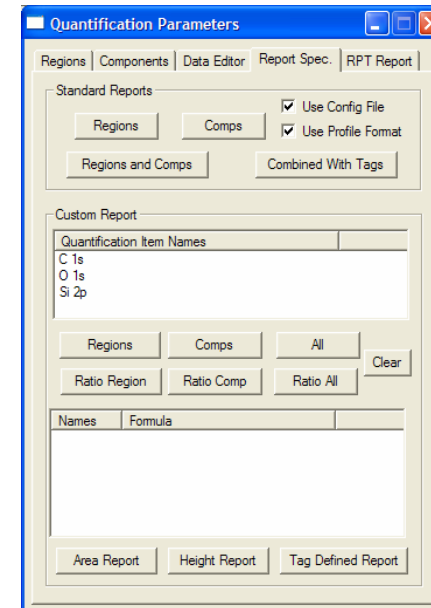


Figure 9: Report Spec Property Page.

Generating Quantification Reports

Differences between the compositions of the sample at these four positions can be examined by generating a quantification

report via the Report Spec property page on the Quantification Parameters dialog window. A tabulation of the quantification values determined from the regions defined on the VAMAS blocks selected in Figure 7 is generated by pressing the **Region** button in the Standard Report section of the Report Spec property page shown in Figure 9. The report shown in Figure 10 can be saved to file via the File menu or transferred through the clipboard to a spreadsheet program using the Copy toolbar button (Ctrl C).

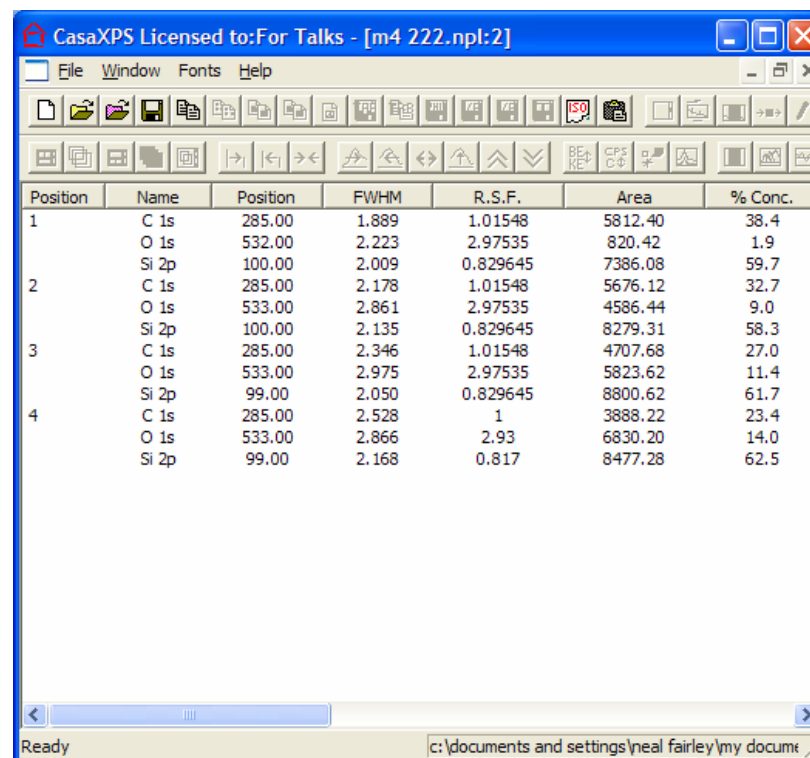
The format for the quantification reports can be defined using the RegionQuantTable.txt file in the CasaXPS.DEF directory. The format for the Standard Report configuration files is described elsewhere in the CasaXPS manual.

Quantification of High Resolution Spectra

High resolution spectra are typically acquired where chemical state information is required or elemental peaks overlap. The lower pass energy used to acquire the spectra achieves better energy resolution for the peaks but at the cost of reduced intensity. The improved peak resolution transforms the broad peaks of the survey mode into peaks for which peak positions are significant in interpreting the data and therefore energy calibration is of greater importance to these high resolution data.

