Quantification of O/In/Sb/C using an Effective RSF and Tags

A common problem encountered in XPS is illustrated by the spectrum in Figure 1, where four elements are identified, but two are not sufficiently well resolved to permit quantification to proceed directly from peak area integration based on regions from the survey spectrum. The O 1s peak overlaps with the Sb $3d_{5/2}$ and so quantification for this sample requires the use of synthetic peaks to measure the area of the O 1s contribution to the data displayed in the inset plot in Figure 1. While oxygen offers O 2s as an alternative to O 1s, the use of the O 2s peak is doubtful on several counts: 1) the O 2s peak lies within the loss structure of In 4d, which causes problems for identifying the background to the O 2s peak, 2) the kinetic energy of the O 2s electrons is higher than the Sb 3d and In 3d peaks, therefore the sampling depth of the material will alter from those electrons used to measure the indium and 3) the O 2s lies in a region for which the transmission of an analyser is difficult to characterise so accurate quantification is limited when using the O 2s transition.
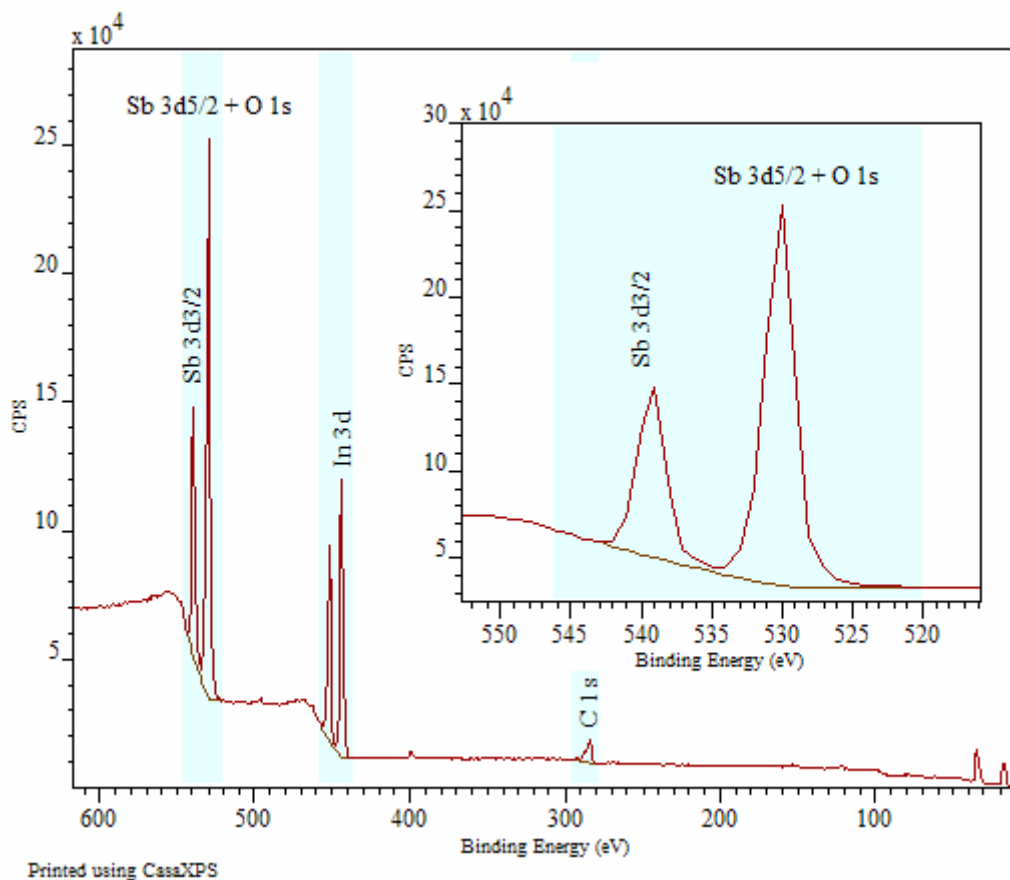

Figure 1: XPS data (Emily Smith, University of Nottingham) from a material containing Oxygen, Antimony, Indium and Carbon.

