

Standard Reports using Tags

Motivation

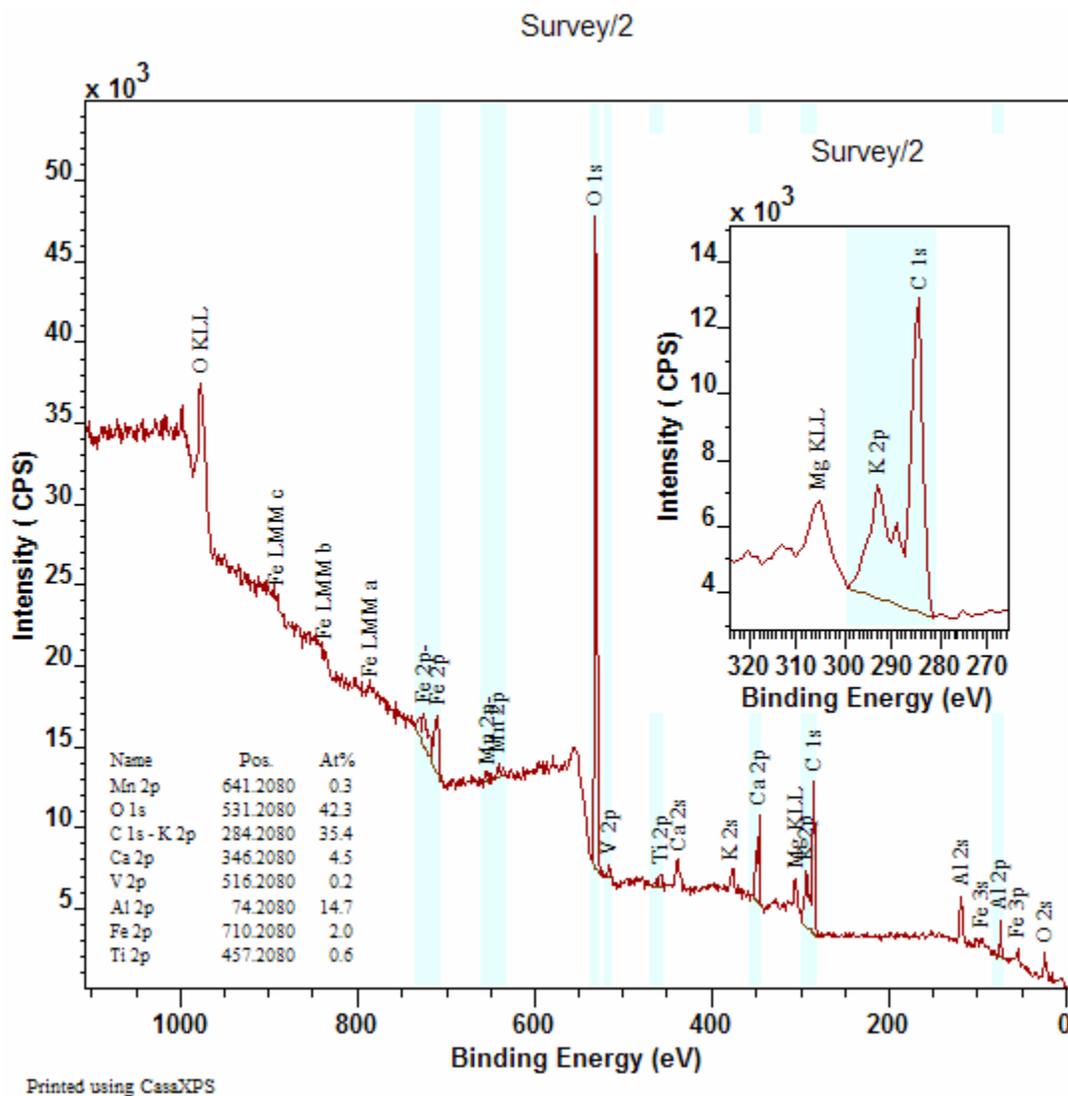


Figure 1

Spectra may include numerous photoelectric and Auger peaks, some of which overlap and therefore prevent a simple compositional analysis of the sample surface. The spectrum in Figure 1 is an example of data acquired at pass energy 160 on a Kratos Axis Ultra, where the K 2p and C 1s peaks overlap. The advantage of acquiring data at high pass energies, namely enhanced signal-to-noise for given acquisition time, is lost when the spectral features can only be separated using less sensitive pass energies with better