The CasaXPS window shown in Figure 11 includes two C 1s spectra acquired from two different samples. The charge compensation for these two experiments is clearly different and therefore the spectra acquired from the two samples must be

adjusted on a sample by sample basis to ensure the appropriate C 1s peaks appear at the same binding energies. Locating a peak accurately for the purposes of energy calibration often required peak modeling of the data envelope. Once a peak energy offset has been established, the same energy calibration offset must be applied to other data acquired under the same experimental conditions.



Position	Name	Position	FWHM	R.S.F.	Area	% Conc.
1	C 1s	285.00	1.889	1.01548	5812.40	38.4
	O 1s	532.00	2.223	2.97535	820.42	1.9
	Si 2p	100.00	2.009	0.829645	7386.08	59.7
2	C 1s	285.00	2.178	1.01548	5676.12	32.7
	O 1s	533.00	2.861	2.97535	4586.44	9.0
	Si 2p	100.00	2.135	0.829645	8279.31	58.3
3	C 1s	285.00	2.346	1.01548	4707.68	27.0
	O 1s	533.00	2.975	2.97535	5823.62	11.4
	Si 2p	99.00	2.050	0.829645	8800.62	61.7
4	C 1s	285.00	2.528	1	3888.22	23.4
	O 1s	533.00	2.866	2.93	6830.20	14.0
	Si 2p	99.00	2.168	0.817	8477.28	62.5

Figure 10: Standard Report generated by pressing the Region button on the Report Spec property page.