While the survey spectrum in Figure 1 will ultimately provide the atomic concentration quantification for the sample, the resolution of the data in the survey does not lend itself to precise peak modelling. For chemical state information and also to provide a good foundation on which the O 1s intensity can be determined, a high resolution spectrum over the antimony/oxygen region is typically acquired. A pass energy 20 (PE 20) spectrum in Figure 2 shows the antimony and oxygen peak positions as defined in the element library together with a peak model consisting of two sets of doublet pairs modelling the Sb 3d data and a single O 1s synthetic peak.
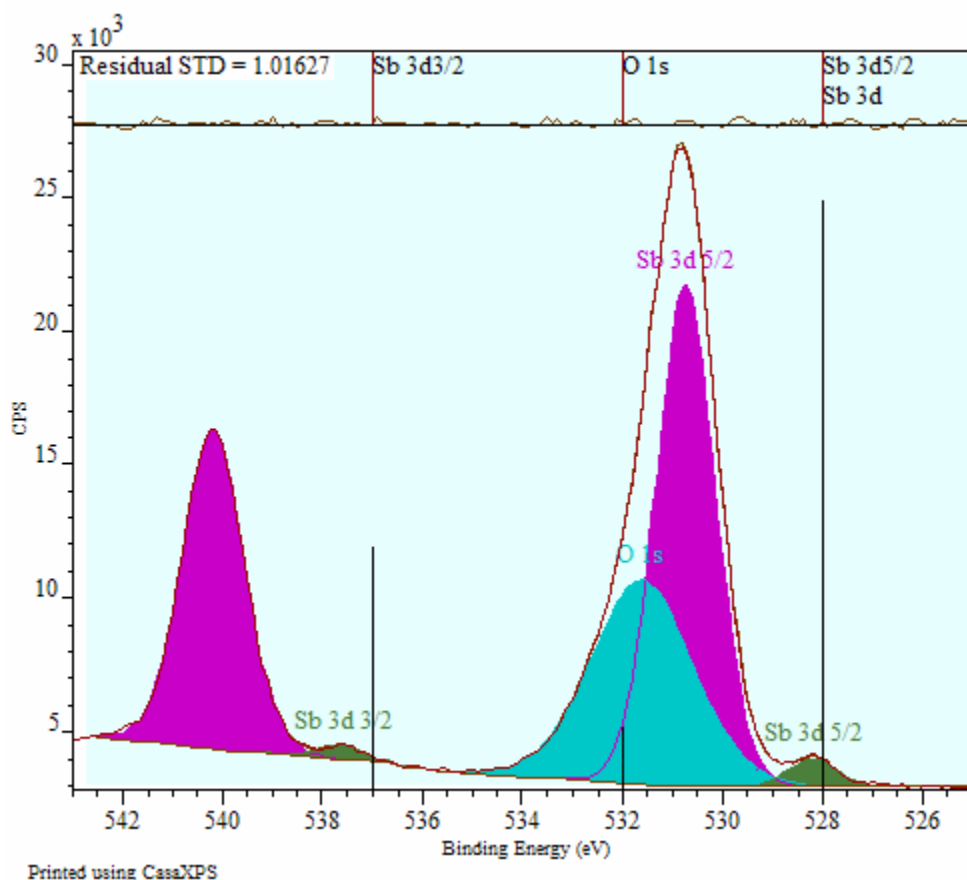

Figure 2: High resolution spectrum suitable for modeling the Sb 3d and O 1s contributions.

Due to the physics of doublet pairs, the Sb $3d_{3/2}$ peaks provide a strong basis on which to model the Sb $3d_{5/2}$ peaks and therefore a good estimate for the O 1s contribution to the data envelope can be readily obtained. Nevertheless, the data acquired at PE 20 requires scaling before a comparison with the survey data which was acquired using PE 80. While a properly calibrated instrument would allow the comparison of data acquired at different operating modes, a method for managing data without regard to the calibration between operating modes is available in CasaXPS.

The procedure for quantifying the data in Figure 1 makes use of the high resolution spectrum in Figure 2 in two ways. Firstly, the peak fit in Figure 2 together with the RSFs for O 1s and Sb 3d allow the determination of an Effective RSF suitable for a partial

