

Curve Fitting and Polymers

The availability of data from well-characterized samples such as those offered by Beamson and Briggs [1] owe much to the popularity of XPS as a tool for understanding the chemistry of polymers. A typical C 1s envelope [2] (Figure 1) includes structure that offers chemical information about a sample, but without some initial starting point it is difficult to construct an appropriate model for such a data-envelope.

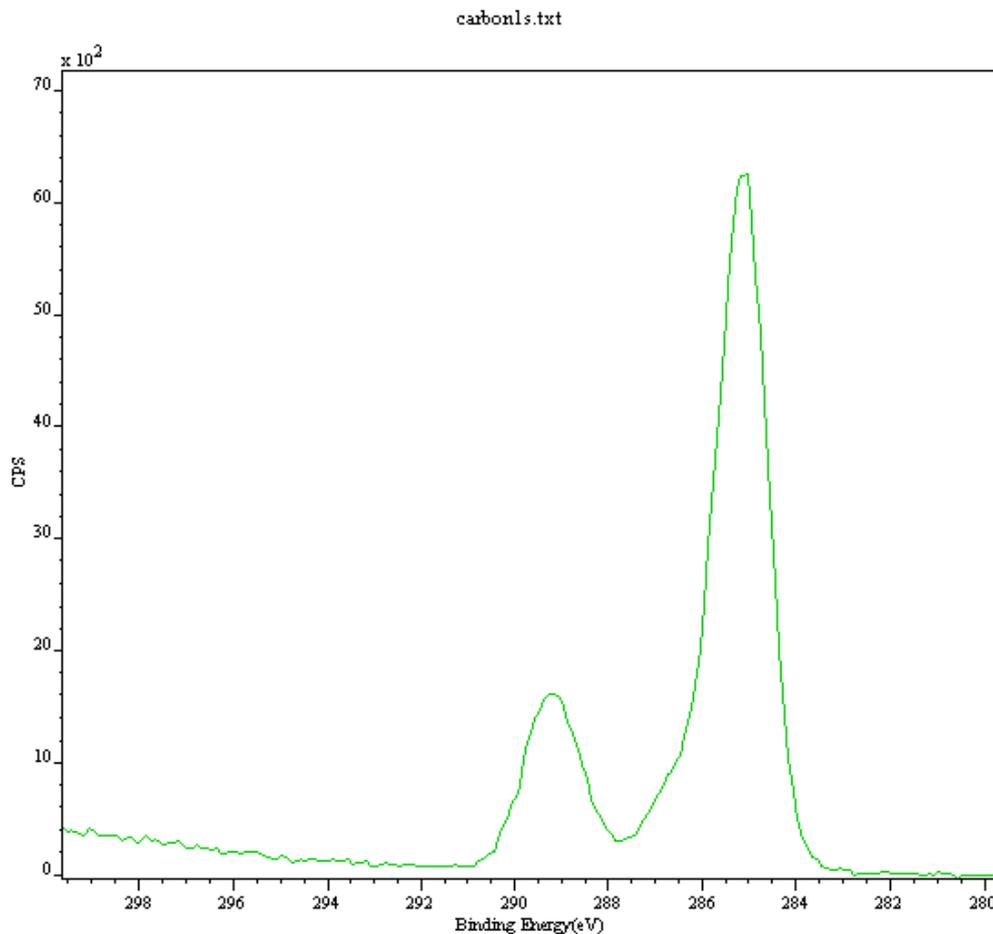


Figure 1: C 1s high-resolution spectrum taken from a polymer-based sample using a VG ESCALAB 220i at University College London, UK.

The high-resolution spectrum in Figure 1 derives from poly (acrylic acid) PAA reacted with inorganic material (or partially reacted) in an acid-base reaction. If Gaussian/Lorentzian (GL) line-shapes are added in an arbitrary way, the curve fit yields little information about the sample other than to say that it deviates from the published data for PAA and therefore demonstrates the presence of additional chemistry at the surface. Figure 2 shows a synthetic model for this data envelope where three GL peaks have been added, then fitted using a Marquardt-Levenberg [3] optimization algorithm. No constraints have been applied and the result is a reasonable fit to the experimental data but the fitting parameters are not readily open to chemical interpretation. For example, the FWHM are much bigger than would typically be expected from C 1s profiles the given instrumental resolution. The three-peak model suggests further synthetic components are required before the sample can be fully understood.

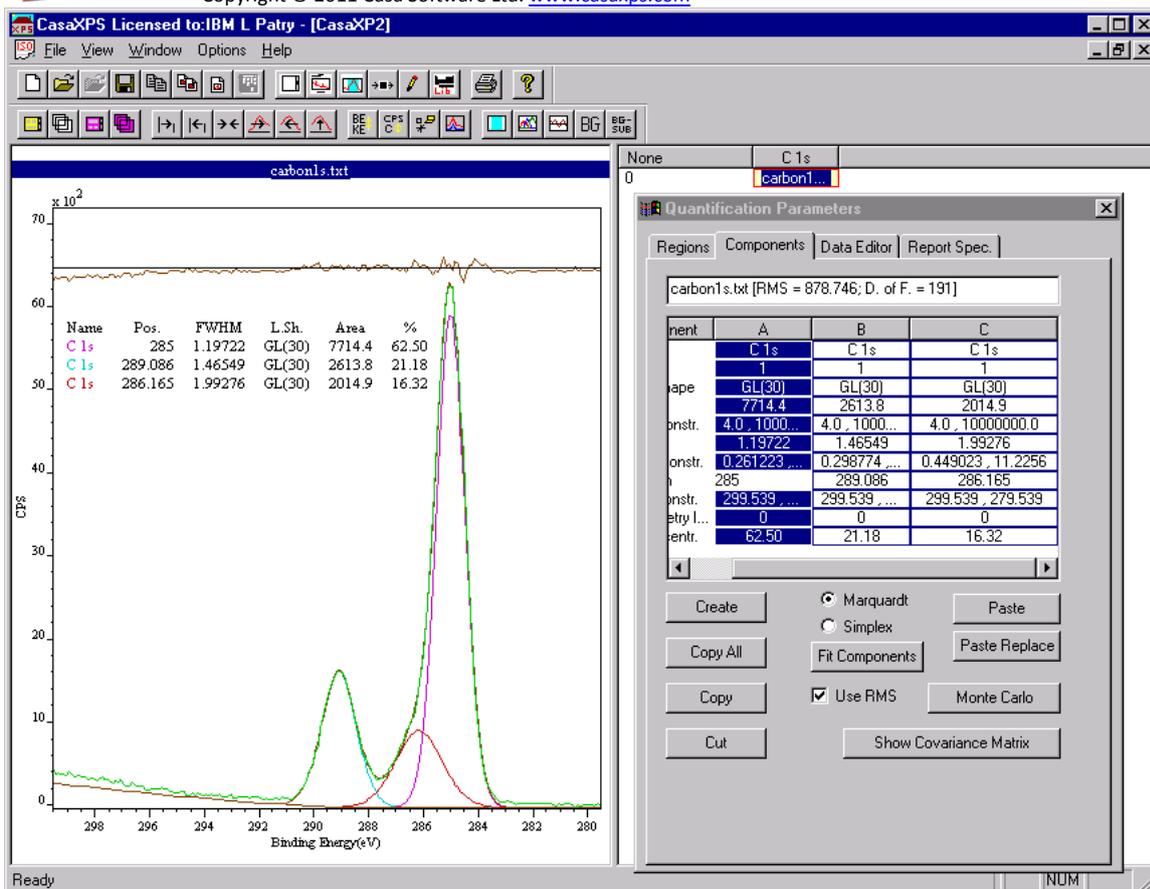


Figure 2: An initial fit to the C 1s spectra shown in Figure 1.

If it is assumed that the FWHM for a C 1s photoelectron peak is 1.1 eV (only a guess), then applying peaks with said constraint results in a peak fit shown in Figure 3. Two additional peaks appear in the model and further more three of the peaks look like they may have something to do with pure PAA. The PAA stoichiometry is still doubtful but the essential positions for a pure PAA envelope have more or less appeared. Further input is required to make sense of the new synthetic model.

To constraint a parameter so that it does not adjust during an optimization step, set the constraint interval to have the same value as the fixed value. E.g., if it is required to set the FWHM value to 1.1, the constraint interval should be entered with the value "1.1,1.1". Actually, it is sufficient to set the parameter value outside the constraint range currently defined for the parameter.

Spectra from Beamson and Briggs ("The XPS of Polymers Database") offer the opportunity to examine more complex polymer data in the context of known synthetic models. Figure 4 is an example of such data where a set of three line-shapes has been used to model the clean PAA C 1s data envelope. The important feature is that the stoichiometry and chemical shifts for the C 1s lines can be incorporated into the model and this information is then transferable to other polymer spectra. The peaks in Figure 4 are linked in area, but only the position of peak "C 1s b" and "C 1s a" are constrained by an offset.

