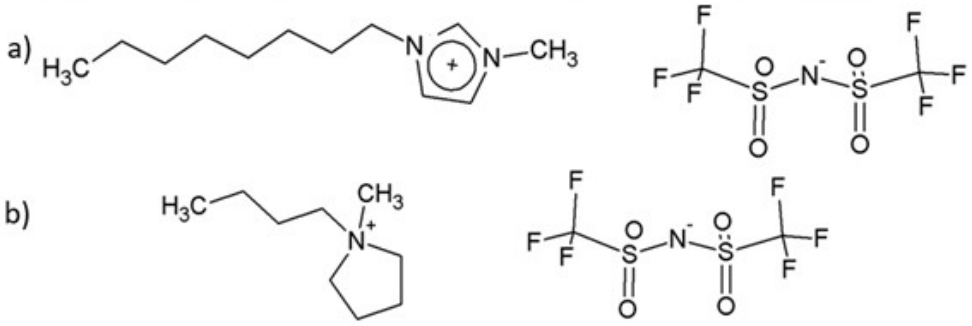
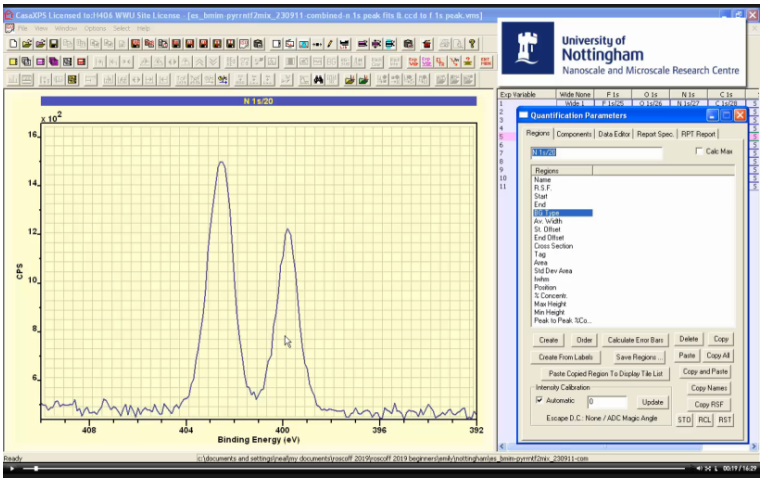
Creating Peak Models: Quantification Parameters Dialog Window Components Property Page

Within in the video a peak model is created based on a spectrum for N 1s photoemission from a sample formed from a mixture of two ionic liquids of known composition. This spectrum is one of eleven N 1s spectra measured from a set of ionic liquid samples representing mixtures of these two well defined ionic liquids and represent a data set for which it can be shown how parameter constraints are created and how these parameter constraints influence optimisation outcomes when fitting components to data.

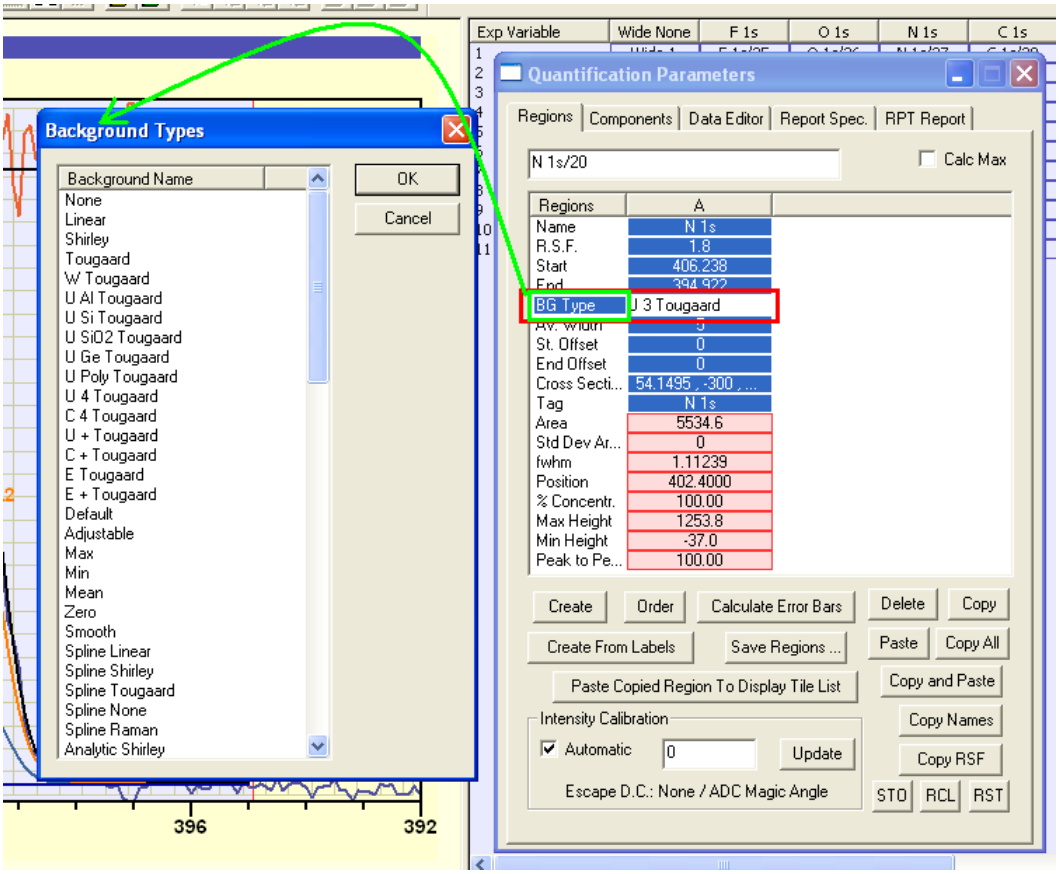
Structures for a) $[C_8C_{1i}m]$ $[Tf_2N]$ and b) $[C_4C_1Pyrr]$ $[Tf_2N]$ used in the mixtures experiments and ionic liquid samples on the Kratos sample bar, left-right 1) 100% $[C_8C_{1i}m]$ $[Tf_2N]$ and mixtures increasing towards 11) 100% $[C_4C_1Pyrr]$ $[Tf_2N]$