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quantification of the survey spectrum. That is, the atomic concentrations for C and In are obtained by applying the Effective RSF (computed for the combined data for O 1s and Sb 3d using the peak model in Figure 2) to the region inclusive of both transitions in the survey spectrum in Figure 1. The Effective RSF is displayed in the text-field at the top of the Component Property Page in Figure 3. The Effective RSF is computed (from the component areas, the component RSFs and the region area) to ensure the correct contribution to the atomic concentration calculation from the Sb 3d/O 1s data envelope is supplied to the partial quantification table calculated from the survey spectrum (Figure 4).
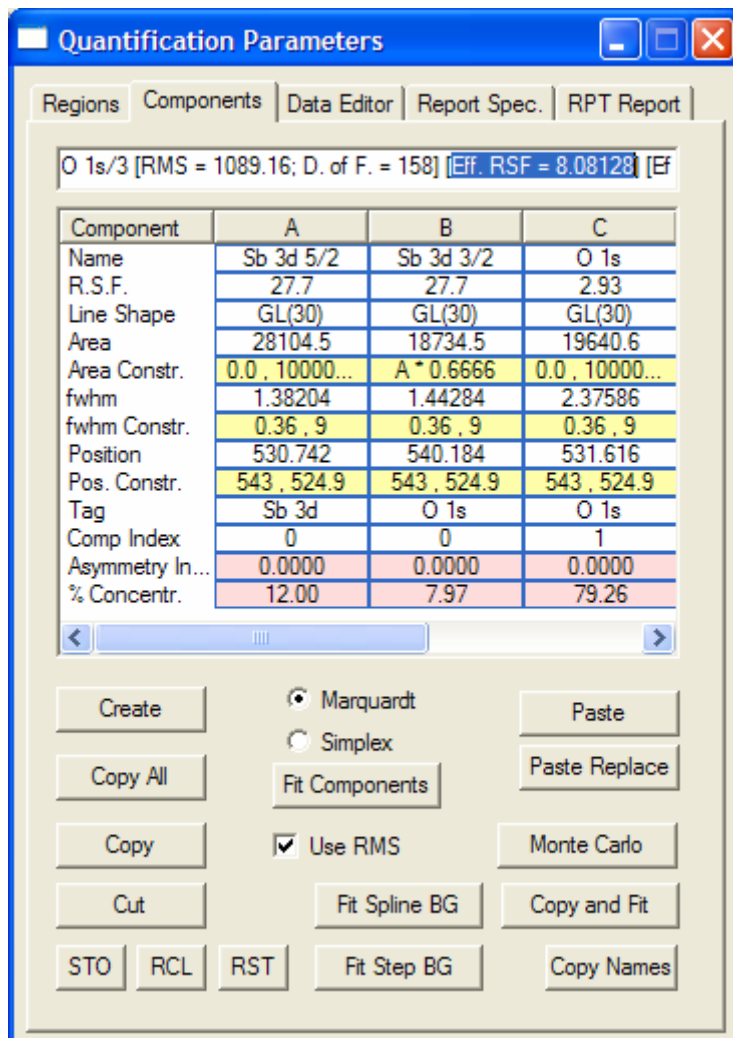

Figure 3: Components Property Page showing the Effective RSF computed from the RSFs and components on the property page.

The quantification table over the spectrum in Figure 4 is referred to as a partial quantification table because the atomic concentration for the Sb 3d/O 1s region is not resolved into the two elemental components comprising the peaks. The atomic concentrations for In and C are fully computed from the data and in the final form, therefore a further step is required to present the fully quantified table of results.
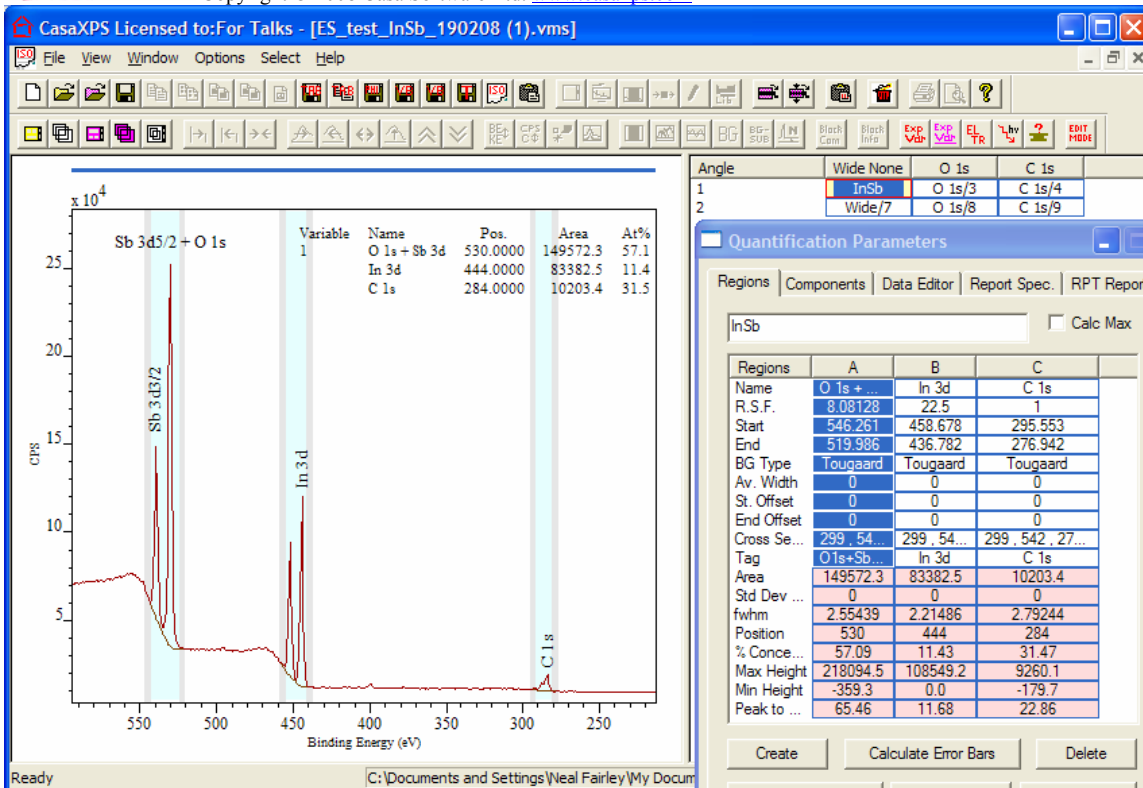
Figure 4: Partial quantification table based on the Effective RSF computed from the component in Figure 2 and Figure 3.