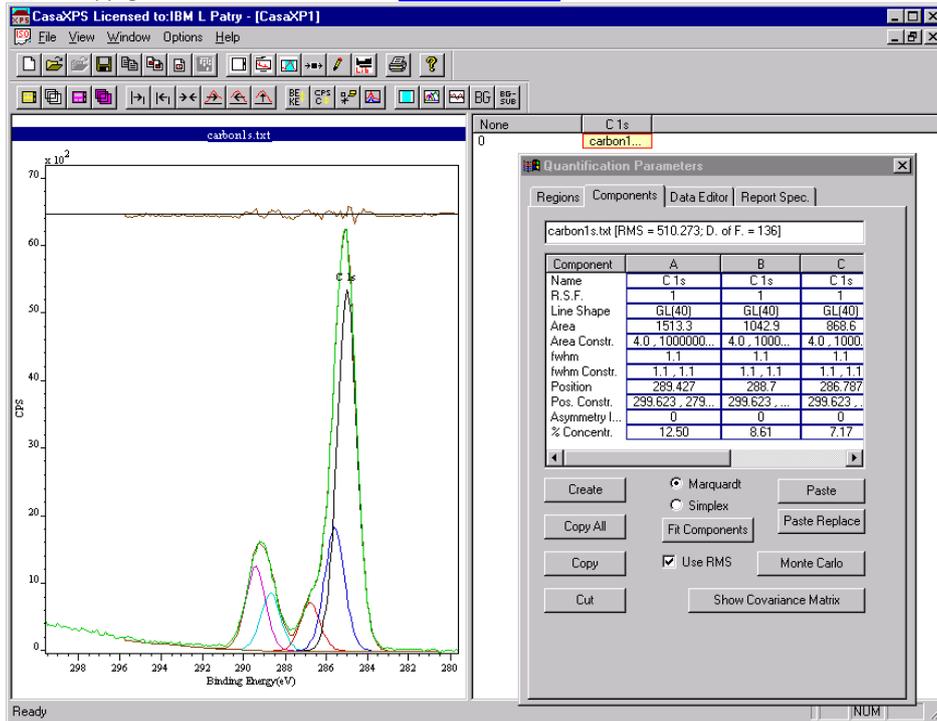


Figure 3: Same C 1s envelope as Figure 2 but the synthetic peaks are all constrained to have FWHM equal to 1.1 eV.

To link a component parameter the constraints must be adjusted as follows. Each synthetic component defined on the Quantification Parameter dialog, Components Property Page, appears as a column of parameters in the scrolled list shown in Figure 3. These columns are headed "A", "B", "C" and so on. To constrain the area of the component in column B to be half of the area of the component in column A, the area constraint in column B should be set to "A * 0.5". Similarly, to offset a component in column C by 0.2 from the component in column B, enter "B+0.2" in the position constraint field in column C.

PAA516.

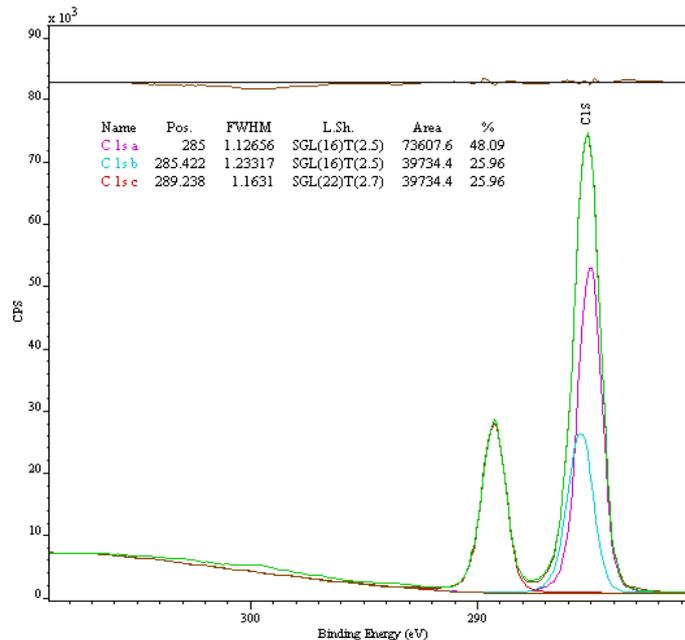


Figure 4: C 1s envelope from clean PAA acquired on a Scienta-300, RUSTI, Daresbury Laboratory UK.

The peak shapes from a Scienta ESCA-300 may differ from a VG ESCALAB 220i (the source of the real data in Figure 1) or any other manufacturers instrument, but the essential structure should be suitable as a basis for the new model. Copying the pure PAA model into the data in Figure 3 leaves a residual that requires an adjustment for the two non-PAA peaks together with the introduction of a third peak. The new peak in Figure 5 is constrained to be the same width and position as the saturated PAA C 1s peak located at 285 eV (BE). The area of this new peak is allowed to adjust at will and accounts for carbon with the same characteristics as the PAA peak at that position. The consequence of introducing the new peak is that the PAA synthetic model can adjust without breaking the stoichiometric relationships for pure PAA, while differences in the intensity of the saturated peak from the PAA structure are allowed for by this additional constrained component (Figure 5).

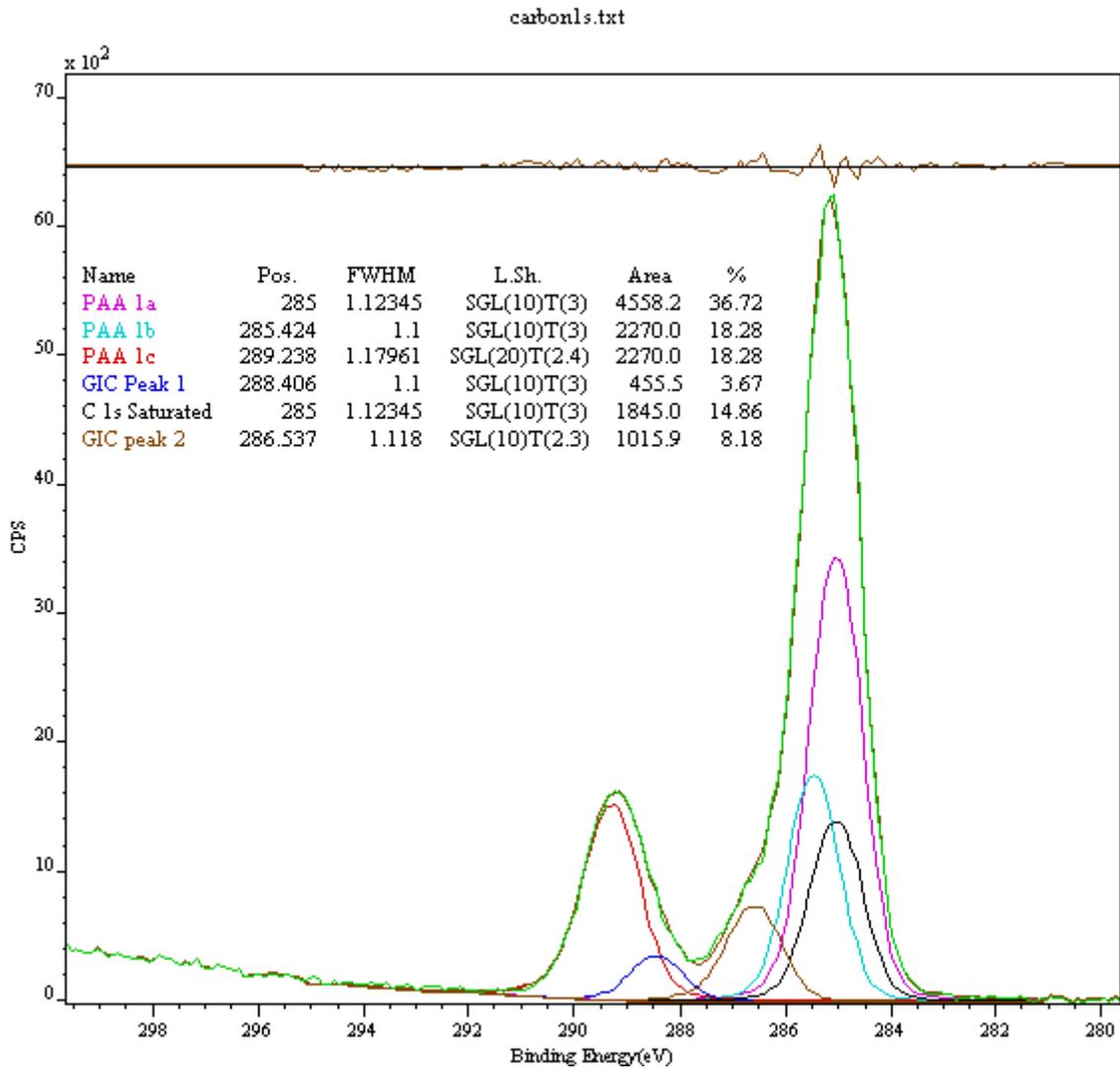


Figure 5: Final form for the synthetic model. The Glass Ionomer Cement (GIC) [2] C 1s envelope containing three peaks from PAA plus three additional peaks not seen in a clean PAA spectrum.

Synthetic models such as the one in Figure 5 can be tested using Monte Carlo simulation techniques [4] to assess the stability of the peak parameters with respect to noise in the data. Once a set of peaks and constraints has been developed, the Monte Carlo procedure simulates repeated identical experiments on the same sample, and for each simulation a new fit is determined for the peak

parameters. The result of this procedure is a set of distributions for the individual parameters from which scatter plots may be constructed that highlight the way noise influences the data model. Figure 6 is a scatter plot for the normalized peak areas of the non-PAA peaks against the saturated C 1s peak from the pure PAA model. The peaks at 288.4 eV and 285 eV have areas that are anti-correlated with the pure PAA model (all the peak areas within the PAA model are constrained to one another), but the synthetic component at 286.54 eV shows a degree of correlation with the intensity of the pure-PAA area.