energy resolution. For the example in Figure 1, a simple elemental concentration measurement based on integration regions is impeded by the overlapping K 2p and C 1s peaks since the RSF for the combined envelope is depended on the relative proportions of the two elements. The concentration for the overlapping peaks must be obtained by applying an effective RSF computed from an appropriate peak model, which may require higher resolution spectra. The high resolution data in Figure 2 provides the means of computing the effective RSF for the survey spectrum in Figure 1, where the mixing of peak areas and differing RSFs for the transitions involved in the potassium and carbon envelope allow the computation of the weighted RSF for the combined envelope in Figure 1 and therefore permits the partial quantification of the sample. That is, the quantification table in Figure 1 determines the combined contribution to the atomic concentration from the overlapping peaks, thus allowing the remaining entries in the table to report true atomic concentration values.

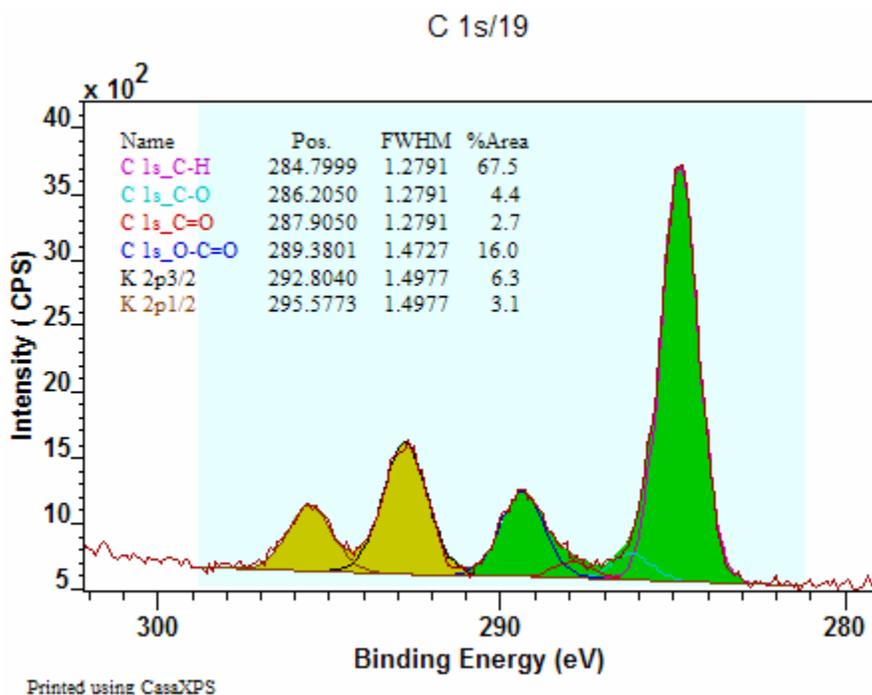


Figure 2

The following discussion describes how to calculate the effective RSF and the use of Tags as a means of combining the survey spectrum with high resolution data to obtain a full quantification of the sample without the need to acquire high resolution spectra for each transition in the quantification. The obvious advantage of limiting the number of high resolution spectra is that of time spent collecting the data.

A new feature in version 2.3.14 is the introduction of a configuration file for the standard report generated using Tags. An example highlighting the use of mass concentration will be used to describe the new configuration file.

Quantification using Tags

A full quantification of the data in Figure 1 requires the use of a peak model to differentiate the contribution to the quantification table from the K 2p and the C 1s transitions. As an example, these data are useful because quantification can be performed in either of two ways, namely, 1) using the high resolution spectrum in Figure 2 to construct a well defined peak-model that can be readily adapted to the data from the survey spectrum, therefore directly quantifying the contributions from the regions and synthetic components computed from the survey spectrum alone, or 2) use the proportions for the K 2p and C 1s peaks from the high resolution spectrum to compute an effective RSF for the K 2p/C 1s region, then generate a Tag report containing the partial quantification table augmented with a subdivision of the K 2p/C 1s region as prescribed by the peak intensities from the high resolution spectrum.