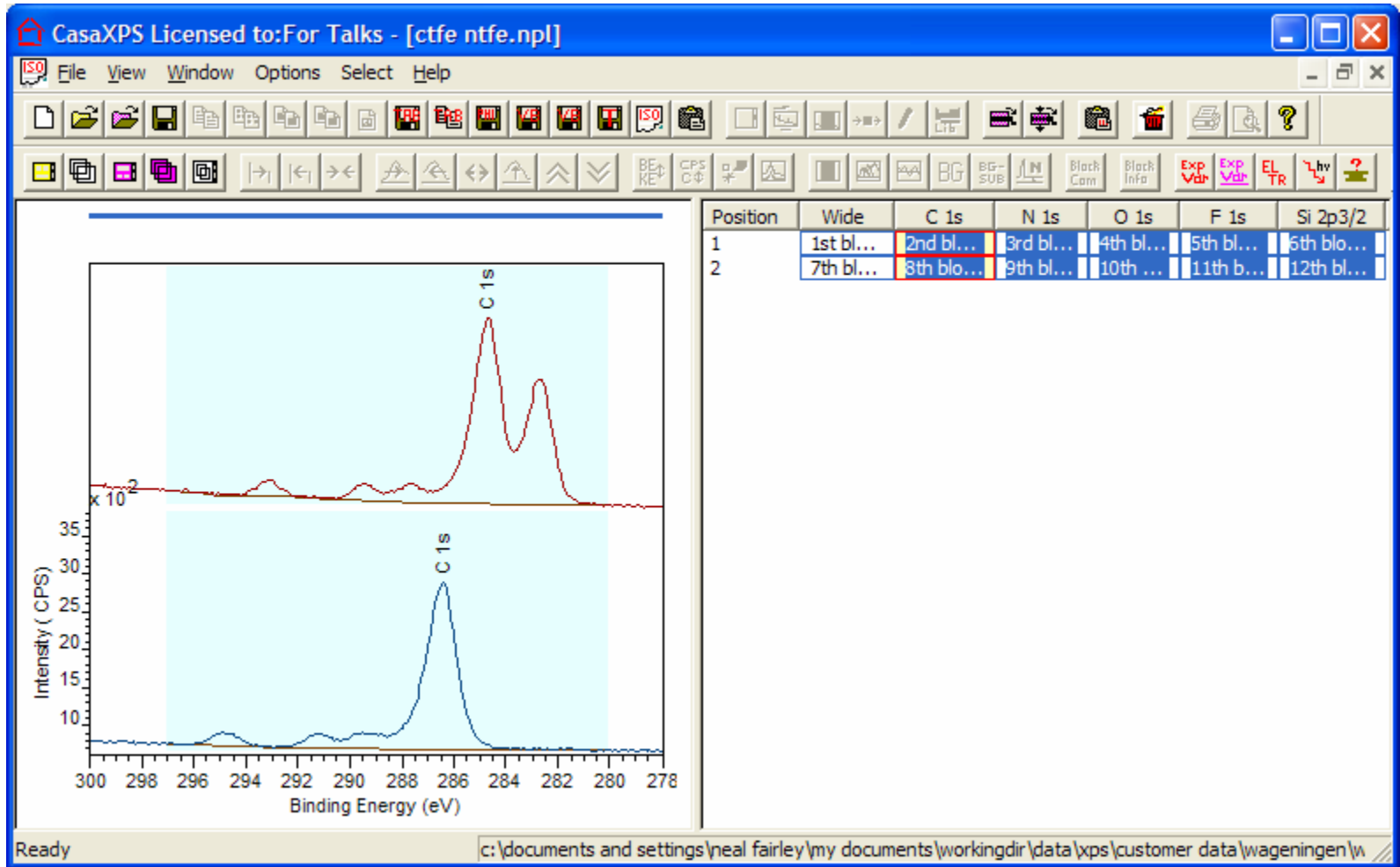


Figure 11: VAMAS file written by SpecSurf including high resolution spectra from two samples.

Creating a Peak Model

The objective in creating a peak model for both the C 1s spectra shown in Figure 11 is to systematically establish the position of the largest peak in each of the C 1s spectra as a reference for calibrating the other high resolution data acquired under the same experimental conditions as the respective C 1s spectrum.

Before synthetic peaks can be created, a quantification region must be defined on the C1s spectrum. The purpose of the quantification region is to specify the background type and the limits over which the background approximation should apply. The Regions property page on the Quantification Parameters dialog window (Figure 6) is used to create the region required by the peak model. Creating a quantification region for the C 1s spectrum is made simpler by virtue of the correct assigned to the spectrum of the element/transition fields in the VAMAS file. This is in contrast to the survey spectra, where it is not possible to assign an element/transition owing to the fact that all elements and transitions are present in the survey data.

The data in the VAMAS file are organized in the right-hand-side of the experiment frame using the element/transition fields to arrange the data into columns, whereas the rows of VAMAS blocks are defined by the experimental variable value, hence the arrangement seen in Figure 11. Given that the element/transition is correctly assigned, in the sense that the

combined string “C 1s” matches the name field in the element library, on pressing the **Create** button on the Regions property page a quantification region is created using the RSF derived from the element library.

Both C 1s spectra in Figure 11 display regions defined with a Tougaard background created via the **Create** button on the Regions property page. Background types are defined using the **BG Type** field on the Regions property page. The default background type is the most recently used background type and can be altered by entering the character “L” for Linear, “S” for Shirley or “T” for Tougaard before pressing the Enter key. Many other background types are available and are describe elsewhere in the CasaXPS manual, however for everyday use these three as normally sufficient. Of the three most commonly used background types, the Tougaard background is the least used, however for the data in Figure 11 the background begins to rise in such a way that both the Shirley and linear background fail to include the left-most C 1s peak.

The peaks in a peak model are created using the Components property page illustrated in Figure 12. The creation of component peaks is achieved by pressing the **Create** button on the Component property page. Again, since the element/transition fields defined in the VAMAS block containing the C 1s spectrum match the correct entry in the

element library, the RSF derived from the element library is assigned to each component as it is created.