At first glance the behavior of the GIC 2 peak at 286.54 eV is unexpected since one might think that two peaks next to one another should produce anti-correlated area distributions. The constraints have altered the concept of “next to” since the PAA sub-model spreads across the entire envelope and it becomes difficult to judge by eye what the influence of noise might be on the final result. This type of insight can only help to understand what constraints do to a fitting procedure as well as provide a rule-of-thumb estimate for error bars.

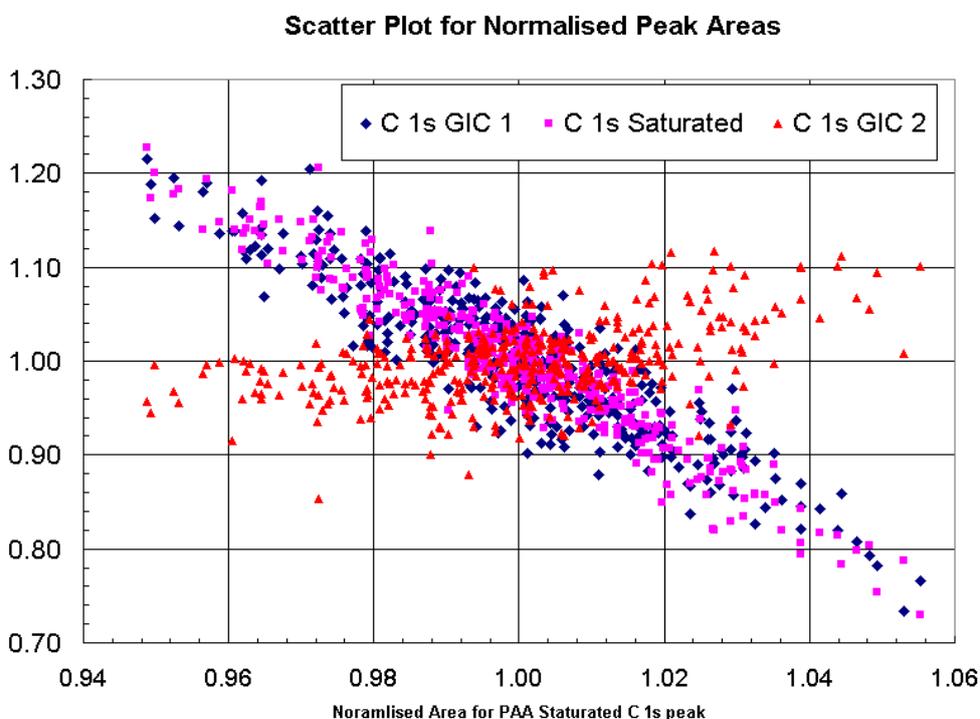


Figure 6: Monte Carlo simulation results for normalized peak areas. The three peaks associated with GIC are plotted against the saturated C 1s peak area from the pure PAA model.

The exact meaning for the model in Figure 5 is left to the experimentalist and may need changing in view of other input, however such a model is only possible when peak fitting routines offer mechanisms for fixing parameters with respect to one another. The role played by the pure PAA synthetic model is that of a foundation shape from which differences in the unknown polymer can be assessed. These additional peaks may still require further interpretation, but with the aid of chemical knowledge and supporting evidence a meaningful model can emerge from seemingly intractable data.

[1] Beamson G. and Briggs D., “The XPS of Polymers Database” Surface Spectra Ltd (2000)

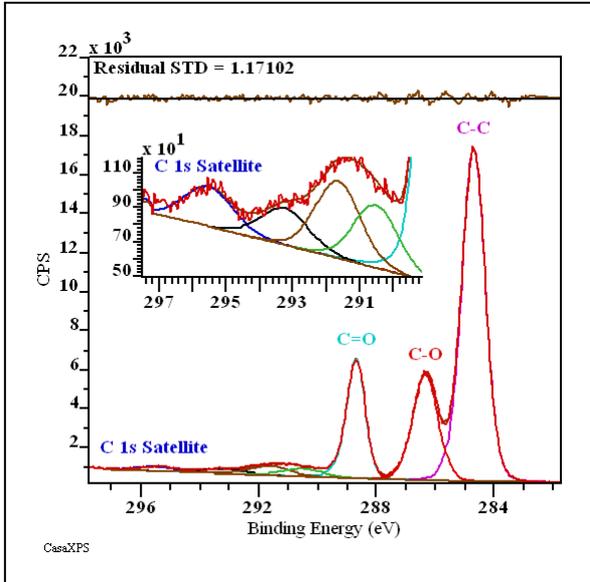


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- [2] Jones F.H., Hadley P.C., Hutton B.M., Eccles A.J., Steele T.A., Billington R.W. and Pearson G.J., "Fluoride uptake by glass ionomer cements: a surface analysis approach" ,. Submitted to Biomaterials.
- [3] Press W.H. et al, "Numerical Recipes in C", Cambridge University Press (1988)
- [4] Cumpson P. J. and Seah M. P., "Random Uncertainties in AES and XPS", Surface and Interface Analysis, 18 361 (1992)

Calculating Precision Errors in Atomic Concentration measured using Peak Models

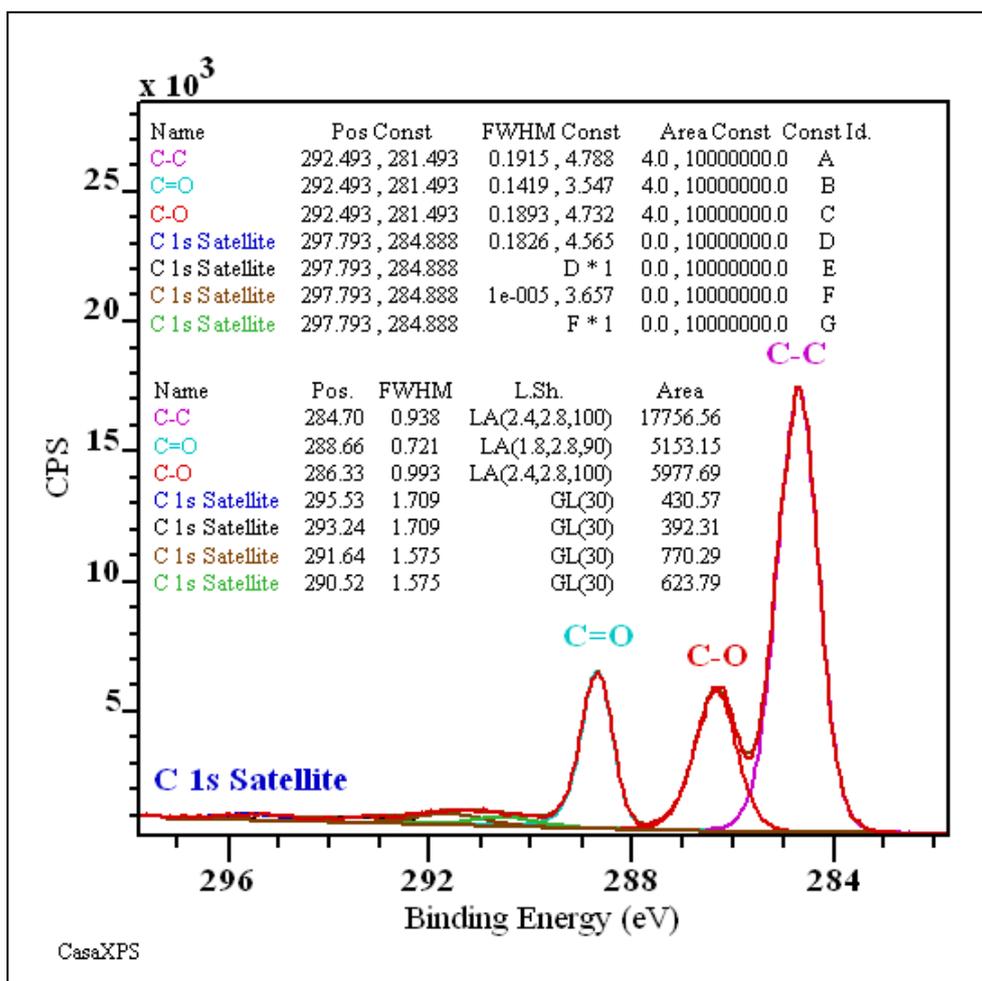
Uncertainties for percentage area calculated for Poly (ethylene terephthalate) (PET) will be used to illustrate the steps leading to the display of the results with error estimates. Further points relating to peak parameter uncertainties are discussed in the context of Poly (ether ether ketone) (PEEK) and silver deposited on silicon.



The Beamson and Briggs XPS of Polymers Handbook fit three primary peaks and four satellite loss peaks to the C 1s spectrum of PET. The primary peaks are well resolved and so the error in peak area as measured by three synthetic component peaks is expected to be reasonably good. The satellite peaks on the other hand are highly correlated and therefore subject to greater uncertainty in terms of peak area.