Observations:

1. While the data are sufficiently well separated in this example to permit a fit of the peak-model in Figure 2 to the survey spectrum in Figure 1, in general, peaks may overlap in ways that the survey spectrum produces poor precision when fitted to synthetic components.
2. Without the high resolution K 2p/C 1s spectrum, it would be difficult to confidently prepare a peak model based entirely on the K 2p/C 1s region from the survey; therefore both methods rely in the high resolution spectrum to perform the quantification.
3. The survey spectrum was acquired using a pass-energy of 160 eV while the high resolution spectrum structure is due to a smaller step-size and a pass-energy of 40 eV. Issues associated with changes in the transmission efficiency between these two operating modes, even with transmission calibration, prevents quantification begin performed directly using both spectra, that is mixing intensities measured from the two different operating modes. Theoretically, a properly calibrated instrument should allow quantification using data from different operating modes, in practice, mixed mode quantification is not recommended.

Quantification using Regions and Components

The Standard Report options on the Report Spec property page offer the means to quantify spectra based on Regions only, Components only as well as mixing intensities from Regions with Components in the same report. Ordinarily, performing a peak fit to poorly resolved data is imprecise so would not generally be employed for survey spectra; however for the example data set in question, the availability of the high resolution spectrum provides a means of characterising a peak model which can be copied, constrained and fitted to the K 2p/C 1s region as shown in Figure 3. The principal reason for performing the quantification using both regions and components is to illustrate the equivalence of quantification using Tags to the more common use of regions or components. The second survey spectrum shown in the right-hand-side of the Experiment

Frame in Figure 3 is simply a copy of the first survey spectrum. The two survey spectra are identical apart from the quantification items defined on the two data blocks.