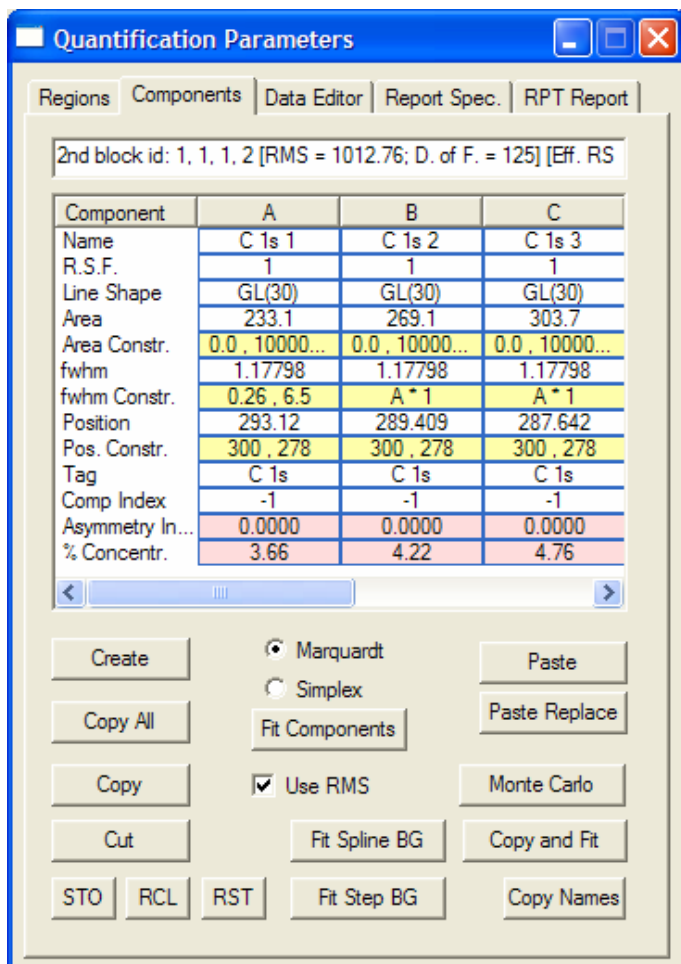


Figure 12: Components Property Page

The components appear as columns on the Components property page, where the parameters are initialized using information gathered from the C 1s data. The components are defined in terms of a lineshape plus area, FWHM and position parameters. Constraints are applied to the numerical parameters either as intervals or by expressing the relationship between two component parameters using the alphabetical labels above the columns on the Components property page. For example, the components defined on the C 1s spectrum corresponding to the property page in Figure 12 are constrained to all have the same FWHM. The *fwhm Constr.* field shown in Figure 12 indicates that the parameter for column **B** and column **C** are calculated from the FWHM value in column **A** using the string **A*1**. Similarly, a known relationship between the area parameter for two peaks can be applied with strings using the column headers. For example, a doublet pair such as Si 2p_{1/2} and Si 2p_{3/2} can be constrained in relative area using **B*2**, say, where the Si 2p_{1/2} component appears in column **B**, the component for Si 2p_{3/2} appears in column **A** and the string **B*2** is entered into the *Area Constr.* field in column **A**. For position constraints, the separation of two peaks can be defined similarly using strings of the form **A+0.25**, say, in the *Pos. Constr.* field.

Once a set of components are defined on a spectrum with appropriate constraints, the **Fit Component** button is pressed to optimize the fit to the data. Figure 13 shows the result of fitting for the C 1s spectra in Figure 11. The constraint applied to the FWHM provides a stabilizing influence on the peak-model which permits the same model to apply to both C 1s spectra in Figure 11. By constructing a peak model suitable for

both sets of data, a consistent peak position can be established for component C 1s 5, which in turn can then be used as the reference point for calibrating the energy scale for both sets of spectra.

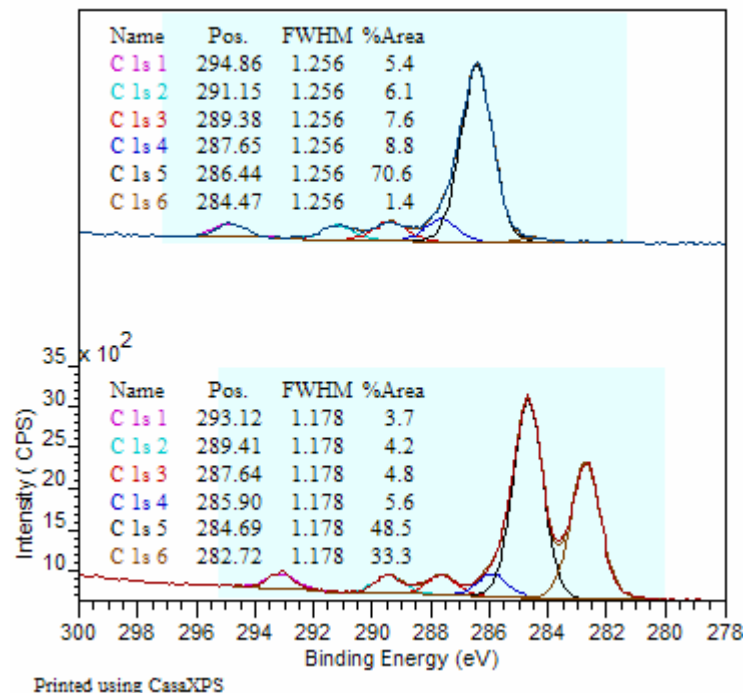


Figure 13: Optimized components representing chemically shifted C 1s transitions.