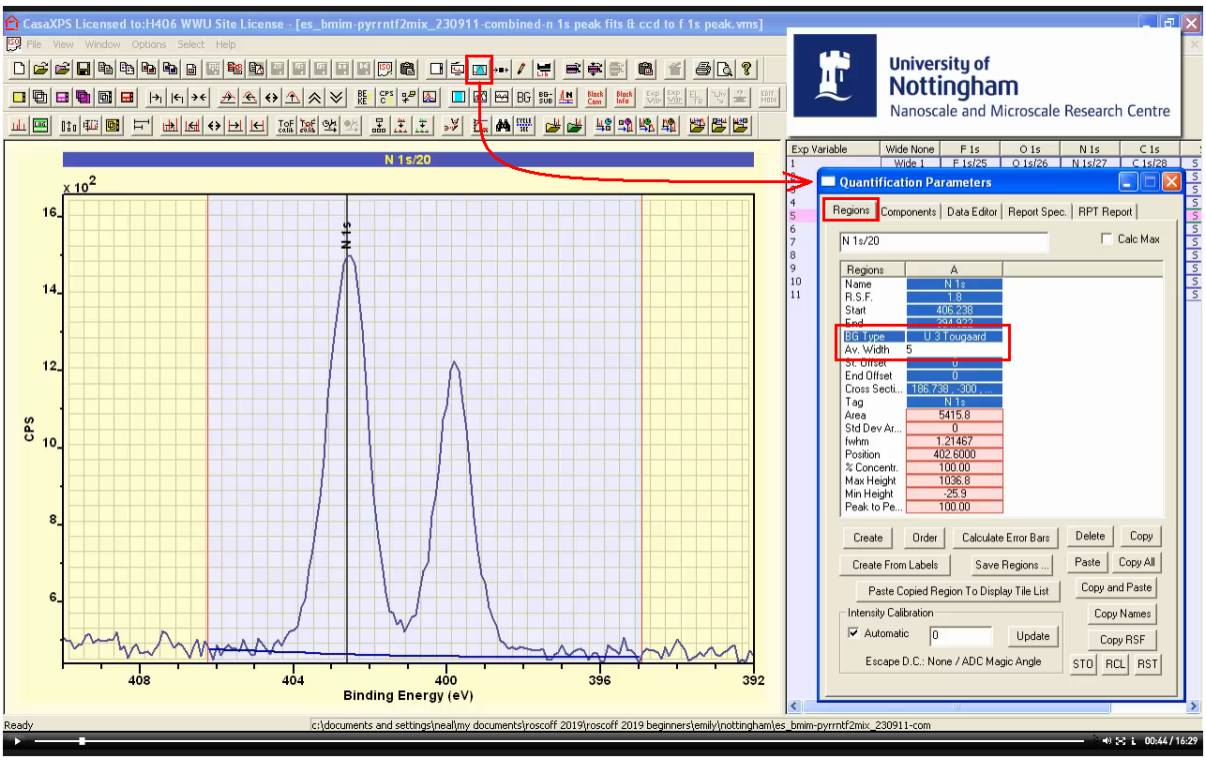


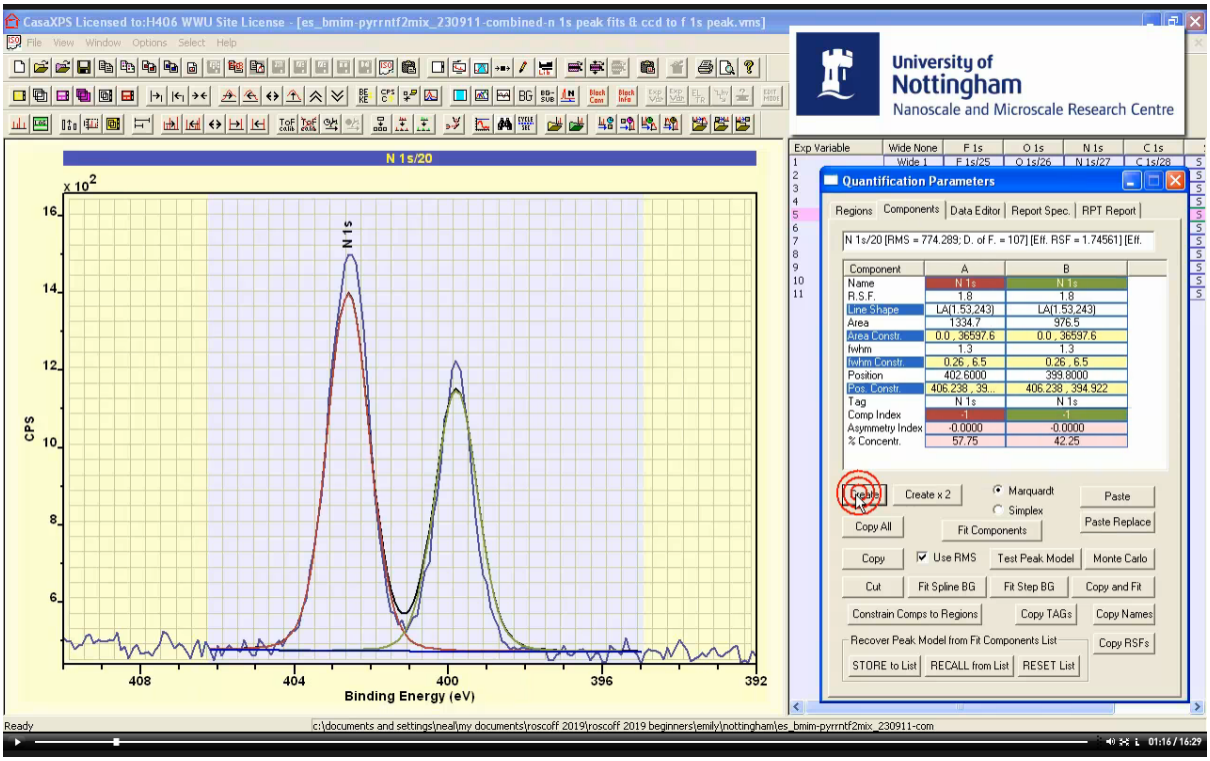
A peak model is constructed using the Quantification Parameters dialog window. The Regions property page is used to define a background required to remove the influence of inelastic scattering and other energy loss processes not attributed to photoemission from N 1s electrons.



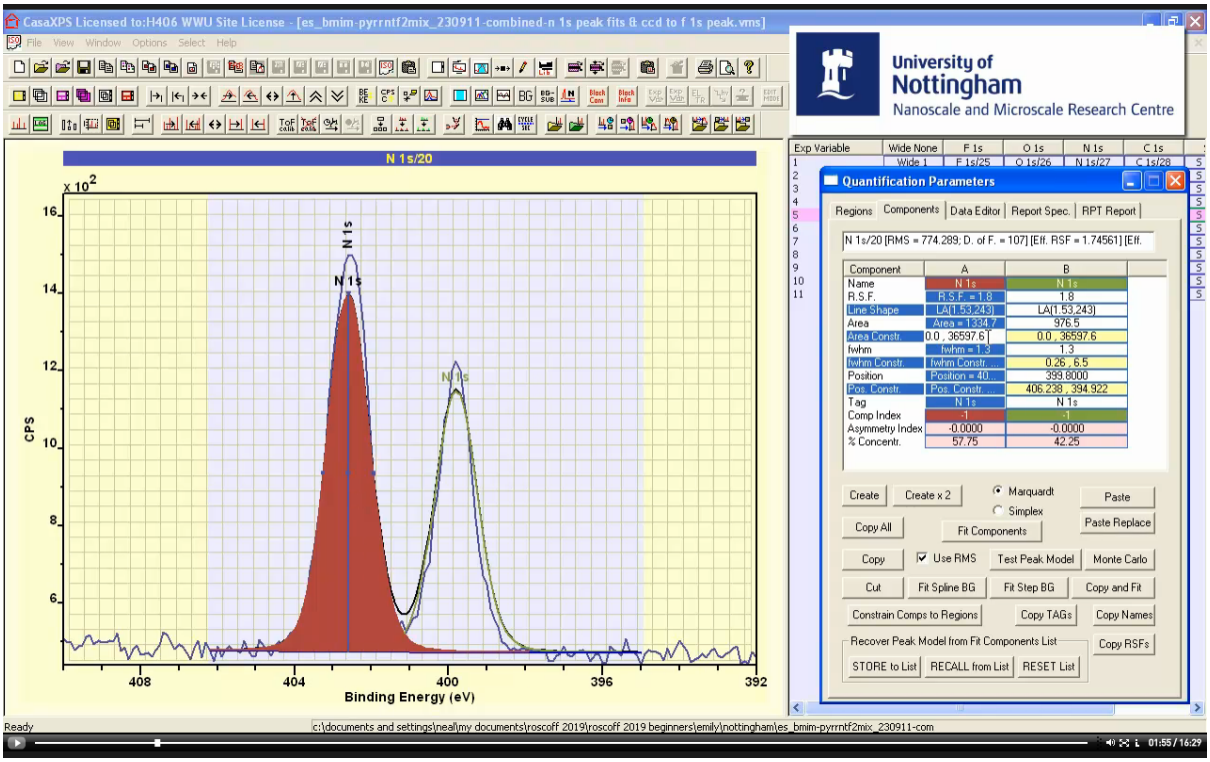
The basic forms for backgrounds include linear, Shirley and Tougaard Universal Cross-section. Many other background approximations are available, but for these data where the background is flat beneath these N 1s photoemission peaks the selection of background type is not as important because all three basic background types turn out similarly flat.



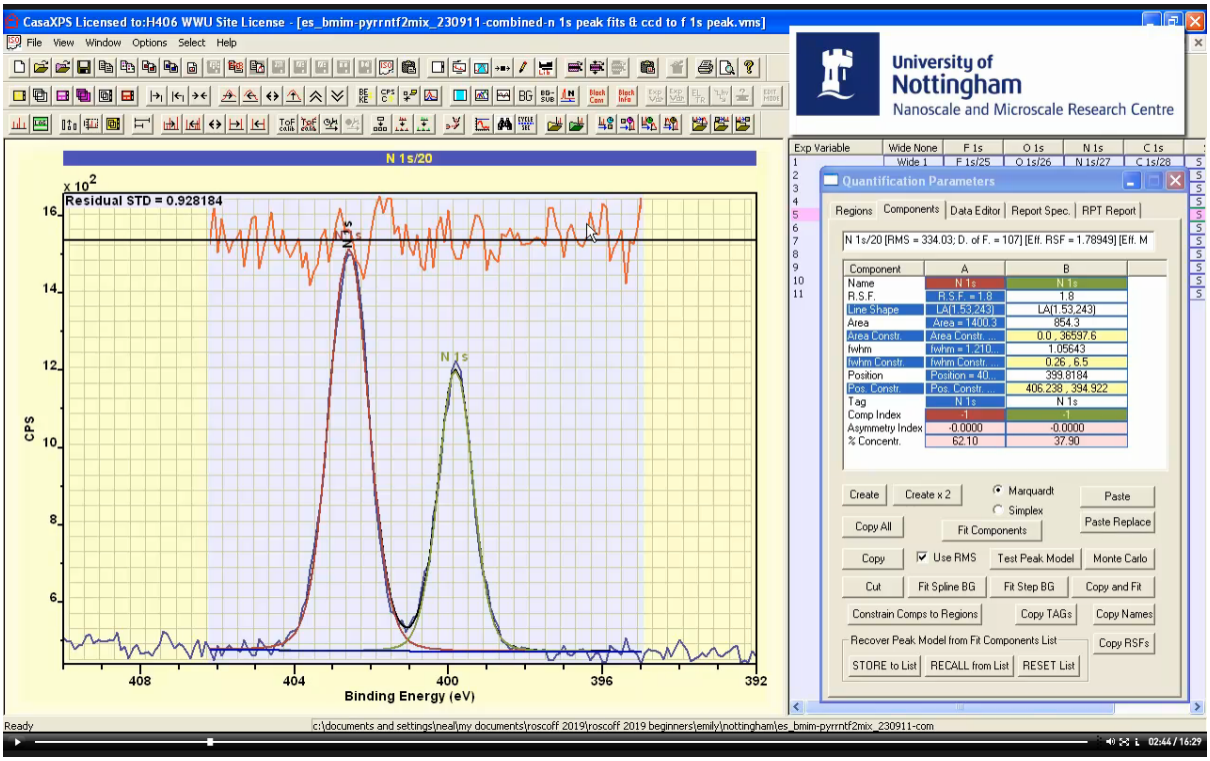




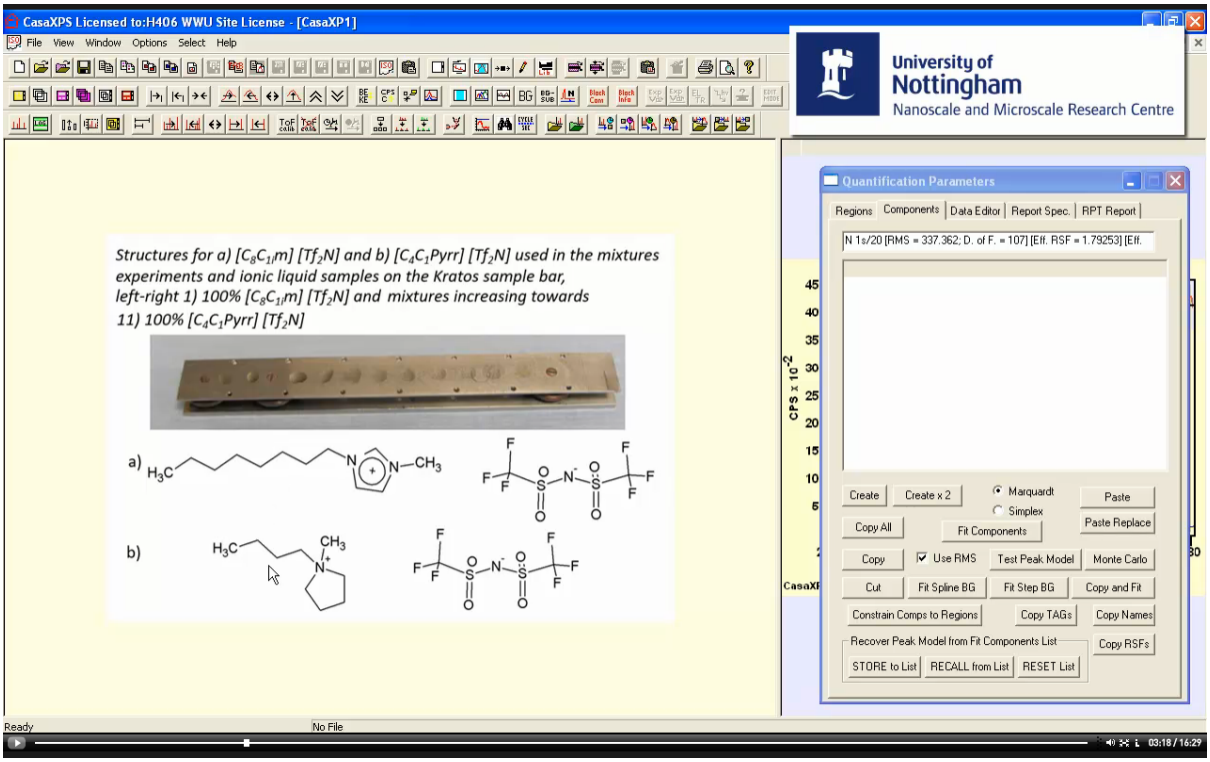
Component peaks are added to a peak model by pressing the Create button on the Components property page. Each new component is added to the list of components as a column of parameters. At the top of each column of component parameters is an alphabetic label. These labels are used to specify constraints between components. Component constraints are illustrated during the video.