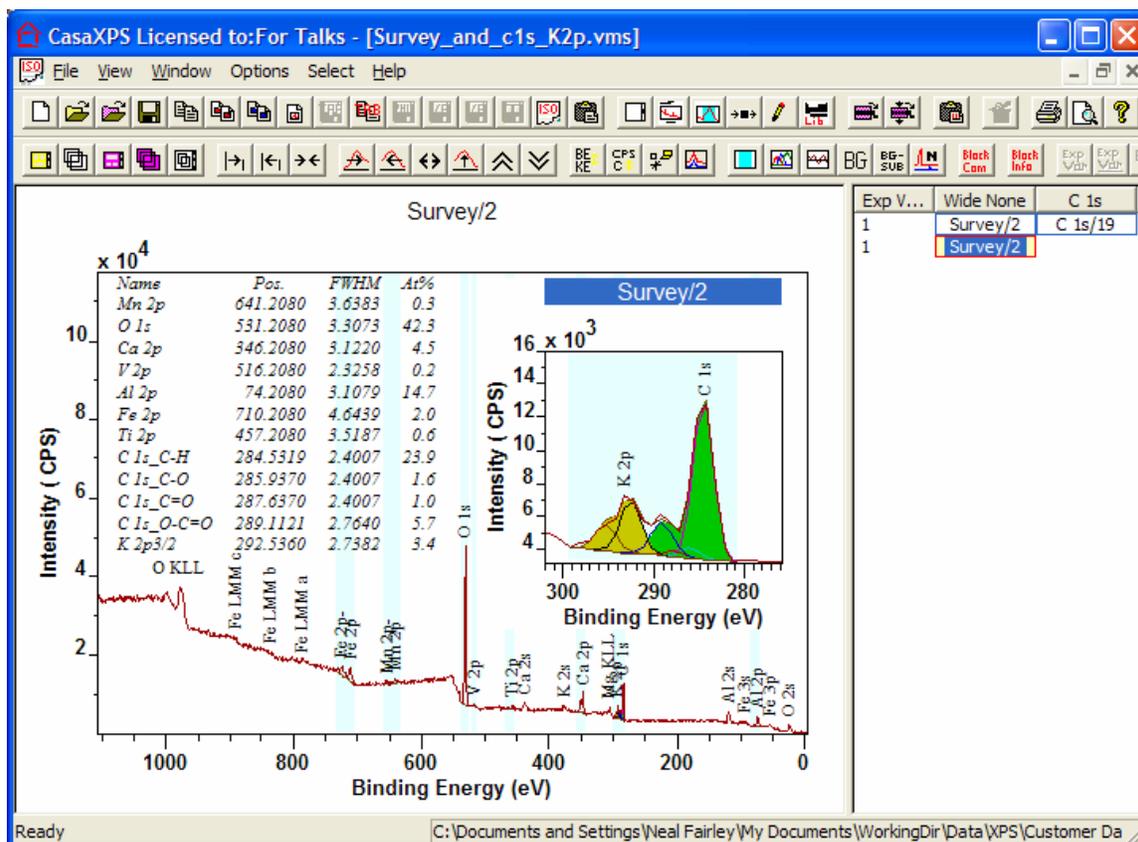


Figure 3: Quantification using Regions and Components defined on the Survey Spectrum.

The peak model created for the high resolution spectrum in Figure 2 is constrained to the extent that only the relative positions of the six synthetic components and their relative FWHM are allowed to be optimised when fitting the model to the K 2p/C 1s region on the survey spectrum. The constraints are tabulated in Table 1. A key step in generating a quantification report involving both regions and components is that the RSF for the region, for which components are used in the quantification, is set to zero. This will prevent the contribution from the intensity measured from the region used to define the background to the peak model being included in the quantification report.

Name	Pos Const	FWHM Const	Area Const	Const Id
C 1s_C-H	302.208 , 279.108	0.28 , 7	0.0 , 10000000.0	A
C 1s_C-O	A + 1.4051	A * 1	A * 0.0650981	B
C 1s_C=O	A + 3.1051	A * 1	A * 0.0398136	C
C 1s_O-C=O	A + 4.5802	0.28 , 7	A * 0.237488	D
K 2p3/2	A + 8.0041	D * 1.017	A * 0.370313	E
K 2p1/2	A + 10.777	D * 1.017	A * 0.185157	F

Table 1

The report generated from the Standard Report button **Regions and Comps** using the survey spectrum in Figure 3 is shown in Table 2. The configuration file located in the CasaXPS.DEF directory displayed in Notepad in Figure 4 was used to create the quantification table.

Tag	Exp Variable	Name	% Mass Conc	Mass	%At Conc
Mn 2p	1	Mn 2p	0.9	54.938	0.3
O 1s		O 1s	34.9	15.9994	42.3
Ca 2p		Ca 2p	9.4	40.078	4.5
V 2p		V 2p	0.4	50.9415	0.2
Al 2p		Al 2p	20.5	26.9815	14.7
Fe 2p		Fe 2p	5.7	55.8458	2
Ti 2p		Ti 2p	1.4	47.8784	0.6
Mixed		C 1s_C-H	14.8	12.011	23.9
Mixed		C 1s_C-O	1	12.011	1.6
Mixed		C 1s_C=O	0.6	12.011	1
Mixed		C 1s_O-C=O	3.5	12.011	5.7
Mixed		K 2p3/2	6.8	39.1019	3.4

Table 2: Quantification using Regions and Components

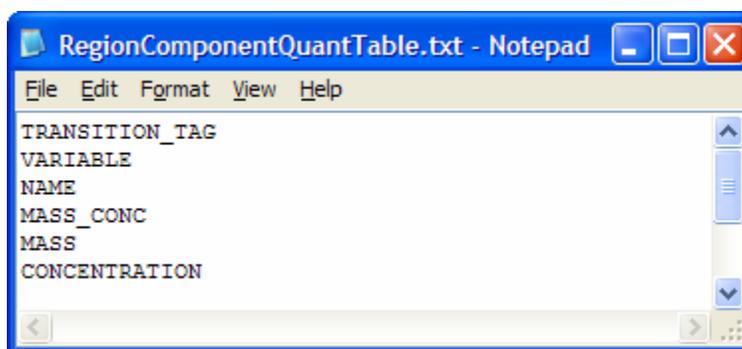


Figure 4

The advantage of generating the quantification from regions and components is that the library RSFs can be directly applied to each region or component in the table. The results presented in Table 2 use the default CasaXPS library and therefore the RSFs used in the quantification are Scofield cross-sections. Since the data are taken from a Kratos Axis Ultra, the Kratos RSF table matching the Kratos transmission function should have been used in practise. For the purpose of the present article, the accuracy of the quantification is not important, only the precision of the calculation.