Calibrating the Energy Scale for an Experiment

The data in Figure 11 are two independent acquisition conditions, which explain the different measured binding

energy for the C 1s peaks in Figure 13. These shifts in recorded binding energy are due to different equilibrium charge states for the sample surfaces. It is assumed the same equilibrium charge state influences the spectra from the same experiment acquired at different binding energies. VAMAS blocks with the same position experimental variable will typically require the same energy calibration therefore the calibration determined for the C 1s spectra must be applied to the other high resolution spectra in the VAMAS blocks belonging to the same row in Figure 11.

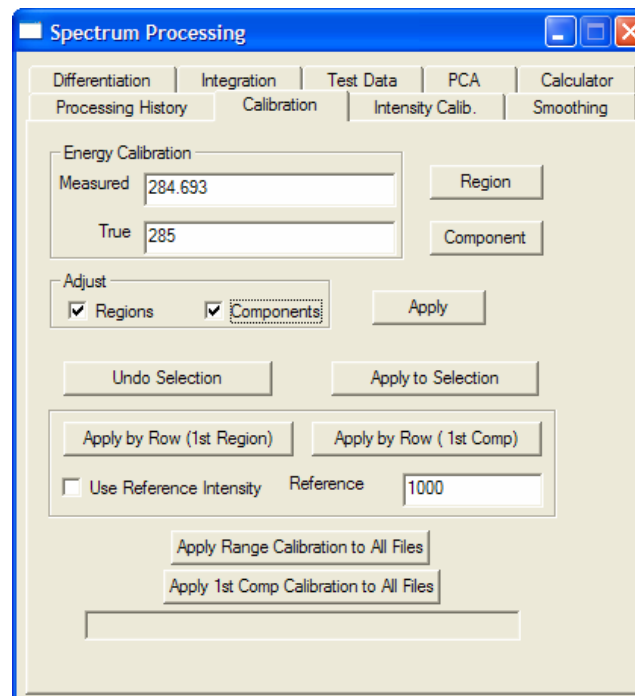



Figure 14: Calibration property page.

The Calibration property page on the Spectrum Processing dialog window  permits the specification of the measured and true binding energies corresponding to a spectrum. Using these two energy values a shift is calculated, which can be applied to a specific VAMAS block or, using the **Apply to Selection** button, to a set of VAMAS blocks. The procedure for calibrating the energy scale for the two rows of data in Figure 11 involves:

1. Display the C 1s spectra in the active tile.
2. Using the Calibration property page, enter the measured value or the component C 1s 5 and the desired true value of 285.0 into the text-field labeled **True**.
3. Select the VAMAS blocks for which the energy calibration is appropriate, i.e. those high resolution spectra in the same row as the C 1s spectrum.
4. Tick the tick boxes for Adjusting the region limits and component parameters. This is required for spectra where regions and/or components are defined prior to energy calibration.
5. Press the **Apply to Selection** button on the Calibration property page shown in Figure 14.

The above five steps must be performed for each of the rows shown in Figure 11. The calibration of the data is recorded in the processing history for each VAMAS block and so can be viewed and modified on a spectrum-by-spectrum basis. The consequence of calibrating the two C 1s spectra using the component C 1s 5 as the reference can be seen in Figure 15. These calibration shifts applied to the other spectra in the file result in relative peak positions shown in Figure 16.