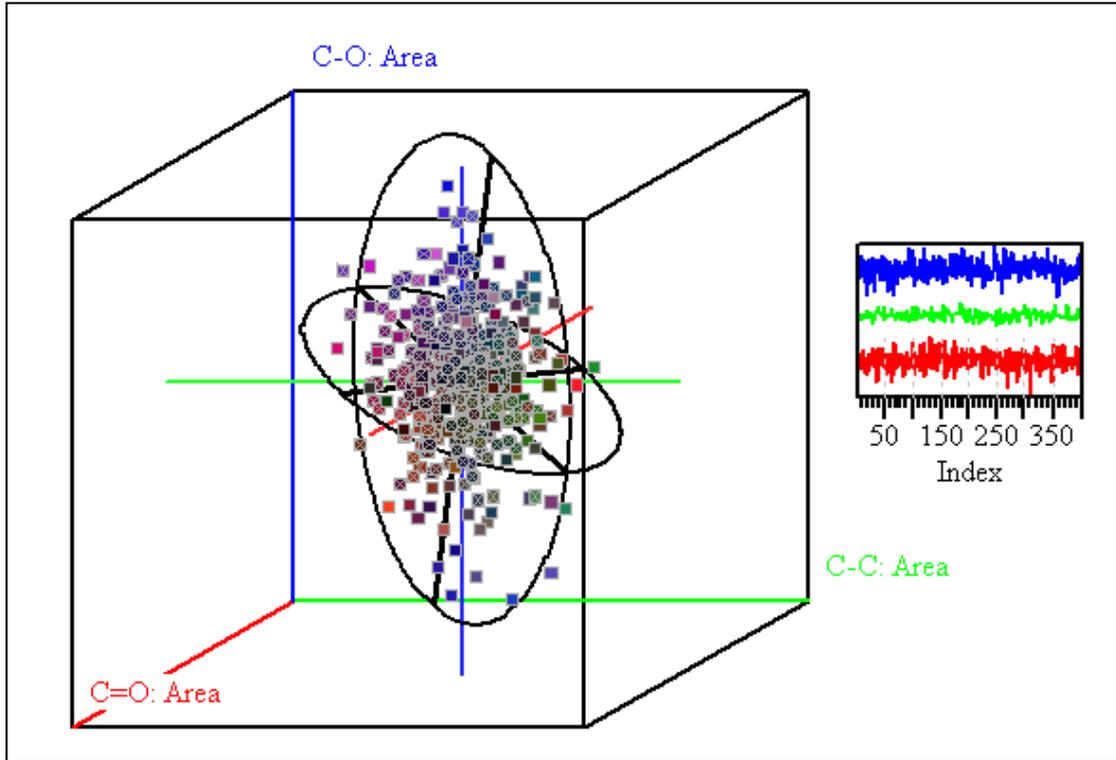
The peak model applied to the data measured from a Kratos Axis 165 follows the design proposed by Beamson and Briggs where asymmetry in the lineshapes is used to model vibrational and other distortions to the C 1s primary lines, and only limited parameter constraints are applied to the satellite peaks in terms of FWHM. Tables overlaying the data show both the peak parameters (position, FWHM and area) for each of the synthetic components and the constraints used to limit the satellite peaks to the appropriate region of energy for these peaks. These parameters are also listed on the Components property page.

Component	A	B	C	D	E	F	G
Name	C=C	C=O	C-O	C 1s Satell...	C 1s Satell...	C 1s Satell...	C 1s Sate
R.S.F.	1	1	1	1	1	1	1
Line Shape	LA(2.4,2.8)	LA(1.8,2.8)	LA(2.4,2.8)	GL(30)	GL(30)	GL(30)	GL(30)
Area	5153.1	5977.7	430.6	392.3	770.3	623.8	623.8
Area Constr.	Area Cons: 4.0, 1000...	4.0, 1000...	0.0, 1000...	0.0, 1000...	0.0, 1000...	0.0, 1000...	0.0, 100000
FWHM	FWHM = 0	0.721097	0.993409	1.70852	1.70852	1.57499	1.57499
FWHM Constr.	FWHM Con: 0.14119, 2...	0.1893, 4...	0.1826, 4...	D * 1	1e-005, 3...	F * 1	F * 1
Position	288.6543	286.3283	285.5323	293.2359	291.6429	290.517	290.517
Pos. Constr.	Pos. Cons: 292.493, ...	282.493, ...	297.793, ...	297.793, ...	297.793, ...	297.793, ...	297.793, ...
Tag	NoTag	NoTag	NoTag	NoTag	NoTag	NoTag	NoTag
Comp Index	0	1	2	3	3	3	3
Asymmetry I...	0.0178	0.0667	0.0178	0.0000	0.0000	0.0000	0.0000
% Concentr.	57.09	16.57	19.22	1.38	1.26	2.48	2.01

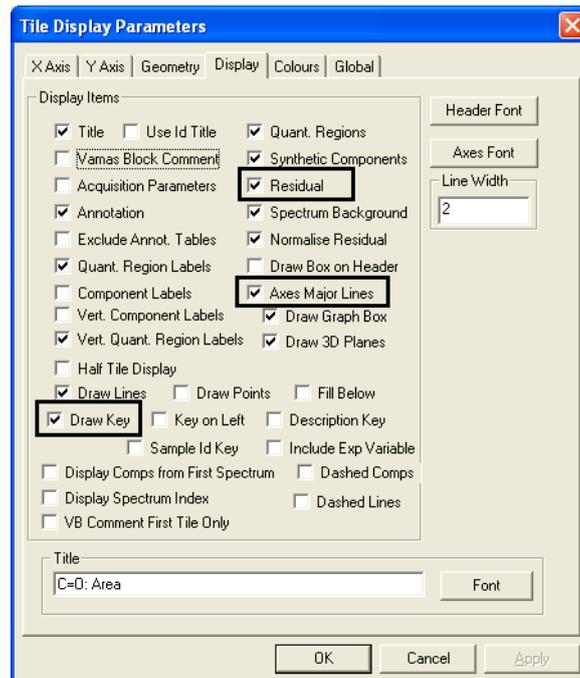


Calculating the standard deviation in the percentage area for a peak model is achieved by pressing the Monte Carlo button on the Components property page of the Quantification Parameters dialog window. Once pressed, the Monte Carlo button causes a sequence of peak-fitting operations applied to sets of synthetic data resulting in two tables representing the simulation results relative to the initial parameter set and an error matrix calculated from the parameter distributions. In addition to these tables of results, a new experiment frame is created in which VAMAS blocks are entered providing the distribution of parameters relative to the initial parameters used to fit the peaks to the data and centred with respect to the initial parameters. The uncertainties in the percentage area for the set of peaks defined on the active VAMAS block is calculated from these centred and normalised parameter distributions.

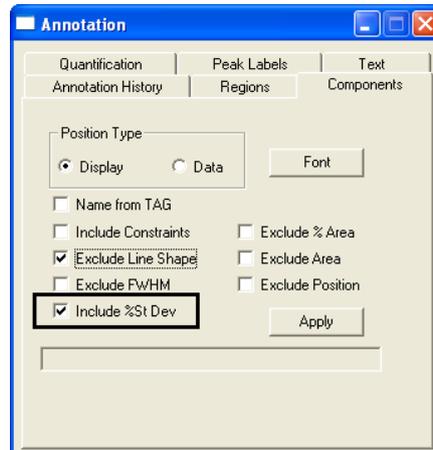
When computing the uncertainties in the peak parameters the problem is that of identifying those parameter sets which lie closest to the distribution centre, and using this distance metric to define a volume containing 68.3 % of the parameter sets. The projection of the extreme parameter values from the identified volume onto the parameter axis provides an estimate for one standard deviation in a given parameter.



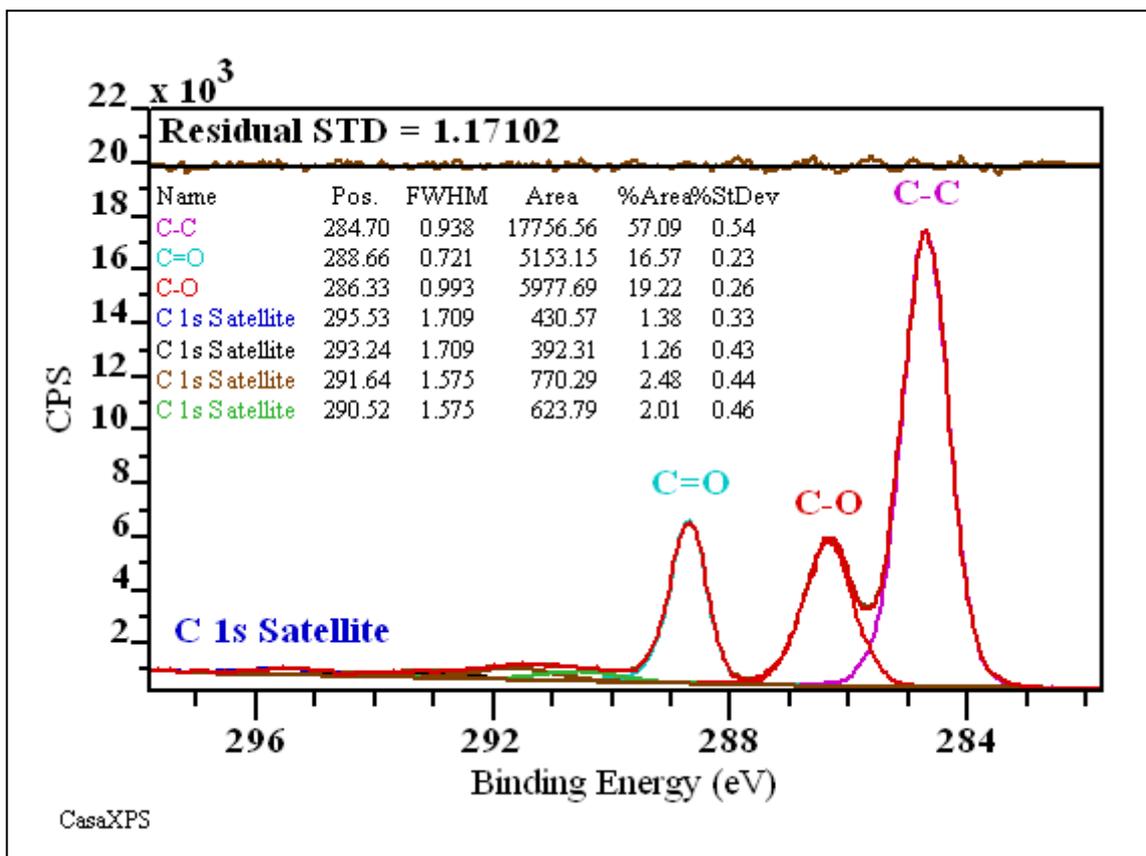
The above scatter diagram is a projection onto a 3D volume of the n-dimensional parameter distribution. A cross is used to indicate those points measured to lie within the 68.3 % n-dimensional volume. To help visualise the structure and shape for a set of parameters, principal axes and the associated ellipses are drawn whenever the residual display option is selected and the axes major lines are enabled on the Display property page of the Tile Display Parameters dialog window. To further annotate the RGB coloured axes with the block id for the distributions plotted the Draw Key tick box is used.



