

Image Processing using PCA and Peak Synthesis

Modern imaging XPS instruments offer a means of collecting data both spatially and energy resolved [1]. These data sets may be viewed as a stack of images acquired from the same location on the sample over a range of energies, or alternatively the data set can be interpreted as an image, where each pixel contains an energy spectrum. Typically these data sets are large and while many images, so acquired, are lacking in features, their existence is useful in the sense these images include information about the noise in the data and are therefore valuable beyond merely defining the background to images taken at peak intensities.

One means of utilizing the full set of data is Principal Component Analysis (PCA), where the set of images are decomposed into an orthogonal set of images, from which the maximum variation in the data is partitioned into the abstract images with the largest eigenvalues. The abstract factor images without features can be attributed to noise. If the set of original images are reconstructed from only those abstract images containing significant information, the result is a new data set where the influence of noise is reduced in magnitude. Data smoothing in the spatial domain is the net result. The consequence of creating the set of images reconstructed from the principal abstract factors is the images may lose some of the sharpness at an interface; however the structure isolated in the principal components is accentuated in all the images. What is more, spectra determined from these reconstructed images are modified by the procedure without moving data between bins in the energy sense and therefore the influence of noise on each energy bin is reduced without need of averaging in the energy domain. If the data is now viewed as a set of spectra recorded at each pixel, the result is a set of spectra with counting statistics determined from the entire acquisition time used to record the image set. That is, smoothed spectra, without damage to the line-shapes. Figure 1 shows both PCA reconstructed spectra and the spectrum from the same pixel without processing.

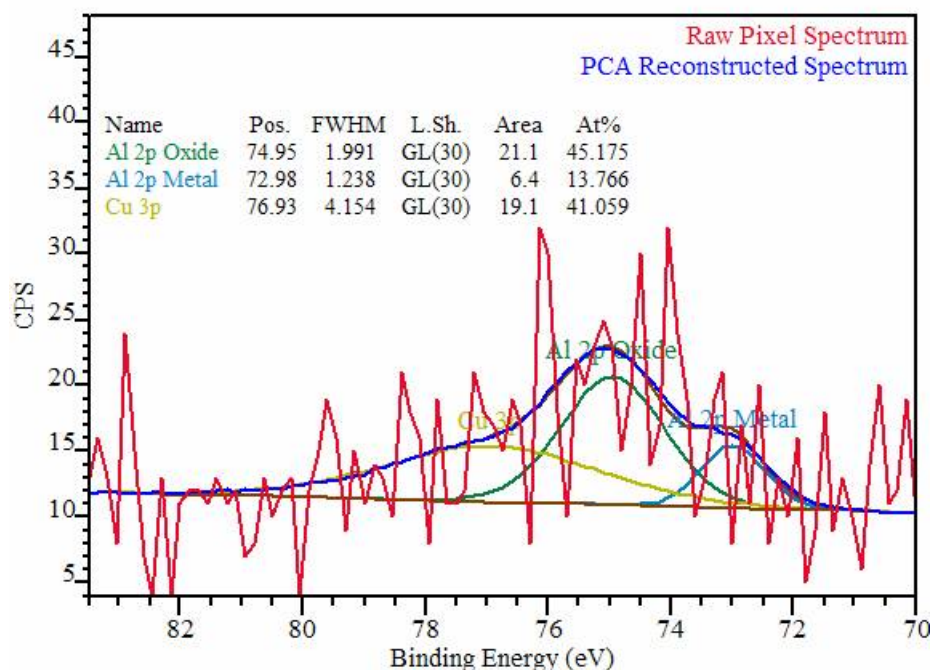


Figure 1: Spectrum at an image pixel. The PCA reconstructed spectrum is fitted with three synthetic components: Cu 3p, Al 2p Oxide and Al 2p Metal

The result of processing the entire image set into spectra following a PCA reconstruction is remarkable and at first hard to believe. The spectra seen in Figure 1 show both the poor signal to noise in the original raw data and the *smoothed* data following the PCA and subsequent projection onto the significant abstract factors in

the spatial domain. The PCA processed spectrum clearly shows the shapes of three underlying peaks, namely, Cu 3p, Al 2p Oxide and Al 2p Metal. Fitting the peaks using synthetic lineshapes allows the intensities attributed to these three state to be partitioned into separate images (Figure 2), which when overlaid supports the spectral information in each pixel by reproducing images consistent with the expected result seen in Figure 2.