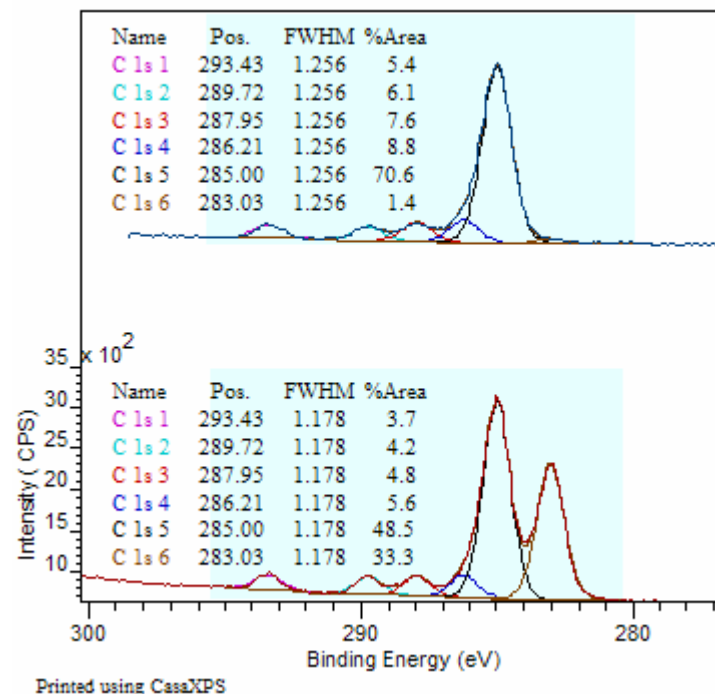


Figure 15: C 1s spectra after energy calibration.

Assuming the calibration peak is correctly assigned for both samples and the sample equilibrium charge state for the Si 2p spectra is the same as the C 1s data, then a conclusion from the energy calibration in Figure 16 is that the silicon chemical state is different between the two samples.

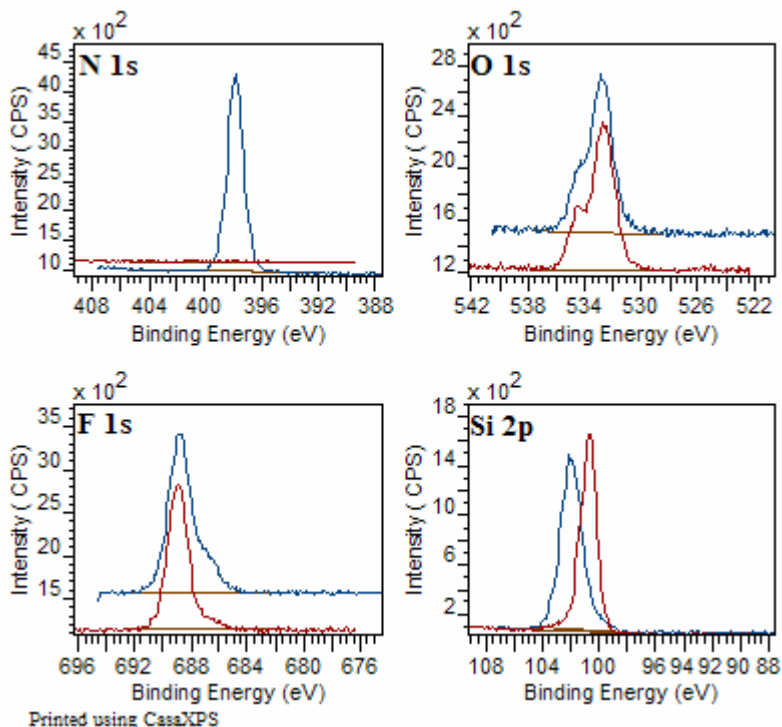


Figure 16: The high resolution spectra from Figure 11 after calibration using the energy shifts performed for the C 1s data in Figure 15.

Standard Report Quantification using High Resolution Spectra

The high resolution data in Figure 11 can be quantified against one another by defining a set of components for the carbon

contribution whilst using quantification regions for the N 1s, F 1s, O 1s and Si 2p spectra. Two observations are worth noting:

1. The high resolution spectra are all acquired using the same pass energy and lens mode. Unless an instrument is rigorously calibrated for intensity, quantification of data from different operating modes should be avoided. Transmission correction is a complex subject and is dealt with in detail elsewhere in the CasaXPS manual. Quantification using TAGs is a method for combining quantification tables from different operating modes, which is again dealt with in detail elsewhere in the CasaXPS manual.
2. The silicon doublet spectrum is assigned incorrectly as element/transition of Si 2p_{3/2}. When a region or component is created using the **Create** button on the respective property pages, the wrong RSF for the doublet pair will be extracted from the CasaXPS library. Either the element/transition fields will need to be adjusted prior to creating the region or the RSF updated after creation using #Si 2p entered in the name field of the region or the component.