To further resolve the contribution from Sb 3d and O 1s to the quantification table calculated from the survey spectrum, the high resolution spectrum must be used a second time. The method relies on the use of the TAG field available for both regions and components. The mechanism requires the components from the high resolution spectrum to be assigned the same TAG field as the corresponding region on the survey. Thus, the string "O1s+Sb3d" is assigned to the TAG field in the survey spectrum (Figure 4) and also to each of the component peaks entered on the high resolution spectrum (Figure 3). Note, the region on the high resolution spectrum must be assigned the TAG string of "NoTag"; this dissociates the components on that spectrum from the region used to compute the background as part of the peak model.

The full quantification table is displayed over Figure 5, where the peak fit from the high resolution spectrum is used to proportion the atomic concentration calculated from the Sb 3d/O 1s region using the Effective RSF. The resulting table provides a full quantification from the survey spectrum, where the high resolution spectrum provides the relative proportions of the overlapping peaks, while the elemental concentrations are consistently calculated from the survey spectrum. It is therefore possible to maintain a relatively small number of calibrated operating modes for an instrument and yet still use the flexibility offered by modern instruments to obtain information from unresolved peaks via un-calibrated high resolution modes.

The quantification table displayed in Figure 5 is created by selecting both the high resolution VAMAS block and also the survey VAMAS block in the right-hand-side of the Experiment Frame and adding an annotation table from the Quantification property page on the Annotation dialog window. The annotation tables offered by the Quantification property page on the Annotation dialog window are displayed based on the VAMAS blocks currently selected in the right-hand-side of the Experiment frame, where each row of VAMAS blocks so selected will produce a set of entries in the quantification table. To quantify data from separate VAMAS blocks, as in the case of the high resolution spectrum in Figure 2 and the survey spectrum in Figure 1, both VAMAS blocks must appear in the same row in the right-hand-side of the Experiment Frame and both must be selected in order to create the table in Figure 5.