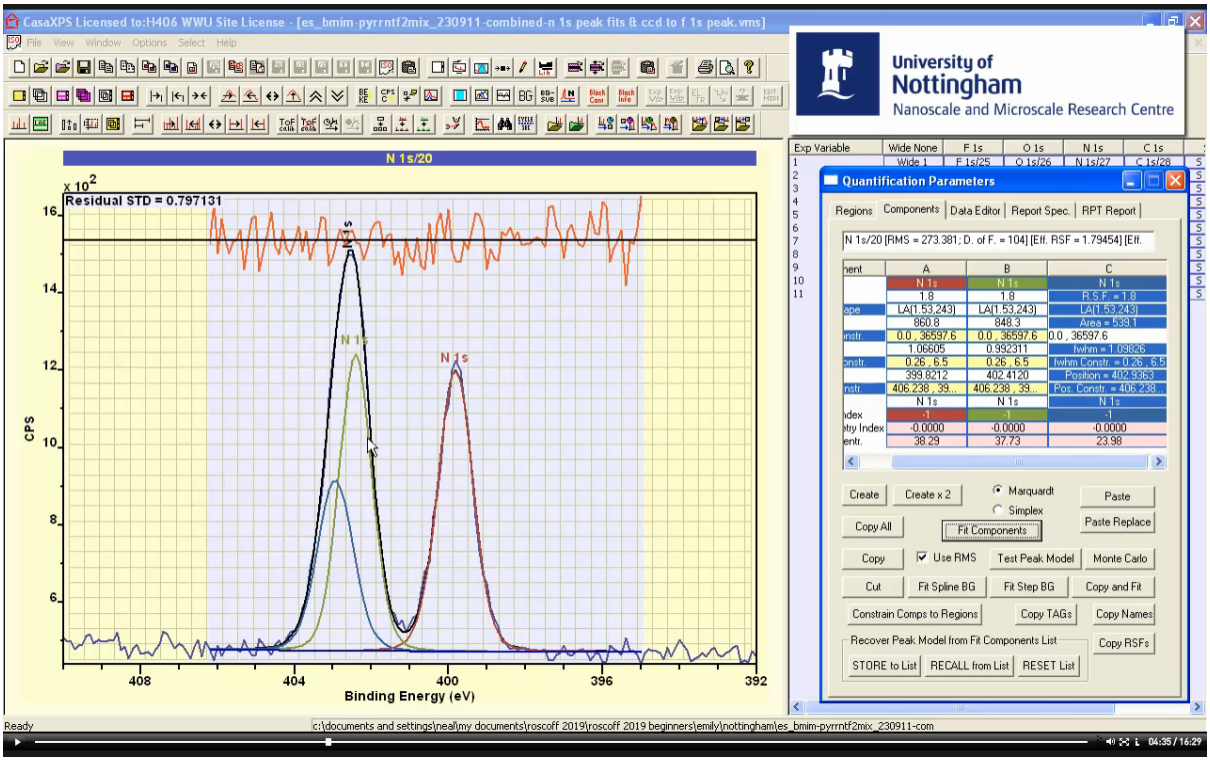
Component peaks are fitted to data by adjusting fitting parameters (Area, FWHM and Position) within intervals for these parameters defined in the corresponding constraints text-field.



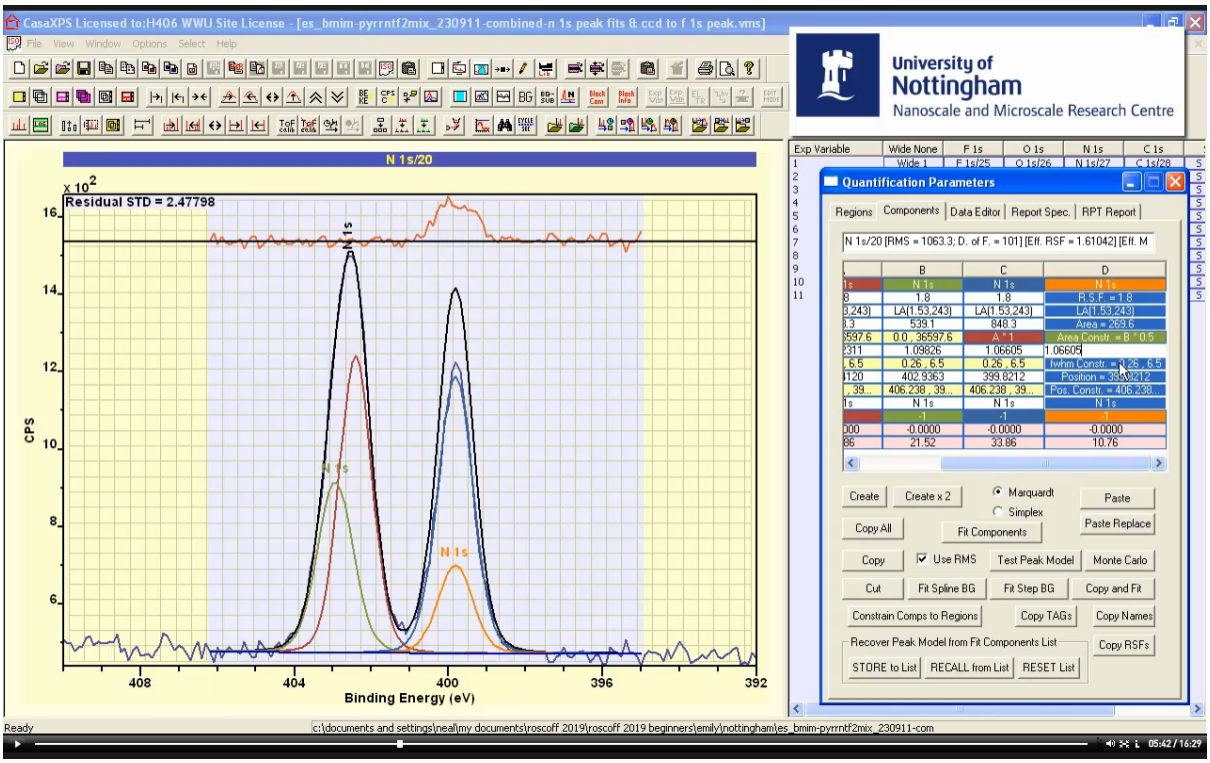
Component peaks are fitted to data in the active display tile by pressing the Fit Components button on the Components property page. Fitting of components to data is also performed by giving focus to the display tile with the use of a left-mouse click within the display tile and then holding down the Control keyboard key before pressing the G key (Ctrl+G).



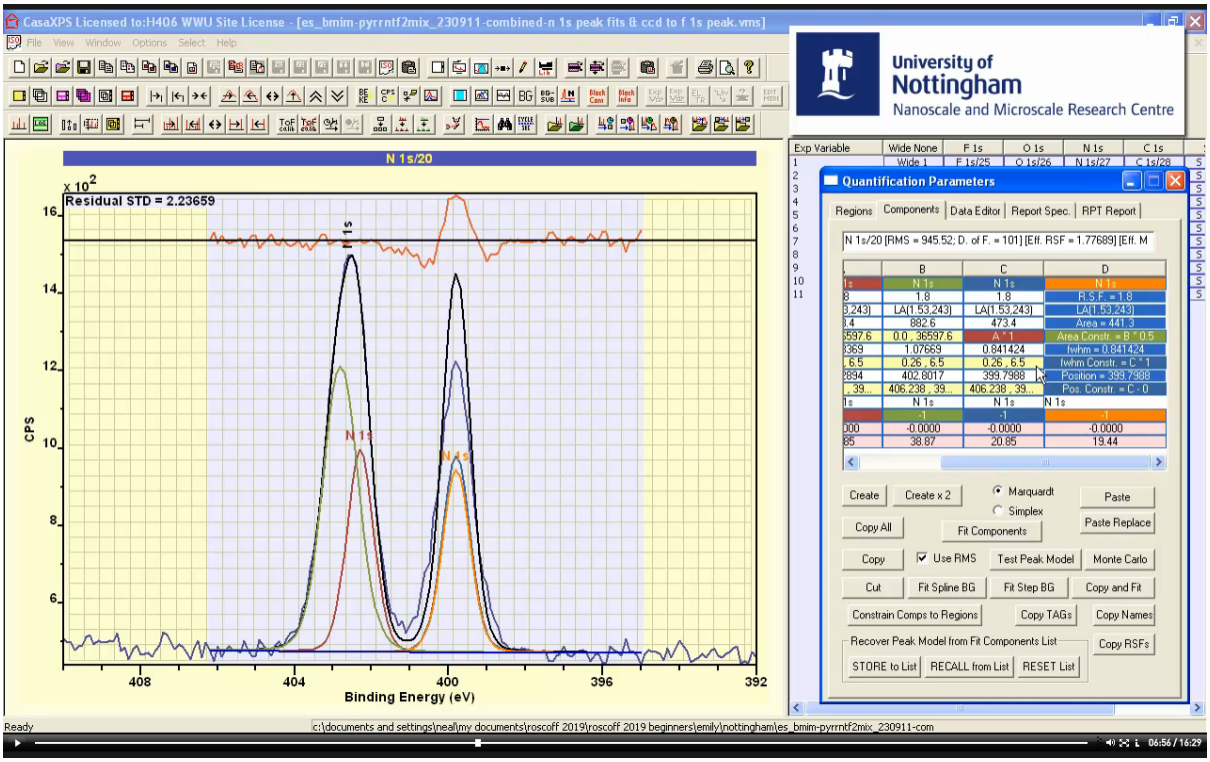
Given that these samples are prepared by mixing two ionic liquids with a common negative ion but different positive ions the number and relative intensities for component peaks should differ from the two peaks currently used to reproduce data from a mixture spectrum.