	C 1s	C 1s	C 1s	C 1s	C 1s	C 1s	N	O	F	Si
Variable	1	2	3	4	5	6	1s	1s	1s	2p
1	2.1	2.5	2.8	3.3	28.2	19.3	0.4	8.9	7.2	25.4
2	1.9	2.1	2.6	3	24.2	0.5	22.1	8.5	8.7	26.4

Table 2: Atomic Concentration Table measured using components for the C 1s and regions for all other spectra.



The quantification table in Table 2 is obtained from the data in Figure 15 and Figure 16 using the **Region and Comps** button in the Standard Report section of the Report Spec property page (Figure 9). The atomic concentrations in Table 2 are computed using both regions from the N 1s, O 1s, F 1s and Si 2p, while the intensity from the C 1s spectrum is measured using the components rather than the region. Given that a region must be defined on the C 1s spectrum, to avoid counting the carbon signal twice, the RSF for the C 1s region must be assigned a value of zero, while each of the components fitted to the C 1s data are assigned the non-zero RSF for C 1s.

Each of the buttons within the Standard Report may be configured using ASCII files located in the CasaXPS.DEF directory; specifically, the **Regions and Comps** button is

configured using the RegionComponentQuantTable.txt file. Provided the **Use Config File** tick-box is ticked before pressing the **Regions and Comps** button, the configuration file determines the format for the report. The report table can be transferred via the clipboard to a spreadsheet program by pressing the Copy button on the top toolbar (Ctrl+C). The clipboard selection dialog window resulting from the Copy toolbar button includes not only the data tabulated using the configuration file, but also a list of other tabulations for the quantification data. Additional formats are also generated within the set of possible quantification tables by also ticking the **Use Profile Format** tick-box. Table 2 derives from one of the profile format tables.