A summary for the parameter analysis in terms of uncertainties in the %Area is added to the display using the Components property page on the Annotation dialog window.



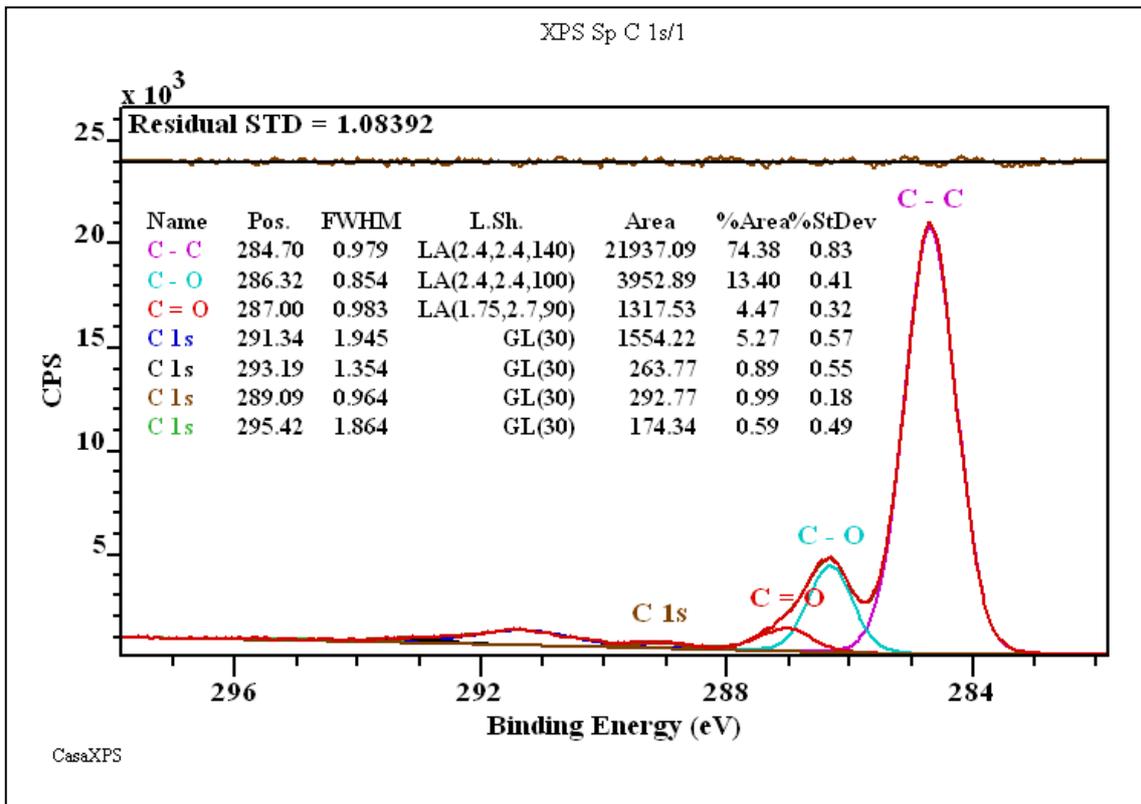
An example of the results for the PET are displayed over the data using the above display options following a Monte Carlo calculation.



The table displayed over the data for PET shows the percentage area uncertainty in the computed area intensity values for the peaks in the synthetic model. While the numerical values for the uncertainties for the peak areas are similar in magnitude, as a proportion of the area as measured, these uncertainties are much less favourable for the satellite peaks than the primary peaks. Since the binding energy for the C=O peak is significantly different from the C-O C 1s binding energy, the

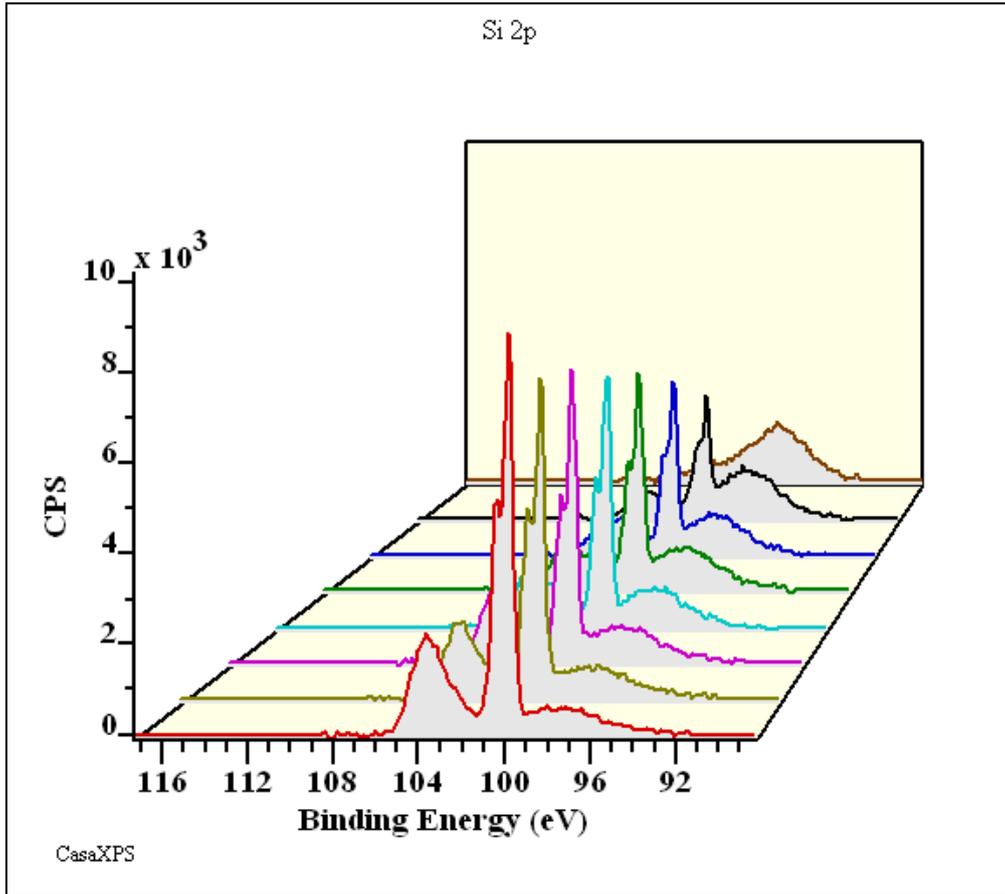
optimisation of the peak parameters for the primary C 1s peaks is relatively stable with respect to noise variations. A similar peak structure from Poly(ether ether ketone) PEEK presents a more challenging problem where three primary peaks are closer in binding energy than is the case for PET. Without applying a constraint to the C=O peak the peak areas would be different due to the overlap between the three primary peaks. Applying such a constraint alters the area and position for the peaks and also changes the uncertainties associated with the peak areas. Without constraint, the percent area for PEEK measured using the same set of peaks for the C=O peak is 2.54 ± 0.53 . With a constraint applied to the FWHM the same quantity is 4.47 ± 0.32 . Apart from improving the precision of the %Area a comparison of these calculations illustrates the real nature of the uncertainties reported in the quantification tables, namely, the accuracy of the measurement is only as good as the model. Changing the model by introducing a constraint alters the result and since the uncertainty reported is a measure of the precision not the accuracy, there is no contradiction in the fact that the two models provide two answers which are not within the bounds of error for each other. Essentially, the two models one with and one without constraints are measuring different quantities, that is, both cannot be used to measure the intensity of the C 1s C=O peak area, since at least one model must be including or excluding some intensity due to the other transitions.

The assertion should be “**IF my peak model is measuring the C=O peak area THEN the %Area for the C=O peak is 4.47 ± 0.32 .**” The value in the precision uncertainty lies in knowing how noise has influenced the outcome when applying the same model to data from different experiments.