Adding more component peaks allows constraints to reflect the expected stoichiometry for these ionic liquid samples.



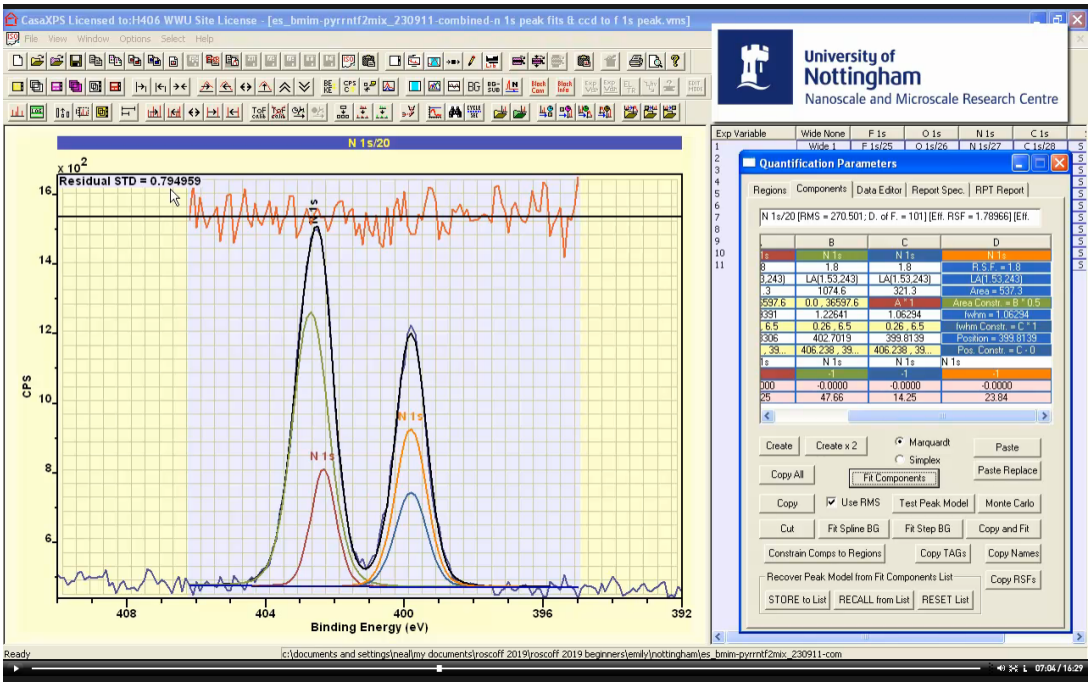
It is expected that two peaks are required for the positive ion contribution to N 1s spectra. It might also be possible to consider signal deriving from negative ions is accounted for by making use of two components provided these two components are linked in FWHM and Position to be identical for both components. Two perfectly correlated peaks would be of little value unless area constraints are also used to force a relationship between negative and positive ions.



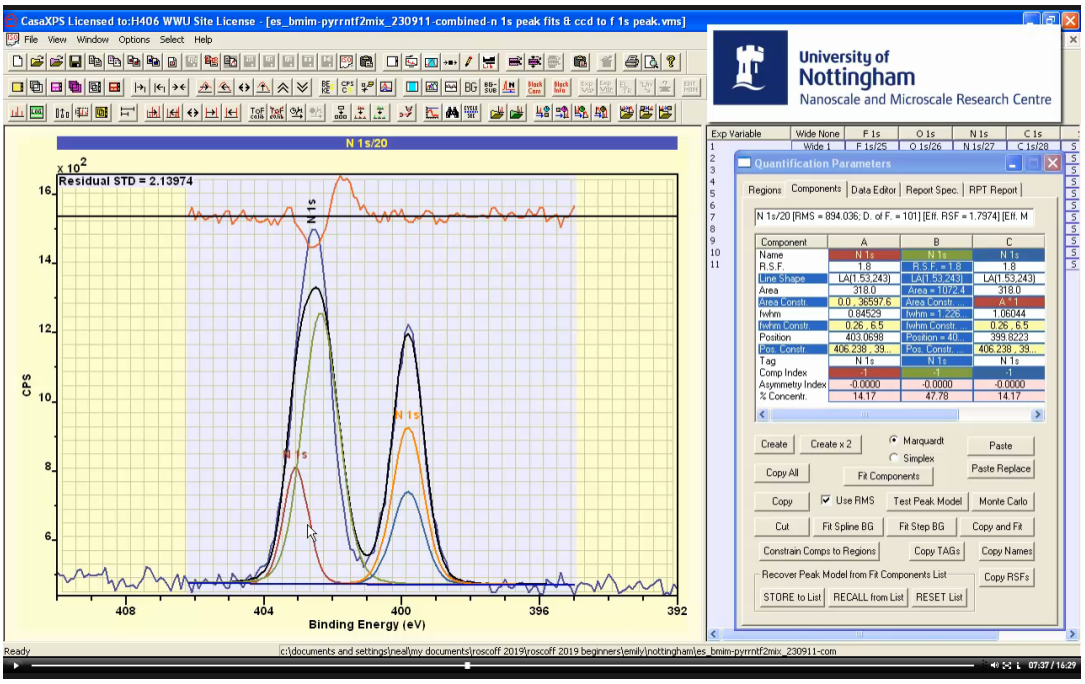
The negative ion N 1s peaks in Column C and Column D are constrained to have identical FWHM and Position by entering into the FWHM constraint field within Column D the string “C * 1” and in the Position constraint field “C + 0”. These two peaks represent all photoemission from negative ions but allowing two area parameters for the same signal permits intensity from two different positive ions to scale the area for these negative ion peaks to be consistent with the two pure forms for the ionic liquids from which these mixtures were formed. While the use of two component peaks for negative ion signal would appear to increase the number of fitting parameters, introducing Area constraints of the form “A*1” and “B*0.5” together with constraining the FWHM and Position parameters reduces the freedom from potentially six fitting parameters for negative ion signal down to two fitting parameters for the combined FWHM and Position for negative ion signal.

Component	A	B	C	D
Name	N 1s IL1	N 1s IL2	N 1s IL1	N 1s IL2
R.S.F.	1.8	1.8	1.8	1.8
Line Shape	LA(1.53,243)	LA(1.53,243)	LA(1.53,243)	LA(1.53,243)
Area	345.3	1040.0	345.3	520.0
Area Constr.	0.0 , 36597.6	0.0 , 36597.6	A * 1	B * 0.5
fwhm	1.08556	1.05761	1.07236	1.07236
fwhm Constr.	0.26 , 6.5	0.26 , 6.5	0.26 , 6.5	C * 1
Position	403.0141	402.4732	399.8226	399.8226
Pos. Constr.	406.238 , 394.922	406.238 , 394.922	406.238 , 394.922	C - 0
Tag	N 1s	N 1s	N 1s	N 1s
Comp Index	-1	-1	-1	-1
Asymmetry Index	-0.0000	-0.0000	-0.0000	-0.0000
% Concentr.	15.34	46.21	15.34	23.11

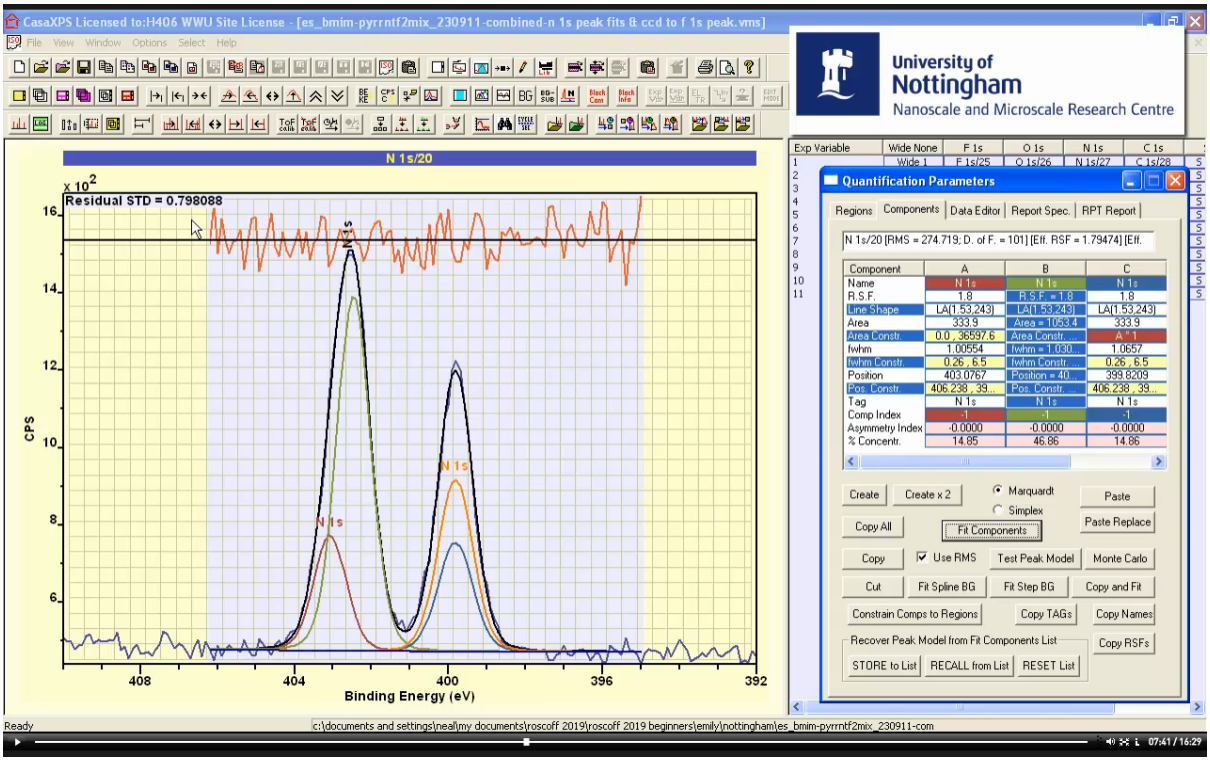
These constraints are introduced based on sample knowledge. Introducing these constraints represents user bias as we assume these ionic liquids once mixed can be considered as unaltered from the ionic composition for the two pure forms of these liquids.