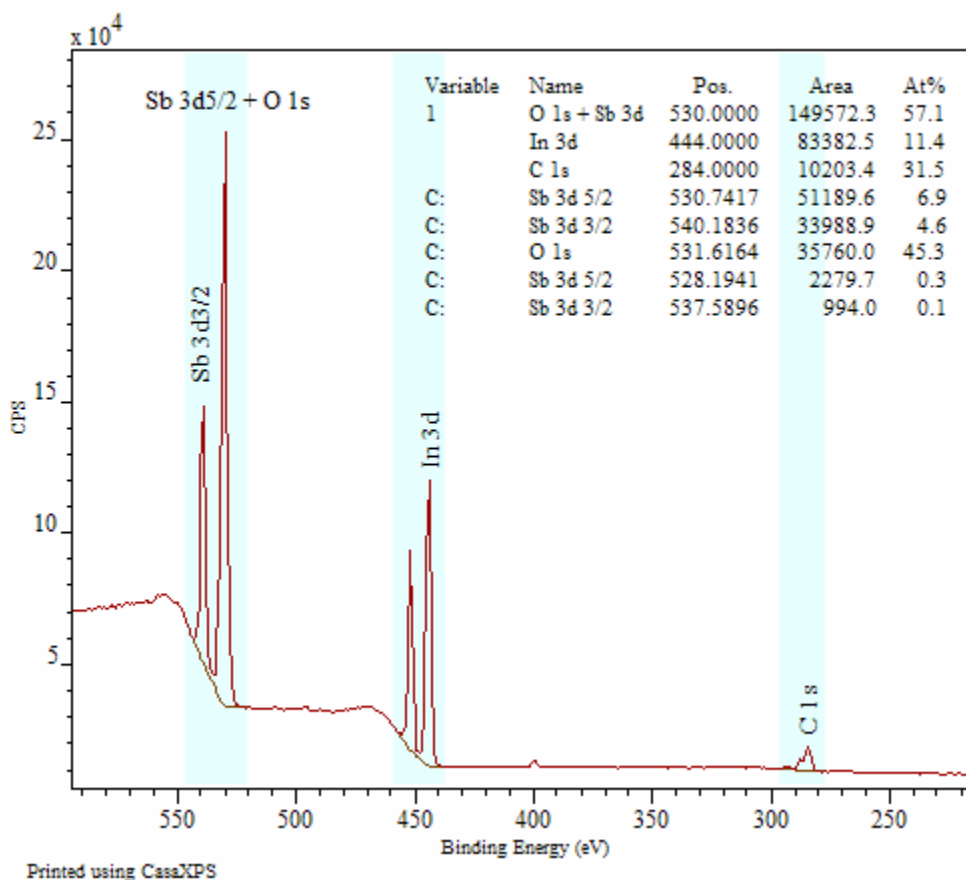| Variable	Name	Pos.	Area	At%
1	O 1s + Sb 3d	530.0000	149572.3	57.1
	In 3d	444.0000	83382.5	11.4
	C 1s	284.0000	10203.4	31.5
C:	Sb 3d 5/2	530.7417	51189.6	6.9
C:	Sb 3d 3/2	540.1836	33988.9	4.6
C:	O 1s	531.6164	35760.0	45.3
C:	Sb 3d 5/2	528.1941	2279.7	0.3
C:	Sb 3d 3/2	537.5896	994.0	0.1

Figure 5: Full quantification table showing the partial quantification table followed by a component based brake down of the Sb 3d/O 1s contribution.

The annotation table added to the spectrum in Figure 5 was defined using the settings in Figure 6. The key settings appear in the "Table Type" section, where the "Use Tag Field" tick box must be ticked and the Comp radio button selected before pressing the Apply button. An alternative to using annotation is to generate a Standard Report from the Report Spec property page on the Quantification Parameters dialog window. After making the VAMAS block selection, the "Combine with Tags" button should be selected.
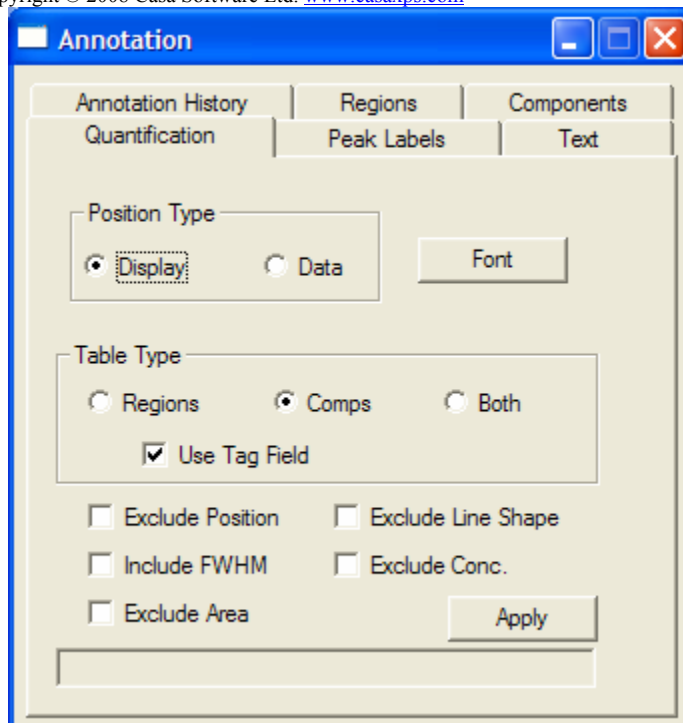
Figure 6: Quantification property page on the Annotation dialog window.