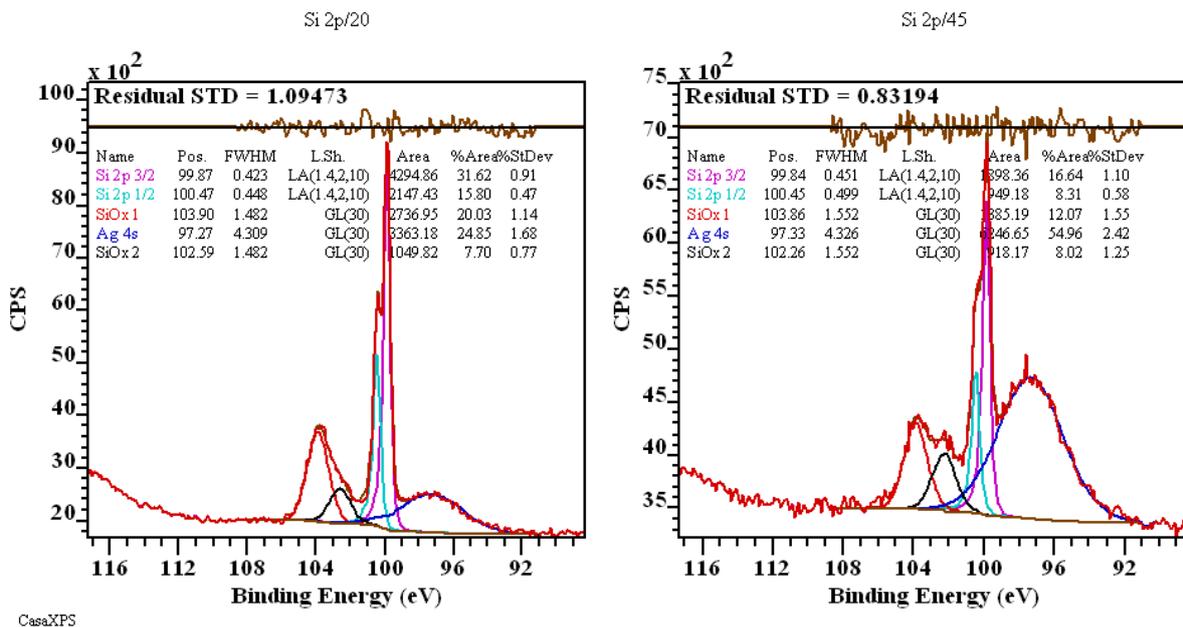


To illustrate the usefulness of precision uncertainty estimates consider a sequence of measurements from a silicon surface after deposition of silver onto the silicon to varying thickness. Spectra measured from the Si 2p energy region include the Ag 4s peak and as the silver layer increases so

does the Ag 4s peak while the Si 2p peaks attenuate due to scattering of the Si 2p electrons by the silver overlayer (University of Iowa, Jukna, Baltrusaitis and Virzonis, 2007, unpublished work).



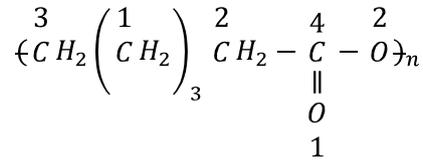
If the objective is to measure the intensity for the silicon oxide peak areas, is it possible to use a given peak model to extract information about the oxide peak areas from a range of these measurements?



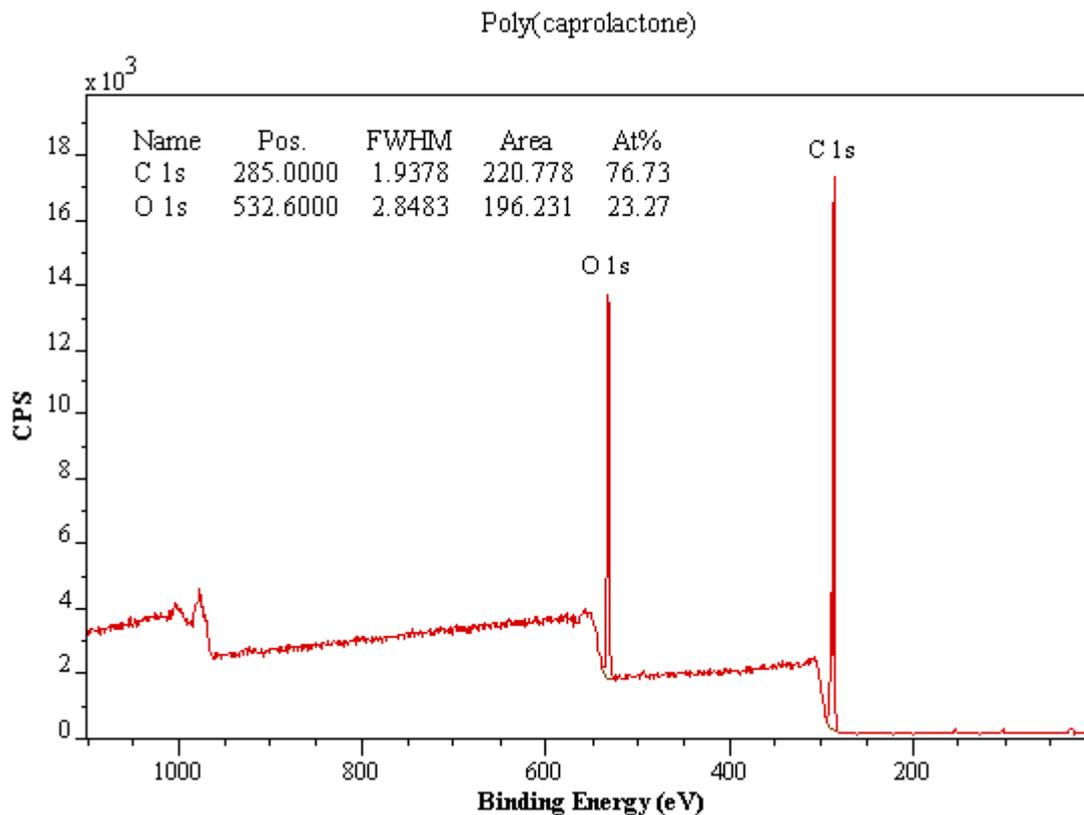
The answer is perhaps surprisingly independent of the precision of the fit between the synthetic envelope and the spectroscopic data. While the residual standard deviation for both spectra fitted to the same peak model appears to be very acceptable, the only warning regarding the precision for the oxide peak areas is evident in the %StDev column in the components annotation table displayed over the two spectra. The peak labelled Si Ox 1, as an example, is measured as a percentage to be 20.03 ± 1.142 for the Si 2p/20 data, however for the Si 2p/45 data, the same peak as measured using identical fitting steps is 12.07 ± 1.548 . As a proportion of the Si Ox1 intensity the uncertainty represents about 6% when fitting the peak model to Si 2p/20 while 13% for the Si 2p/45 data. The residual standard deviation gave no indication of a potential problem in the peak model when used with these data.

Peak Fitting Poly (caprolactone)

The subject addressed in this article relates to constraining peaks from different VAMAS blocks to ensure a valid model results in terms of known chemistry for the sample.



Following the assignments of Beamson and Briggs, the expected stoichiometry for Poly (caprolactone) (PCL) is two oxygen to six carbon.

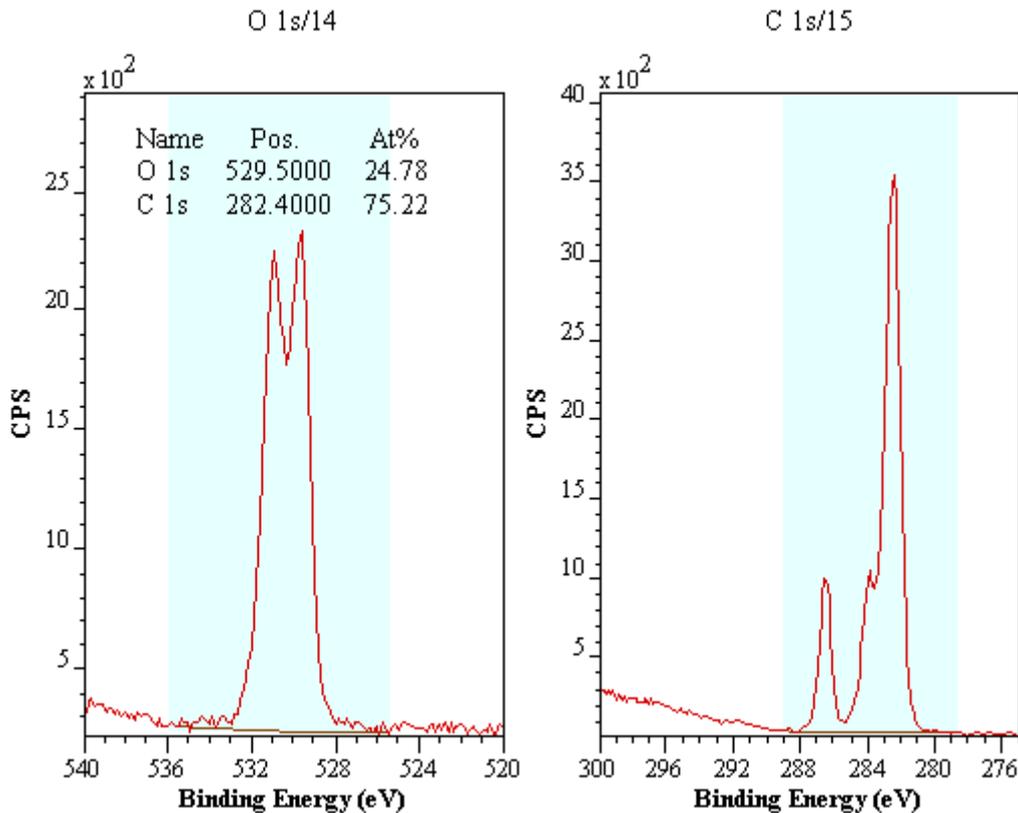


A strategy for enforcing relationships between peaks from different chemical states is as follows. Data acquired from PCL using two distinct acquisition energy regions are used to construct a single VAMAS block for which peaks representative of both C 1s and O 1s electrons are combined with intensity calibration information in such a way to permit the use of Monte Carlo simulation to compute estimates for the atomic concentration uncertainties calculated based on the peak model.