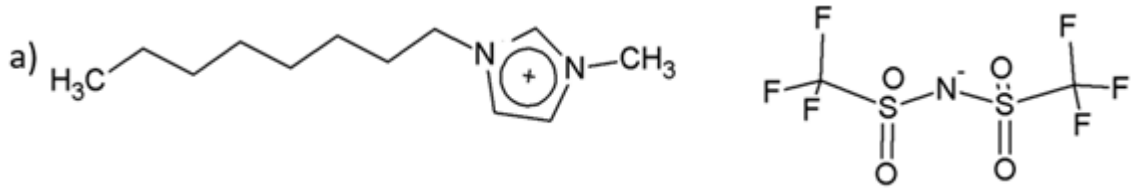
Parameter constraints thus far link negative ion intensity with corresponding positive ion intensity is accordance with the expected relationship for the two pure forms of ionic liquids mixed to create the sample from which these N 1s data are acquired. The two negative ion components are linked via a Position constraint, but to this point the pair of positive ion components may adjust independently of each other in terms of Position and FWHM parameters. Two highly correlated components with freedom to move in binding energy and component width should be a cause for concern.



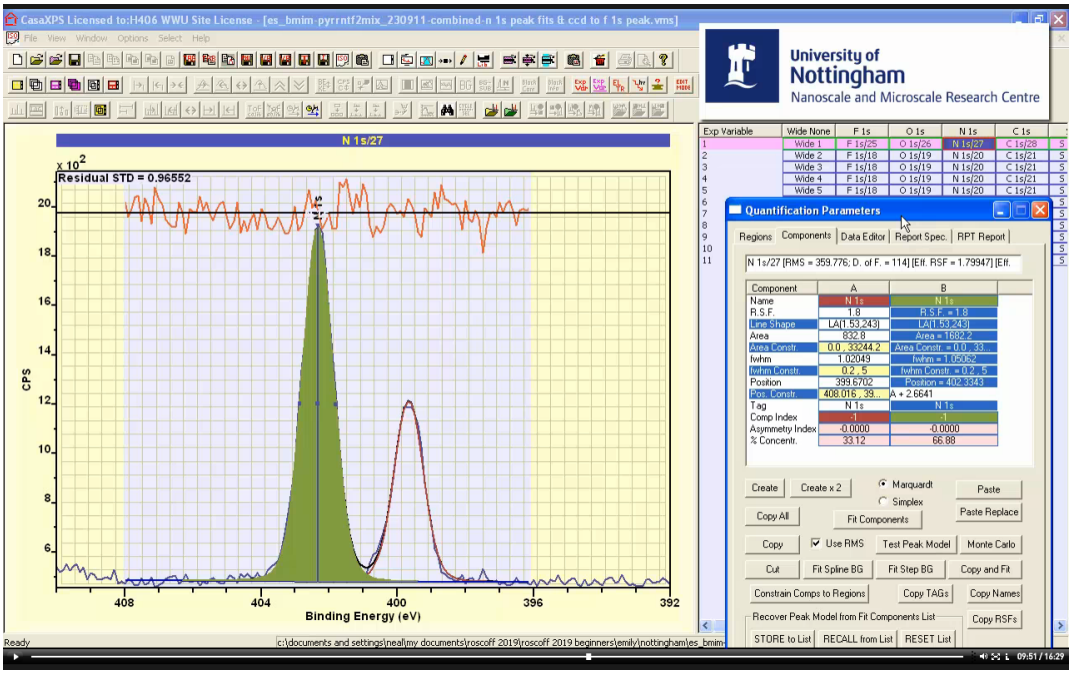
Adjusting the starting conditions for the peak model from the previous optimisation sequence allows us to test if a simple adjustment can produce a fit for these peaks to data with similar quality of fit but for which physically significant information changes to the point of negating the conclusion drawn from the previous fit to the same data.



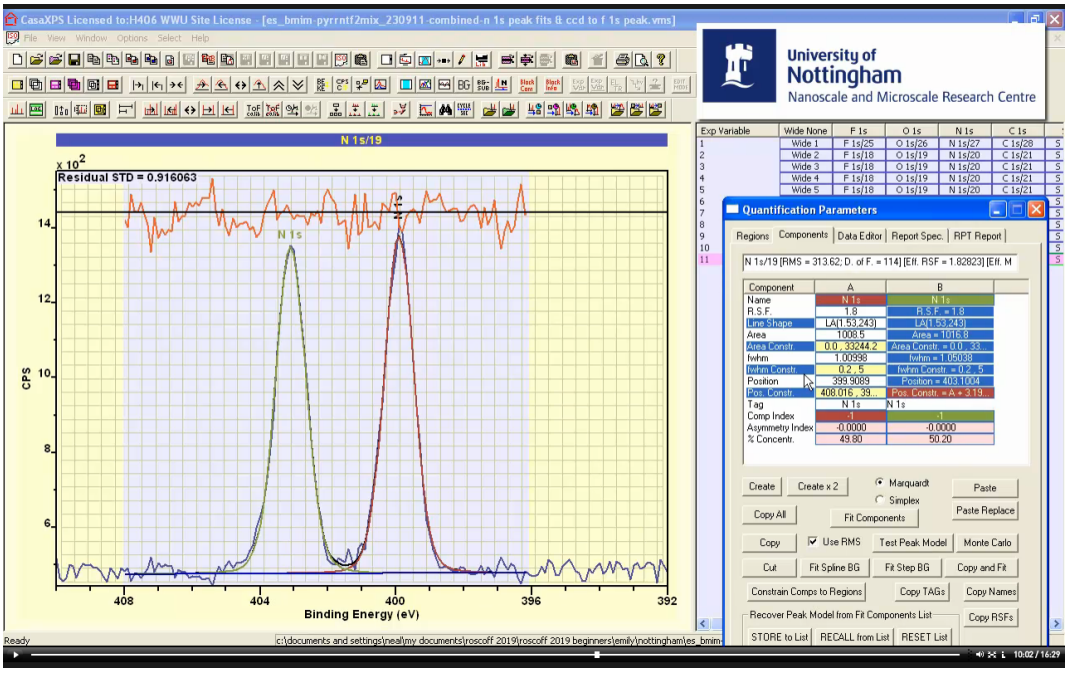
On fitting these same peaks using a different starting position for these two components representative of positive ion signal yields a similar quality of fit as measured by the residual standard deviation, but importantly for the analysis so far, the binding energy for these component peaks is reversed without altering the relative intensity of these components. Two different starting conditions for optimisation produce similar residual standard deviation but the outcome in terms of binding energy is very different. Such a test indicates the peak model, meaning number of peaks and constraints linking fitting parameters, is not capable of separating signal from positive ions for this particular mixture of ionic liquids.



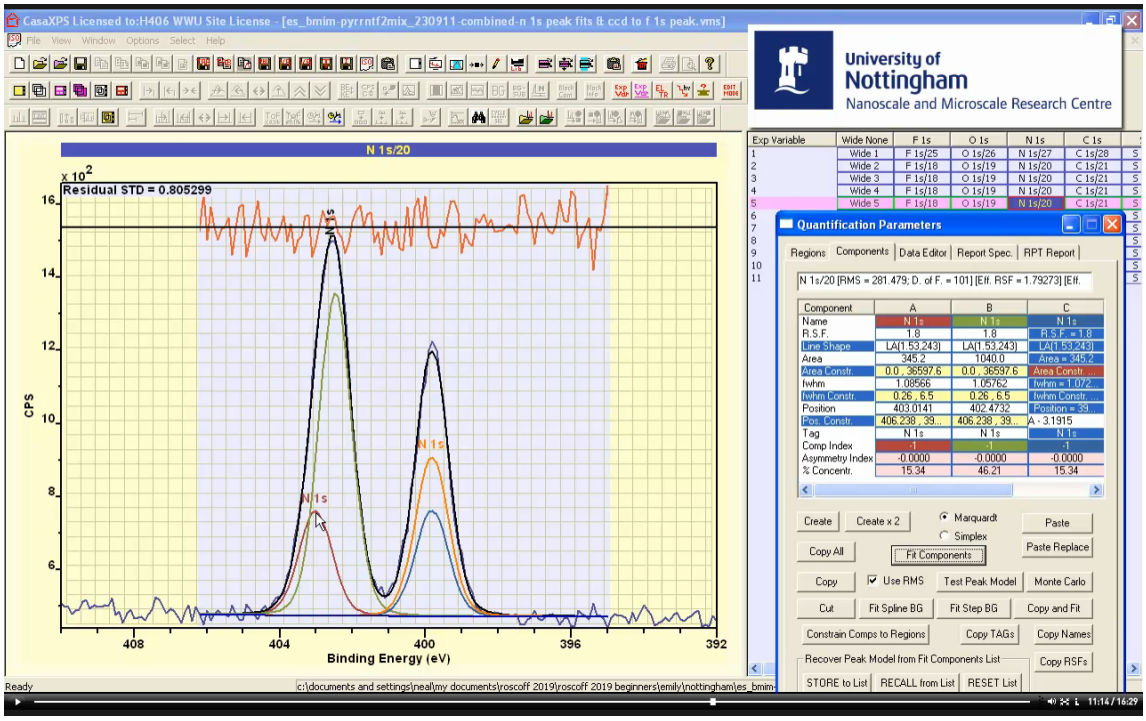
The objective for these data is to measure the relative proportions for positive ions within mixtures formed from the two pure ionic liquids. Currently the peak model would not be suitable for this purpose therefore additional constraints are required. Since data are collected from the pure forms for these two ionic liquids, and in both cases N 1s spectra exhibit well resolved peaks corresponding to positive and negative ions, it is therefore possible to support our assumptions about relative intensities for N 1s component peaks and, more importantly for this analysis, binding energy relationships can be assessed and computed.