Quantification using Combine with Tags

An equivalent quantification for the data in Figure 1 and Figure 2 corresponding to the quantification for the survey spectrum in Figure 3 can be performed using the Tag mechanism. A configuration file, CombineWithTagsQuantTable.txt, identical in contents to the one shown in Figure 4 is defined for the Combine with Tags button and is shown open in Notepad in Figure 5. All the Standard Report configuration files are located in the CasaXPS.DEF directory.

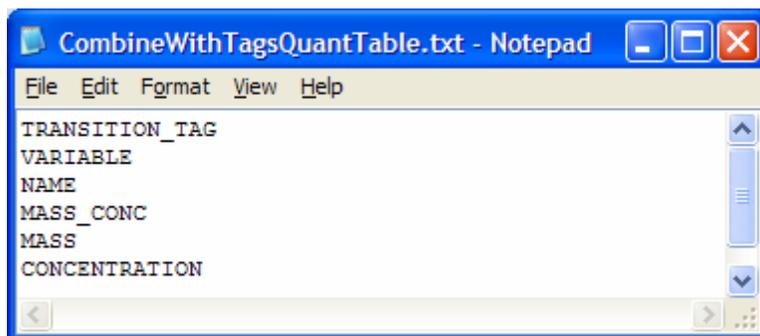


Figure 5

Since more than one VAMAS block are used, namely, the survey spectrum and the high-resolution spectrum, both must appear on the same row in the right-hand-side of the Experiment Frame, and both VAMAS blocks must be selected in the right-hand-side before pressing the **Combine with Tags** button on the Report Spec property page. The resulting quantification table generated using the Tag mechanism is shown in Table 3, where the only different between the Table 3 and Table 2 is the additional entry labeled C 1s – K 2p with Tag set to “Mixed”. The preparation of the region with the name C 1s – K 2p is key to generating a quantification report and will be discussed in more detail below.

Tag	Exp Variable	Name	% Mass Conc	Mass	%At Conc
Mn 2p	1	Mn 2p	0.9	54.938	0.3
O 1s		O 1s	34.9	15.9994	42.3
Mixed		C 1s - K 2p	26.7	14.5917	35.4
Ca 2p		Ca 2p	9.4	40.078	4.5
V 2p		V 2p	0.4	50.9415	0.2
Al 2p		Al 2p	20.5	26.9815	14.7
Fe 2p		Fe 2p	5.7	55.8458	2
Ti 2p		Ti 2p	1.4	47.8784	0.6
Mixed	C:	C 1s_C-H	14.8	12.011	23.9
Mixed	C:	C 1s_C-O	1	12.011	1.6
Mixed	C:	C 1s_C=O	0.6	12.011	1
Mixed	C:	C 1s_O-C=O	3.5	12.011	5.7
Mixed	C:	K 2p3/2	6.8	39.1019	3.4

Table 3: Quantification using Tags

The idea behind the Tag mechanism is that an intensity measured from the survey spectrum can be linked to a peak-model from a high resolution spectrum. The concentration from the survey spectrum is divided between the components fitted on the high-resolution spectrum and reported in the quantification table as a list of concentrations summing to the concentration for the region from the survey spectrum with the same Tag string as the components. For example, in Table 3 the region labeled C 1s - K 2p is assigned the Tag “Mixed”. The components from the corresponding energy interval measured using the lower pass energy are also assigned the Tag string “Mixed”.

The actual Tag string is not important so long as the one used is different from any other Tag strings used for other regions and components which contribute to the quantification report. Regions not part of the quantification report should be assigned the string NoTag; for example the region used to create the peak model on high resolution spectrum should be assigned a Tag field of NoTag.