The success of the approach described below depends on well characterised data in terms of intensity. Physically meaningful constraints are only possible if appropriate sensitivity factors are available, the transmission response of the instrument is known and sampling depth considerations are allowed for when comparing peak intensities from different energy regions within a spectrum. Without a well calibrated instrument, the constraints in terms of peak intensity may be introduced in

an ad hoc regime and serve just as well to add structure to the peak model, but perhaps lack the pleasing nature of the example which follows.

These data are collected on a Kratos Axis Ultra at University of Manchester which has been calibrated using the National Physical Laboratory's XPS instrument calibration procedure. The transmission function calculated from the NPL software allows the use of Scofield cross-sections modified for physical effects such as angular distribution intensity-variations and escape depth dependency on kinetic energy of the detected electrons. Scofield cross-sections represent the scaling factor required to compare peak intensities resulting from excitation processes with differing photoionisation transition probabilities.

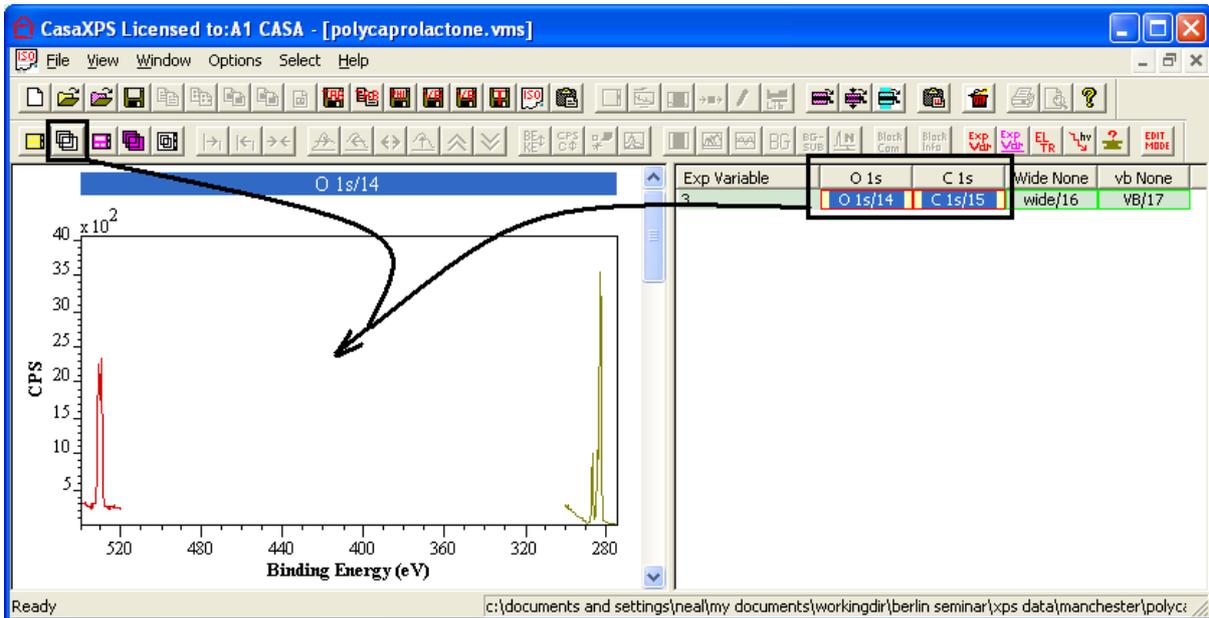


A systematic analysis for a pair of high resolution spectra corresponding to the O 1s and C 1s energy regions is dependent on maintaining the calibration information just described whilst manipulating the data into a suitable form to perform the analysis.

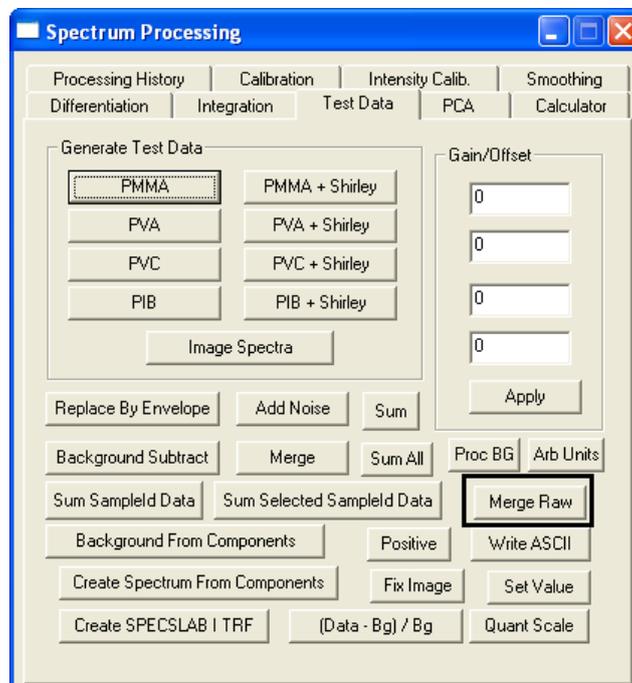
The technique for creating a peak model which describes both the C 1s and O 1s data envelopes is based on merging the two spectra into a single VAMAS block. To perform the merge operation the spectra must be acquired using the same energy step size. The reason the same step size must be used is to ensure the noise within the data is left unaffected when the two spectra are merged. Interpolating data with noise tends to smooth the resulting spectrum since changing the data bins through interpolation will never increase the variation in the data intensities, but can and will reduce the variation. The appropriate merge operation with necessary book keeping steps is performed using the Test Data property page on the Spectrum Processing dialog window.

To merge two or more high resolution spectra with identical energy step-size:

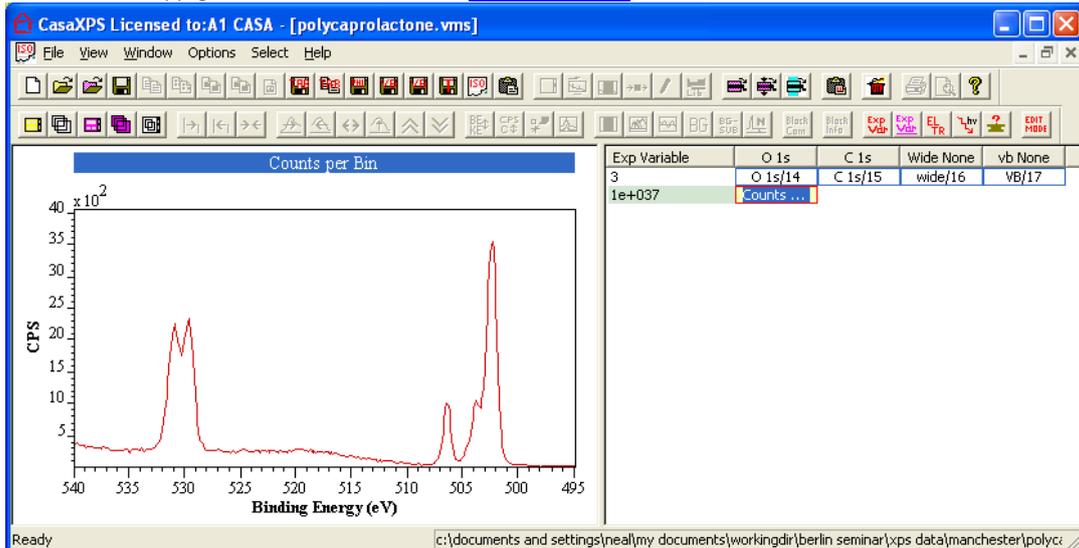
1. Select the VAMAS blocks in the right-hand pane and press the overlay button on the toolbar. The selected VAMAS blocks are displayed in the active tile in the left-hand pane.



2. Using the Options menu or the top toolbar, select the Spectrum Processing dialog window and bring the Test Data Tab to the front. The Merge Raw button on the Test Data property page acts on the spectra overlaid in the active tile and when pressed creates a new VAMAS block constructed by concatenating the data bins from the overlaid spectra in the active tile.