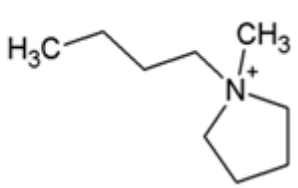
Adding two component peaks to an N 1s spectrum then fitting these components to these data facilitates the calculation for the offset between components. A binding energy offset between two component peaks is introduced using the Position Constraint field for a component by entering the heading label for a second component followed by an offset value in the form “A+2”, meaning set the position for the component in Column B by adding 2 eV to the position of the component in Column A. If the label for a component header is simply entered into a different component constraint and the Enter keyboard key pressed, then the constraint is updated by computing the relative offset between these components. To compute the offset between these two N 1s components the Position Constraint in Column B is entered as A. On pressing the Enter key the Position Constraint is updated with the string “A+2.6641”, thus indicating the binding energy offset is 2.6641 eV.

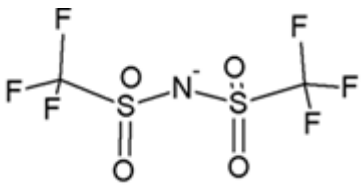


Creating a two component peak model and repeating the same offset calculation for the second pure ionic liquid results in an offset in binding energy of 3.1915 eV between two peaks of equal intensity. Armed with the binding energy offset for two peaks of equal area applying the same offset to equivalent peaks in the peak model for the mixture removes the binding energy issue with the ionic liquid peak model.



b)

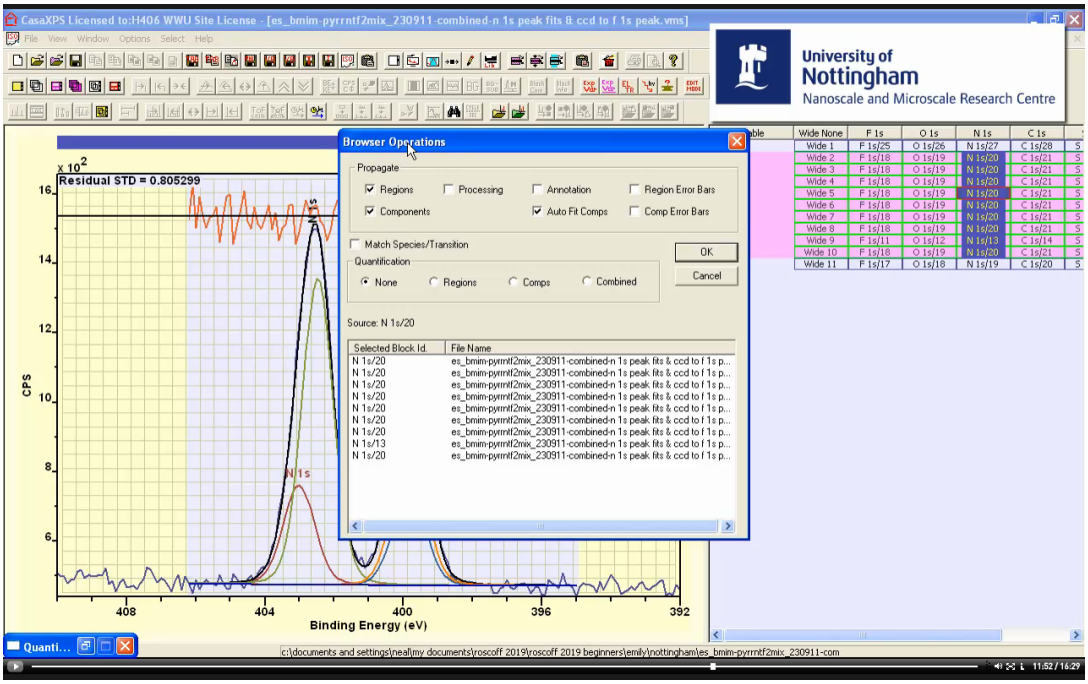




Regions | Components | Data Editor | Report Spec. | RPT Report

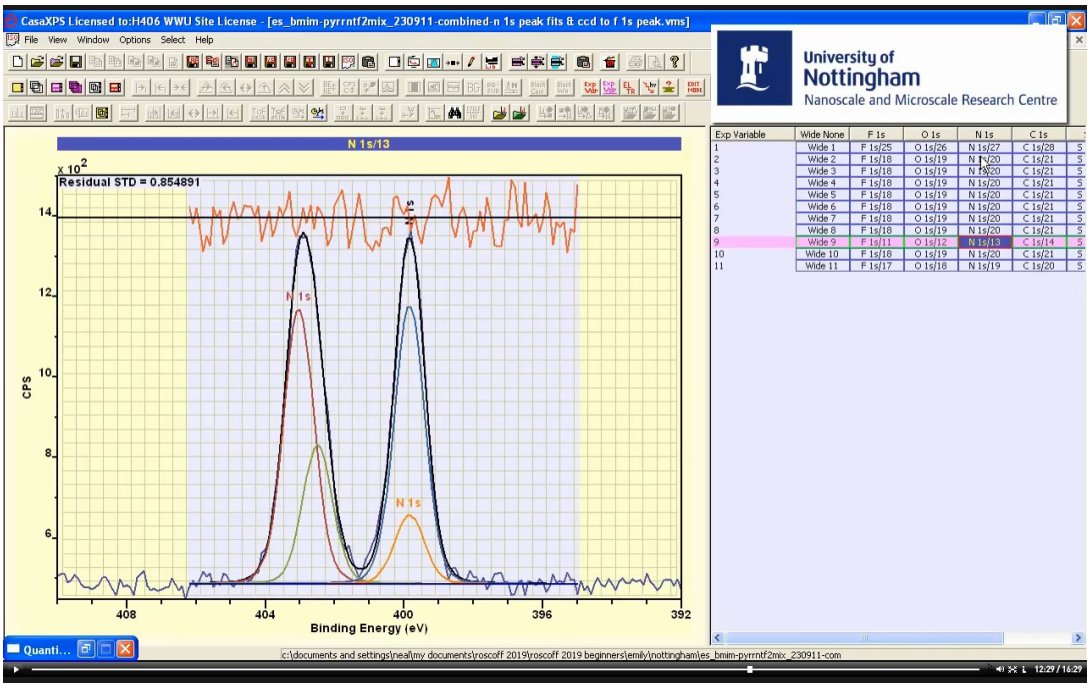
N 1s/20 [RMS = 270.49; D. of F. = 101] [Eff. RSF = 1.79244] [Eff. M

Component	A	B	C	D
Name	N 1s IL1	N 1s IL2	N 1s IL1	N 1s IL2
R.S.F.	1.8	1.8	1.8	1.8
Line Shape	LA(1.53,243)	LA(1.53,243)	LA(1.53,243)	LA(1.53,243)
Area	225.3	1315.7	225.3	657.9
Area Constr.	0.0 , 36597.6	0.0 , 36597.6	A * 1	B * 0.5
fwhm	0.953352	1.00899	1.03903	1.03903
fwhm Constr.	0.26 , 6.5	0.26 , 6.5	0.26 , 6.5	C * 1
Position	402.9048	402.3264	399.7133	399.7133
Pos. Constr.	406.238 , 394.922	406.238 , 394.922	A - 3.1915	A - 3.1915
Tag	N 1s	N 1s	N 1s	N 1s
Comp Index	-1	-1	-1	-1
Asymmetry Index	-0.0000	-0.0000	-0.0000	-0.0000
% Concentr.	9.29	54.27	9.30	27.14

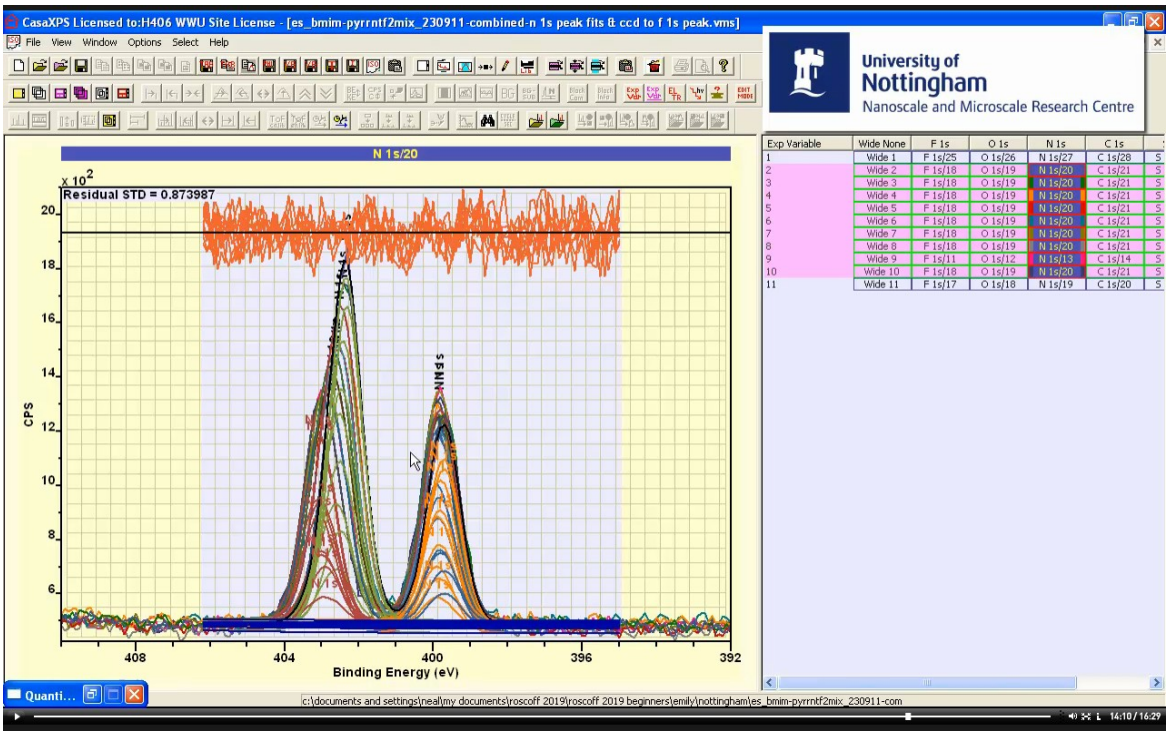


Confidence in a peak model is enhanced by testing the model using spectra with similar peak structure by fitting the peak model to all such data. In this example, N 1s spectra were measured from a range of nine samples formed by mixing different proportions of two ionic liquids. If it is assumed no chemical changes occur within these mixtures, the model as constructed based on this assumption should fit all data with similar data reproduction that has been obtained so far.