Tile Display

1st block id: 1, 1, 1, 1

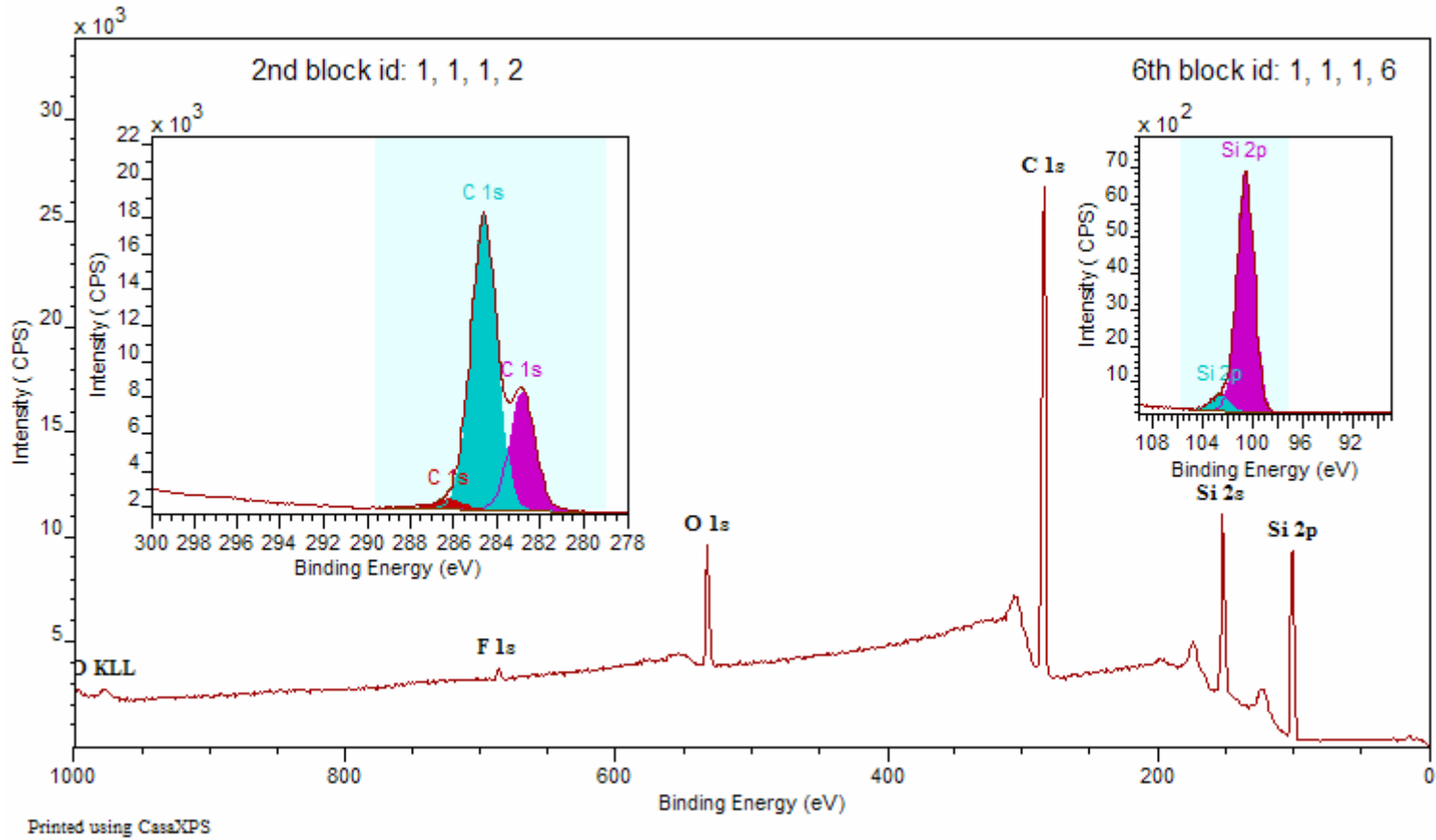


Figure 17: Example of display format using Inset Tiles, Component colouring options and Peak Annotation.

Presentation of data for reports and publication is an important feature to most researchers. The display of data in CasaXPS is controlled via the Tile Display Parameters dialog window, Page Tile Format dialog window and the Inset Tile mechanism. Once a display format has been prepared, such as the one shown in Figure 17, the formatting information can be saved to file and restored to the data at a later time using options on the File menu (Figure 18) of CasaXPS.

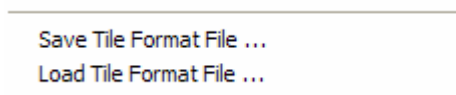




Figure 18: File Menu options for saving and loading tile display format files.

The Tile Display Parameter Dialog is available from the Options menu and also the top toolbar . Display parameters affecting fonts, colours for spectra and components, and selective display options such as labels on the axes are all found on property pages on the Tile Display Parameter dialog window (Figure 19). The number of display tiles per page is

controlled by the Page Tile Format dialog window  (Figure 20). Each property page on the dialog window represents a predefined format for the given number of tiles per page. Figure 16 illustrates the format for four tiles per page. A detailed description of these display options can be found in The Casa Cookbook and elsewhere in the CasaXPS help files.

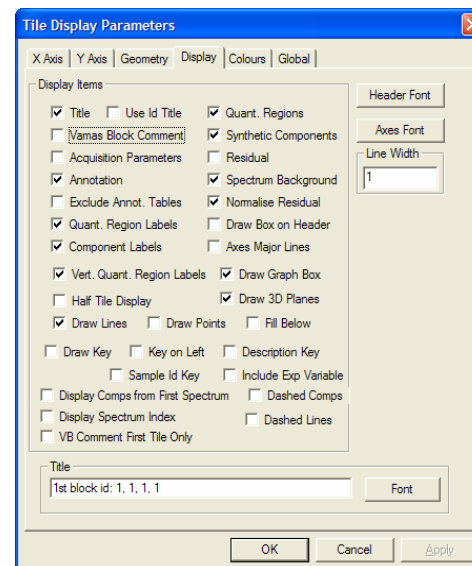


Figure 19: Tile Display Parameter Dialog Window

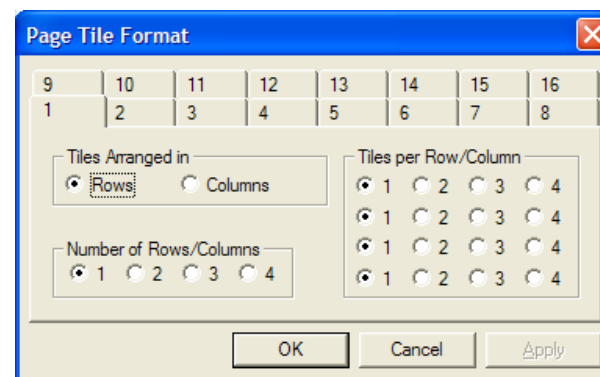


Figure 20: Page Tile Format Dialog Window