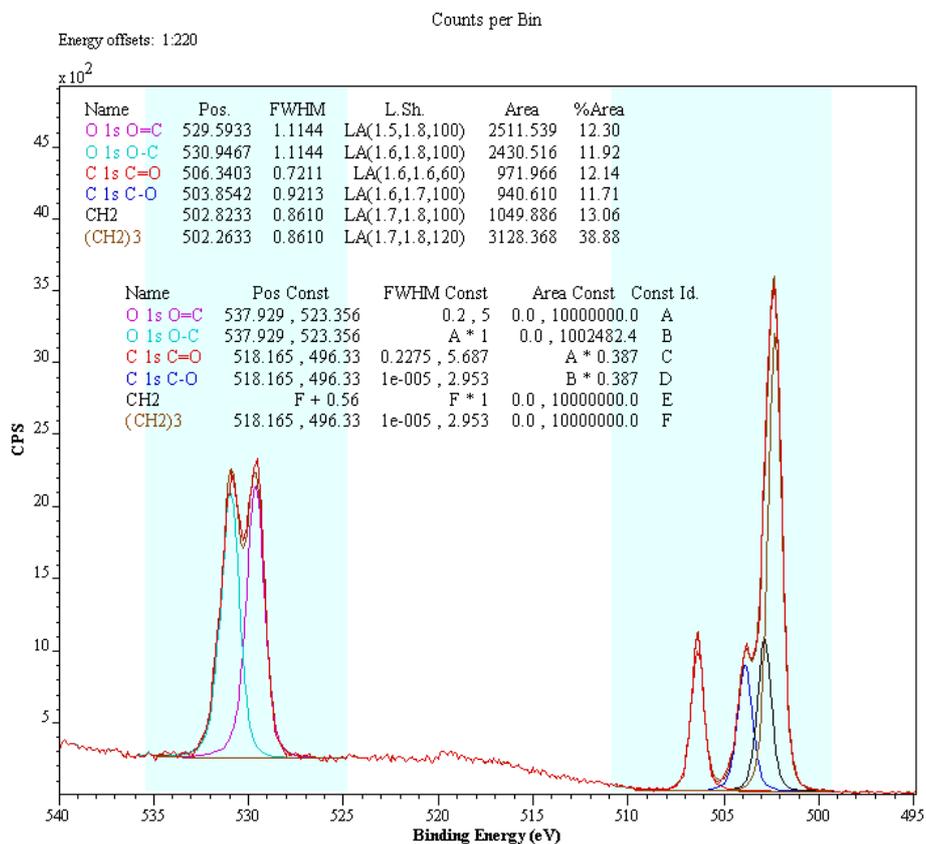


3. Display the newly created VAMAS block in the active tile. The order for the spectra in the new VAMAS block is determined by the order with which the VAMAS blocks were selected in the right-hand pane before overlaying the spectra in the active tile. Note the energy scale is no longer meaningful, but does maintain the relative positions for peaks.

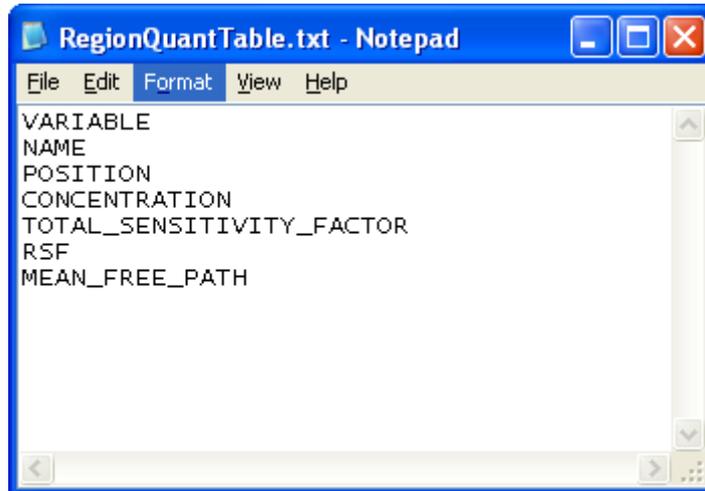


With the data collected in a single VAMAS block a peak model can be prepared which permits constraints between peaks from carbon and oxygen. For the example in use currently, the C=O bond equates peak intensity between an oxygen and a carbon peak. Similarly the second oxygen peak can be equated to the intensity of a carbon peak corresponding to the C-O bond in the PCL polymer. Constraints of this nature are advantageous to the precision achieved for peak areas since the C 1s C-O peak is correlated with the two CH₂ C 1s peaks and the two O 1s peaks are correlated with each other, or alternatively stated these peaks overlap to a significant extent.

The peak model justified by the chemical formula for PCL specified in Beamson and Briggs requires two chemically shifted O 1s peaks and four chemically shifted C 1s component peaks.



Assuming all the intensity adjustments are available and correctly determined for the data, the relationship between the peak areas for O 1s and C 1s components can be obtained by determining the ratio for the total sensitivity factor computed for the quantification regions defined on the O 1s and C 1s high resolution spectra. The total sensitivity factor is a scaling factor determined from the RSF, the transmission function and the escape depth correction and can be obtained by configuring the Standard Report file used with the Region button on the Report Spec property page of the Quantification Parameters dialog window.



Since each operating mode for the instrument results in a different transmission function, it is important to use the Region report generated from the same data ultimately used to create the peak model when calculating the area constraint relationship between carbon and oxygen peaks.

It should also be noted that the current example for PCL is remarkable in the sense that the quantification based on carbon and oxygen high resolution spectra is strangely consistent with the expected stoichiometry for the polymer. In general, XPS data is not so well behaved and so the area constraints may differ from the ideal case presented here, where the quantification for carbon to oxygen measured from the high resolution spectra is 75% carbon to 25% oxygen by atomic concentration.

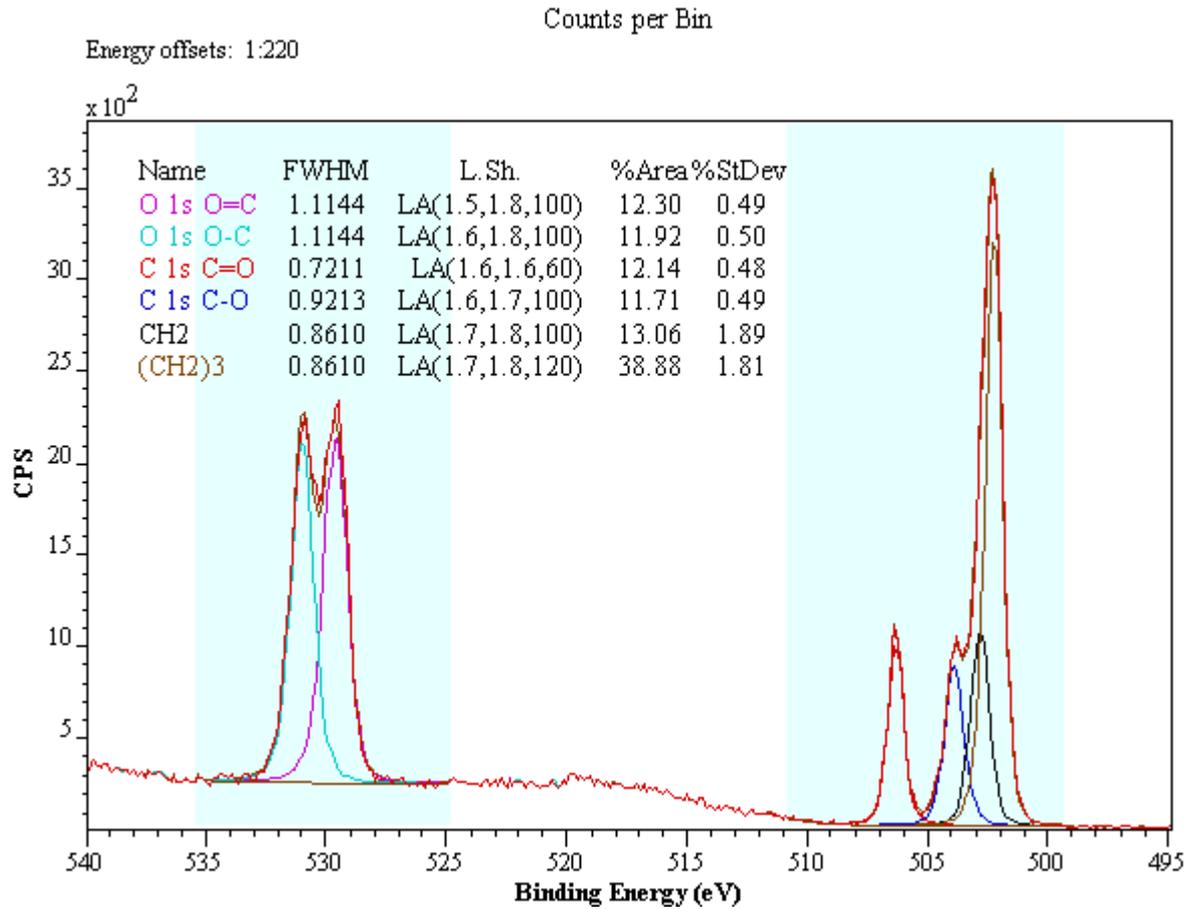
	Name	Position	%At Conc	Total RSF	Library RSF	MFP
	O 1s	529.5	24.62	2.20502	2.93	0.859415
	C 1s	282.4	75.38	0.852369	1	1.00144
C 1s Total RSF / O 1s Total RSF = 0.386558						

$$C\ 1s\ Peak\ Area = O\ 1s\ Peak\ Area \times \frac{C\ 1s\ Total\ RSF}{O\ 1s\ Total\ RSF}$$

Hence the constraint entered for the C 1s C=O component peak in column **C** is **A * 0.387**.

The advantage of performing the analysis using merged raw data is error analysis using Monte Carlo methods is available. The Monte Carlo button on the Components property page coupled with the Components property page on the Annotation dialog window always the results to be displayed over

the data to include an error estimate for the precision on offer for measuring atomic concentration as a percentage.



It is worth noting from the error estimates displayed over the data show the highly correlated CH₂ peaks are significantly less well determined than the peaks constrained in terms of peak area between the O 1s and C 1s data.