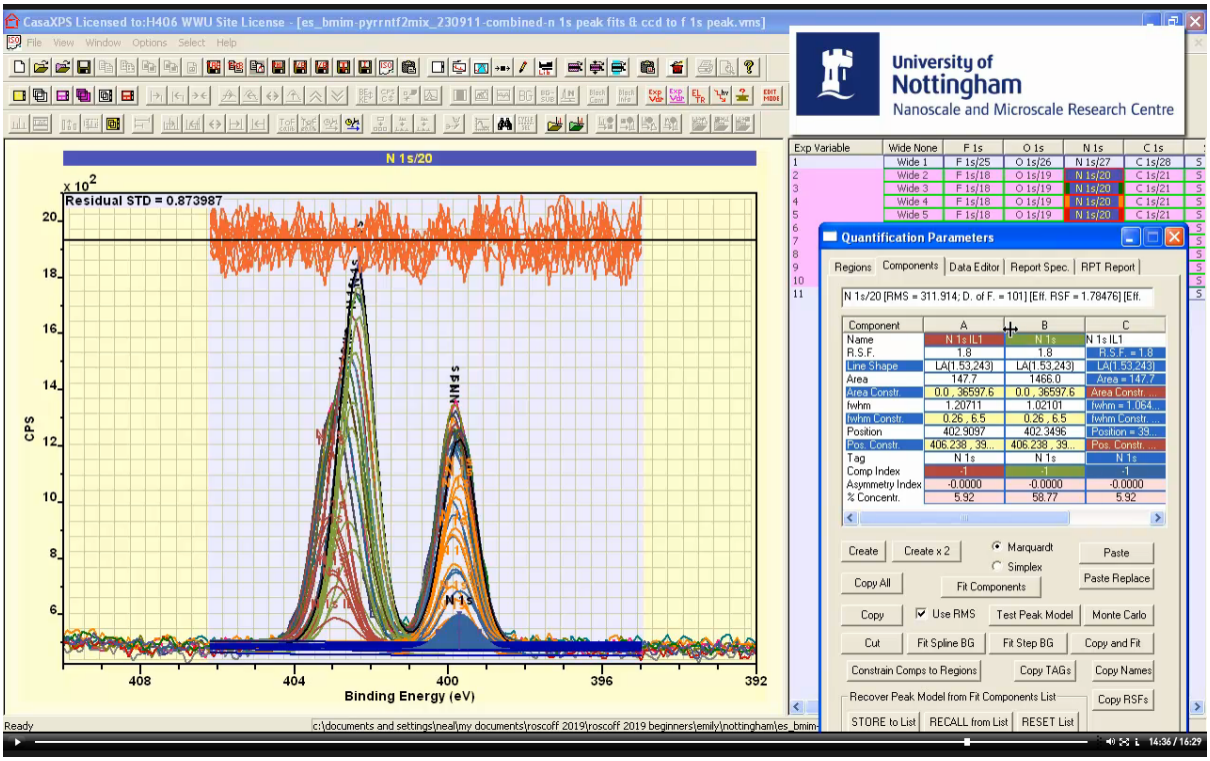
Selecting the set of VAMAS blocks in the right hand pane corresponding to mixtures of ionic liquids before placing the cursor over the active display tile containing the current peak model then pressing the right hand mouse button invokes the Browser Operations dialog window. Selecting the Regions, Components and AutoFit tick-boxes then pressing the OK button propagates the peak model from the active VAMAS block to the set of selected VAMAS blocks.



Visual inspection indicates data reproduction is comparable to the original data used to construct the peak model.

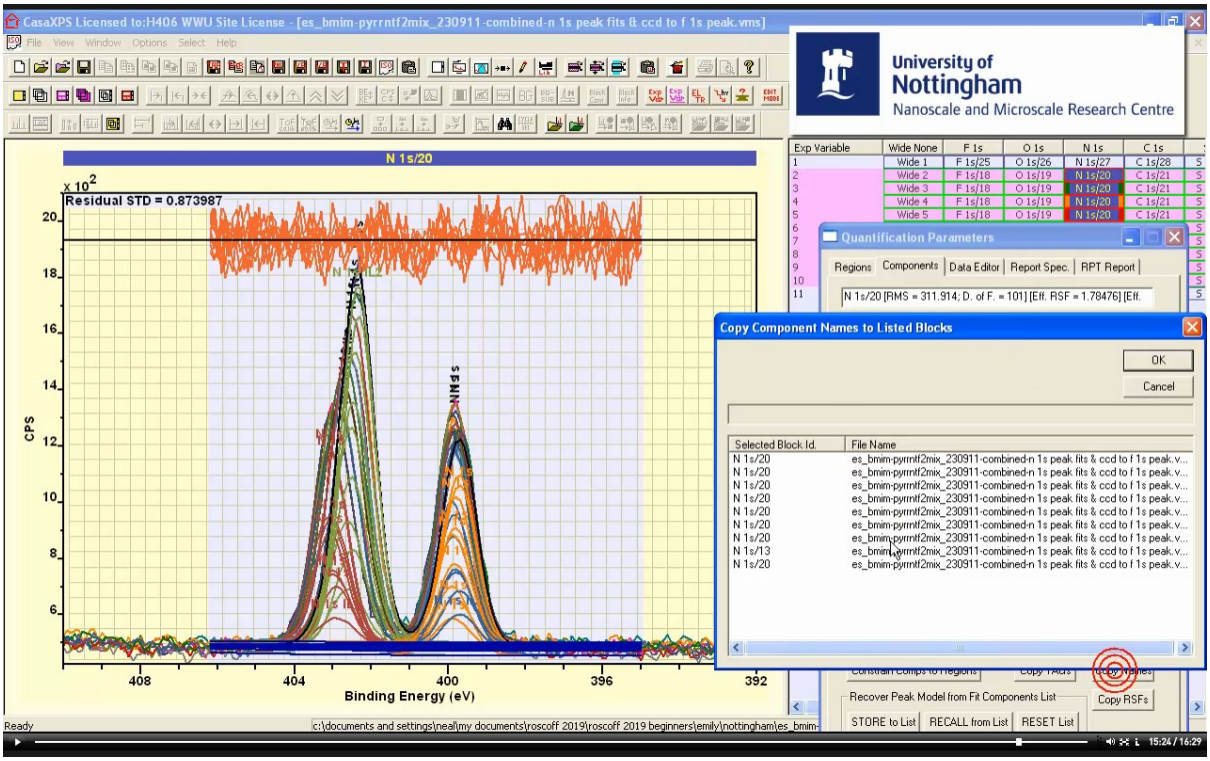


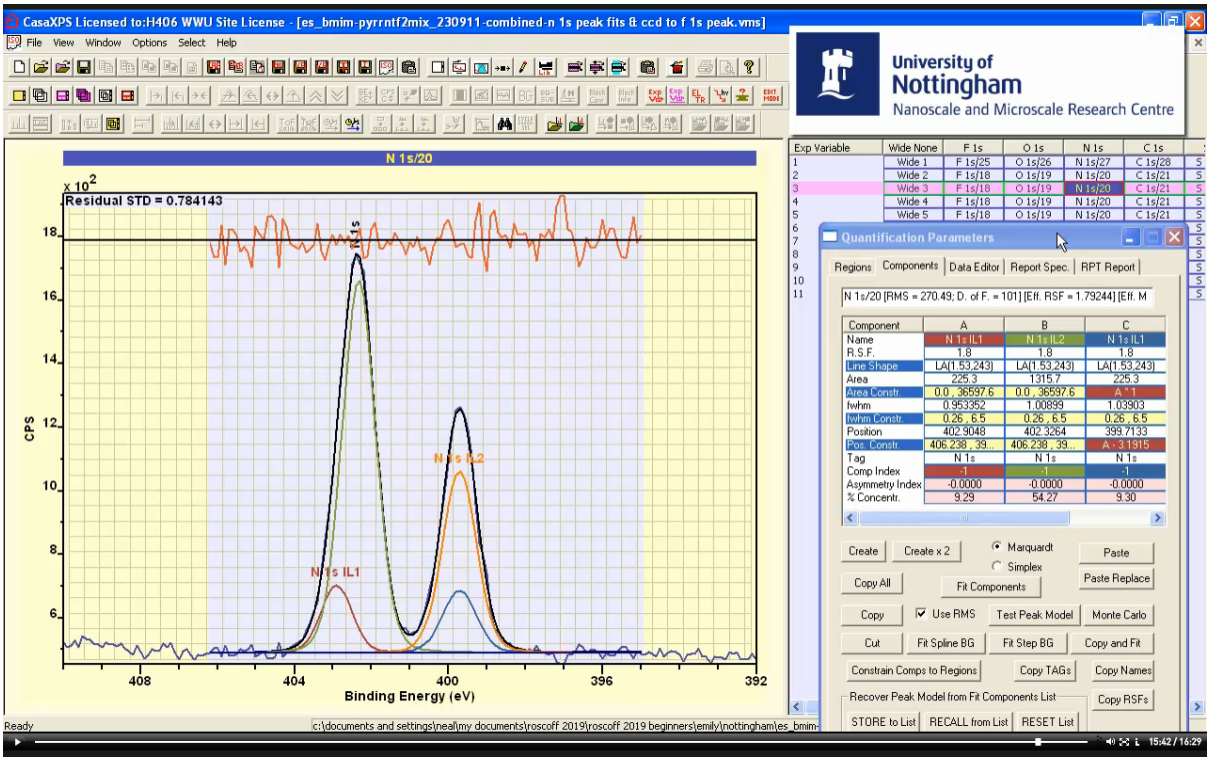
These N 1s spectra measured from different proportions of two ionic liquids exhibit different charge state resulting in shifts in binding energy for different measurements. The peak model prepared for one spectrum was propagated to all spectra without performing any charge correction processing step. The act of fitting this peak model to these data necessarily required the flexibility to shift the model in binding energy as well as adjust relative intensities of component peaks depending on spectrum. These types of adjustments in fitting parameters are the reasons non-linear least squares optimisation is required. Given the target of measuring proportions of ionic liquid mixtures, parameter constraints were necessary for this particular peak model where these constraints were added in turn to limit the flexibility of the model when fitted to data and these development steps demonstrated the need for such constraints for this application. Non-linear least square fitting of components to data is sometimes replaced by linear least squares fitting of standard spectra to unknown data. Linear least square fitting of these two pure ionic liquid spectra would require charge referencing to align all N 1s data in a physically meaningful way. Once energy shifts are performed as an independent exercise from optimisation, linear least squares would be equivalent to linking all fitting parameters within the component peak model with the exception of Area parameters. Finally FWHM and Position Constraints would need to be fixed to specific values before propagating the model to all other data. At which point, non-linear optimisation and linear optimisation are logically performing the identical calculation. Thus in using non-linear optimisation fitting of components to data with the least number of constraints permits a degree of flexibility that at times is required to allow for acquisition differences in spectra.