To summarize the creation steps used to create the Tag report in Table 3:

1. Each element for which a photoelectric transition can be uniquely identified on the survey spectrum, a region must be created from the element library. The reason the element library is explicitly stated is that when a region is created via the element library, not only is the RSF and the Tag field updated, but also the average mass for the element is added to the region information. The quantification table in Table 3 includes the mass concentration and to ensure each entry has the appropriate mass, the table also includes a column displaying the mass specified for each quantification item.
2. For the same reason, the set of peaks used to model the transitions from the high resolution data must also be created using the element library.
3. The Tag field for the region on the survey spectrum and the components from the high resolution spectrum must all be assigned the same unique Tag string. For this example the word “Mixed” was chosen, but any string would do provided it is different from the string NoTag and unique to the one region on the survey spectrum and the set of corresponding components on the high resolution spectrum.
4. The RSF for the C 1s-K 2p region in Table 3 must be computed from the peak model for the high resolution spectrum and manually entered into the region RSF field on the Regions property page. The effective RSF for a peak-model is displayed in the text-field at the top of the Components property page. The value for the effective RSF can be copied and pasted from the Components property page into the RSF field on the Regions property page.

The effective RSF is a weighted average of the RSFs used in the components in the peak model, where the weighting is determined from the relative intensities of the components and provides a scaling for the region intensity measured from the survey spectrum. The effective RSF allows the partial quantification of the survey spectrum using regions only. Similarly, when reporting the mass concentration, an effective mass is required for the intensity associated with the C 1s-K 2p region on the survey spectrum. An effective mass, like the effective RSF, is computed from the peak model defined on the high resolution spectrum and displayed in the text-field at the top of the Components property page (Figure 6).

5. For a quantification report which includes the mass concentration, such as the one in Table 3, the region defined on the survey spectrum accounting for the overlapping peaks must be assigned the effective mass computed from the Component property page. The effective mass is entered to the right of the effective RSF and typically requires the use of the cursor and arrow keys on the keyboard before the effective mass string is made visible. The effective mass can

be selected as seen in Figure 6, copied and pasted into the Tag field for the corresponding region on the survey spectrum. The format for the keyword string entered into the Tag field is Mass = <real number> as seen in Figure 7. On pressing the Enter key on the keyboard, the mass so specified is updated in the region and the previously assigned Tag string is returned to the Tag field. If the Tag field does not return to the previously assigned Tag string, then the mass failed to be updated due to a syntax error.