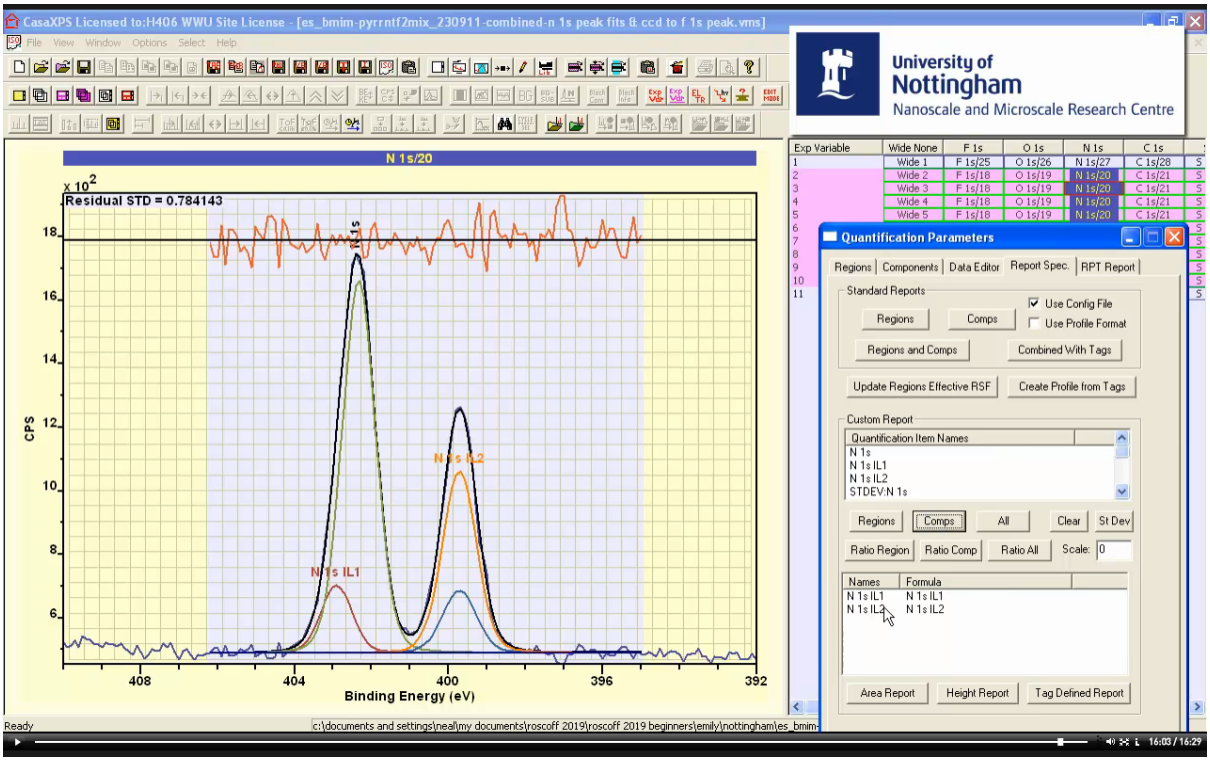
Once these spectra are fitted using the current peak model the next step might be to profile these samples in terms of component areas determined by the peak model for each of the standard ionic liquids used in the preparation of these mixtures. The Report Spec. property page includes a sections used to define Custom Reports for combining intensities from regions and components defined on VAMAS blocks selected in the right hand pane. The Custom Report allows the profiling of signal gathered from different components representative of the same material. Any component or region with the same name will have intensity summed to form the composition reported by the Custom Report section. Thus to make use of the Custom Report to calculate the proportions for these two ionic liquids in the mixtures, components representative of an ionic liquids must be assigned a unique name. Component name fields are therefore adjusted to “N 1s IL1” for one ionic liquid and “N 1s IL2” for the other. Note the region name is “N 1s” so it is important to make these component names different from that of the region name, otherwise component and region intensity will be summed incorrectly. A warning message is issued in the event a Custom Report is prepared with regions and components with identical names.

Changing name fields on the Components property page only adjusts names for components on the active VAMAS block displayed in the active tile. All component names for the models fitted to each of the mixture N 1s spectra must be updated too. Once the name field are updated with N 1s IL1 and N 1s IL2 on the active VAMAS block the alternative to propagating and fitting afresh is to use the Copy Names button on the Components property page. Component names are transferred to VAMAS blocks selected in the right hand pane for any peak model matching the number of components defined on the active VAMAS block. Copying names does not incur the cost of refitting components to data.

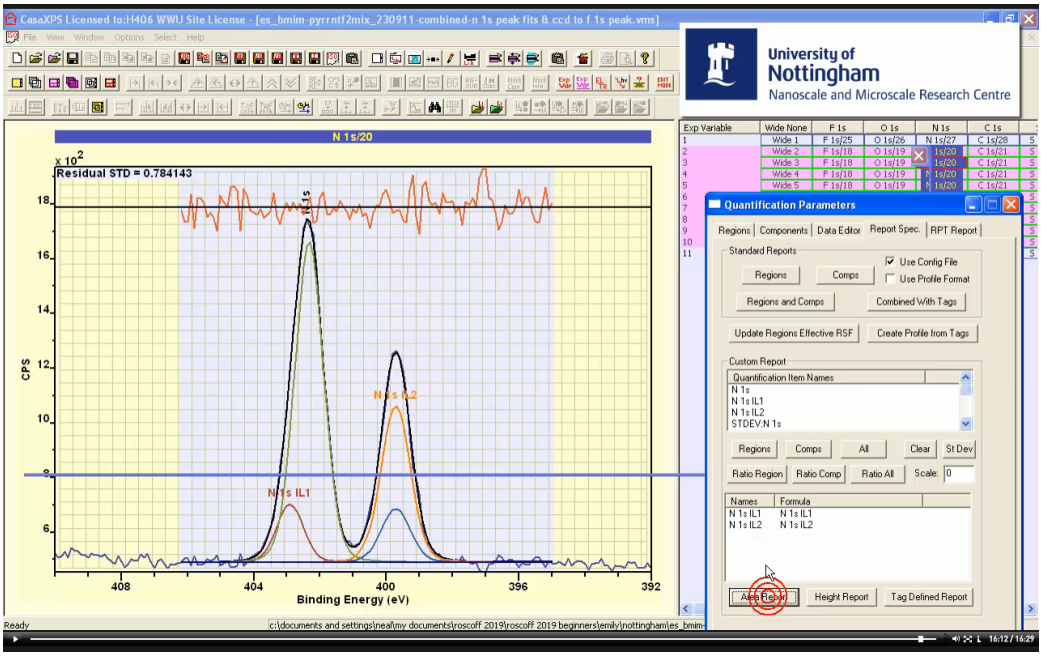




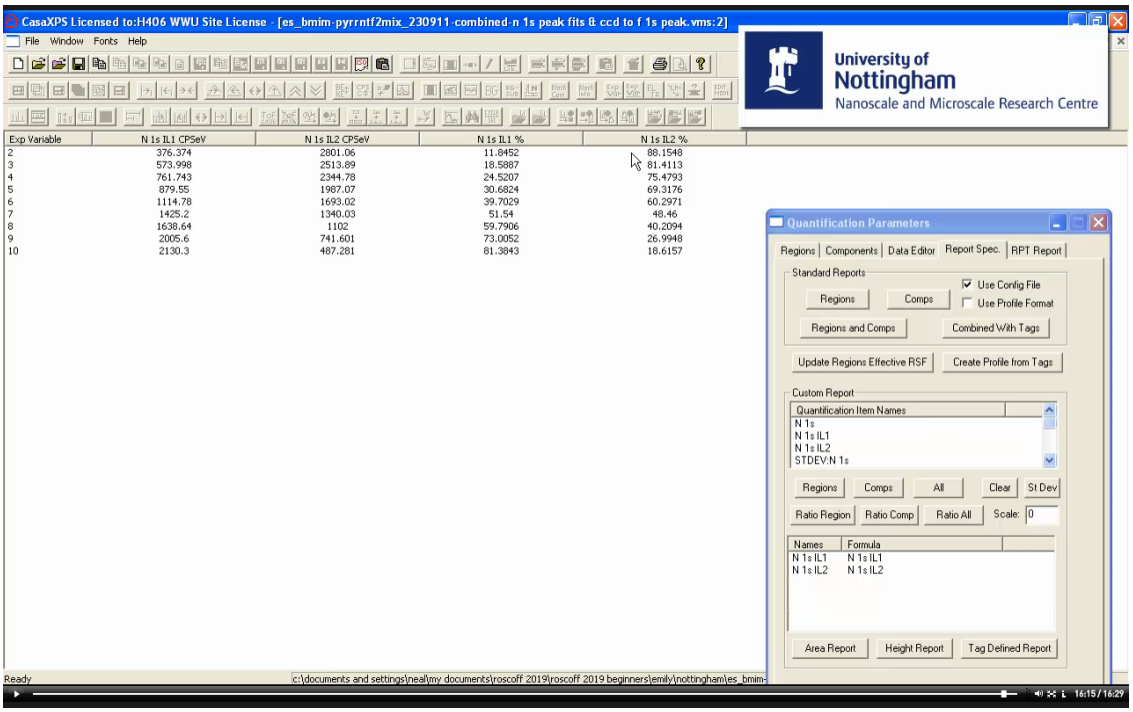
After names are copied using the Copy Names button, stepping through the VAMAS blocks previously selected before pressing the Copy Names button verifies names are appropriate for use with the Custom Report.



Quantification Parameters dialog window, Report Spec property page makes use of VAMAS blocks selected in the right hand pane. The Quantification Items table is a list of names assigned to components and regions defined on the selected VAMAS blocks. The Names/Formula is a subset of these quantification items that will be used to compute a quantification table. The Names columns is a user defined string not necessarily the name of a component or region. The Formula column is an expression defined in terms of component or regions names that allows the intensity to be specified from more than one region or component, if necessary, but in this example these formulae are simply the names for components assigned to each of the ionic liquids.



A quantification table making use of the Name/Formula table applied to selected VAMAS block is created by pressing the Area Report button.



Text from the report can be copied to the clipboard as tab spaced ASCII data suitable for use in a spreadsheet program.