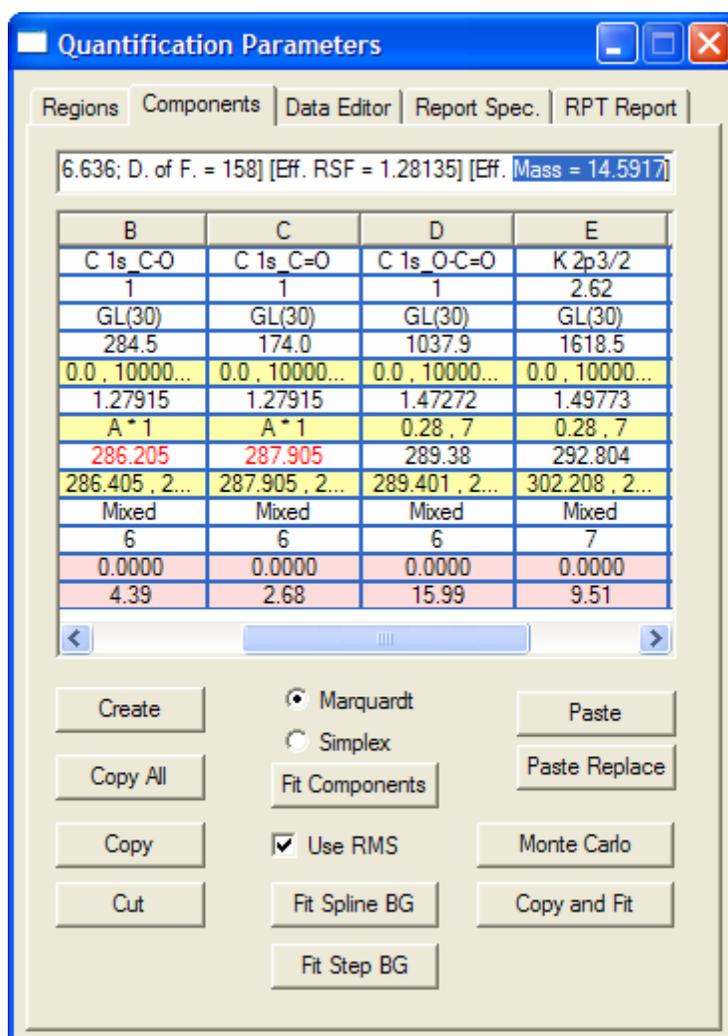


Figure 6: Effective Mass

- The report in Table 3 is obtained using the configuration file in Figure 5 by pressing the Combine with Tags button on the Report Spec property page located in the Standard Report section.

While the quantification using Tags is more complicated than the report using regions and components, often overlapping peaks are difficult to fit using a survey spectrum so Tags provide a means of obtaining quantification which would otherwise be difficult to perform.

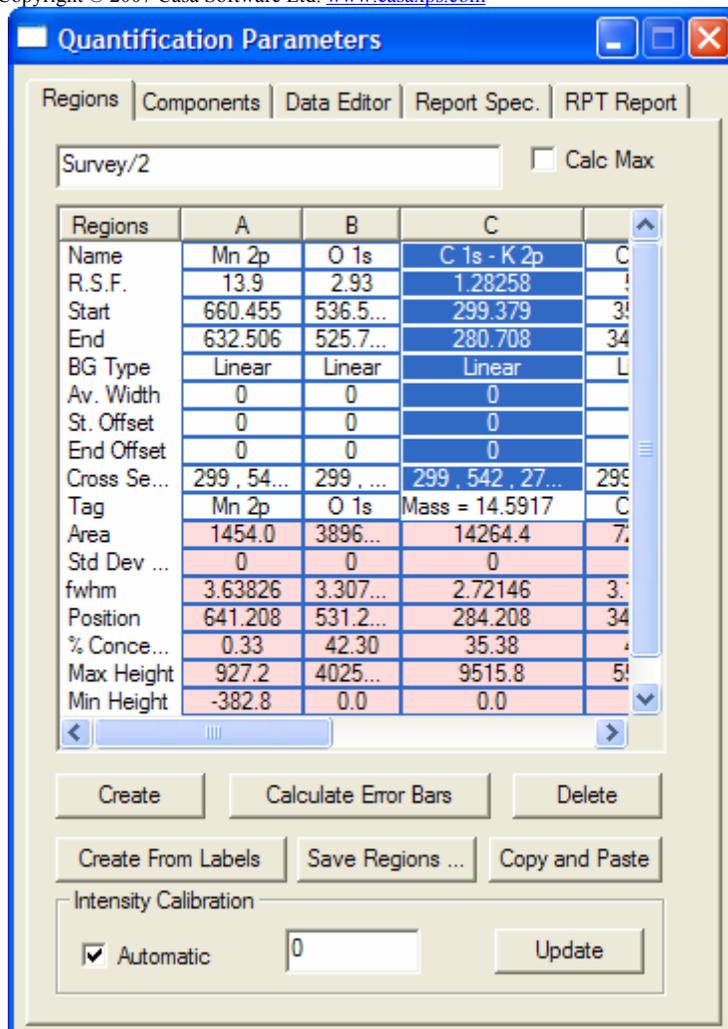


Figure 7: Entering the effective mass into the C1s-K2p region.

A Note on Component Display

The display of the components in Figure 2 is new to version 2.3.14 of CasaXPS. Components are assigned a Comp Index, which is seen below the Tag field in Figure 6, where the Comp Index for the C 1s components is assigned the value of 6, while the K 2p components are assigned the value of 7. These integer values refer to the colour palette entries used to display the components available from the Colour property page on the Tile Display Parameters dialog window. Tick boxes on the Colour property page allow the enabling of these Comp Index values for the purpose of selecting the colour with which a component is drawn and also whether or not the components with a common Comp Index are filled with the specified colour. These features are discussed in more detail elsewhere.