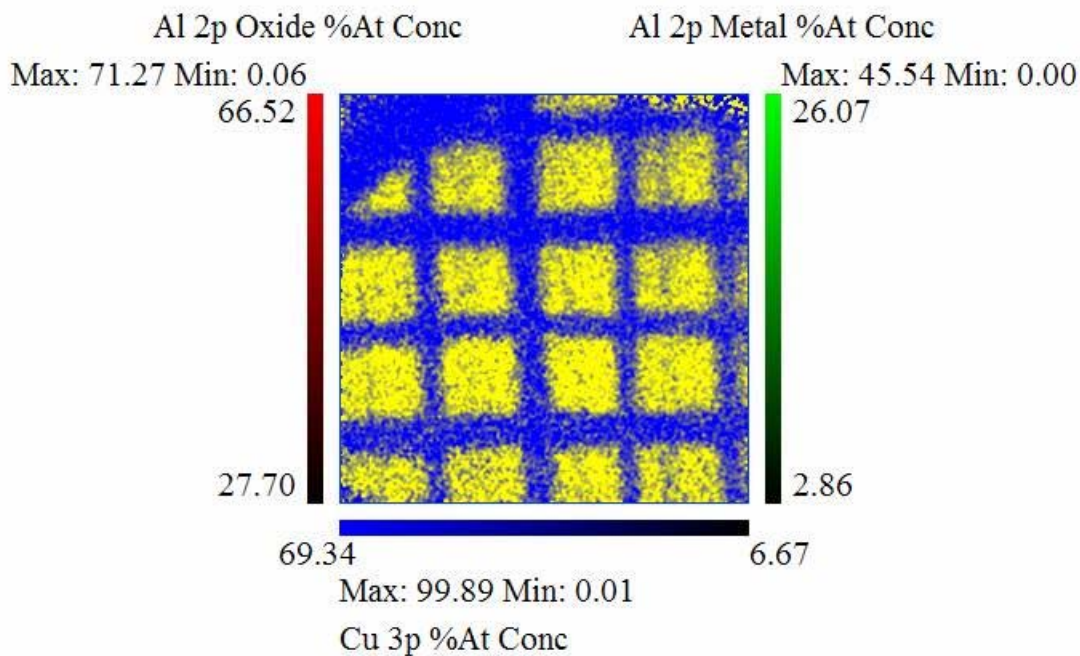
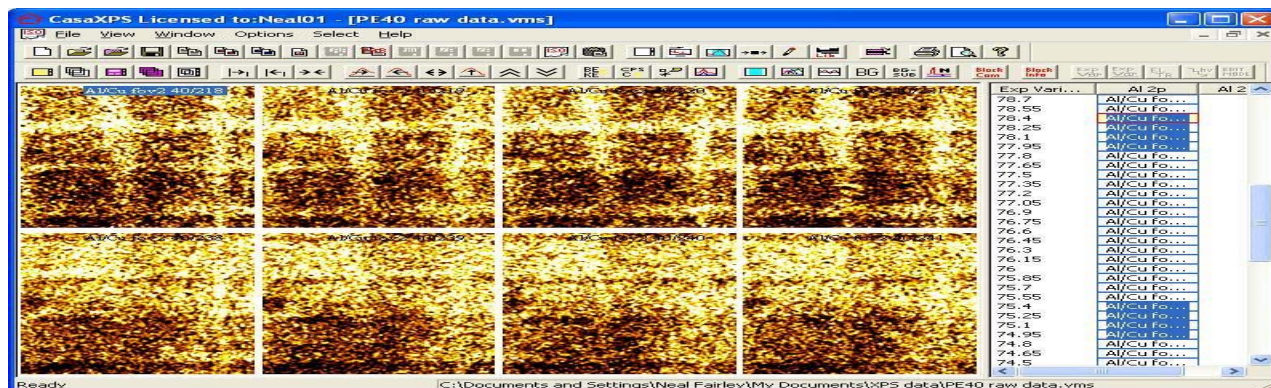


Figure 2: Cu grid on Al foil after peak-fitting spectra at each pixel using the model shown in Figure 1. Note the two Al 2p peaks result in positive visual information in the background to the Cu grid. No such information was apparent in the original set of images. Data was acquired on a Kratos Axis Ultra upgraded with a pulse counting delay line detector.

The image of the copper grid seen in Figure 2 should be compared to the original data displayed in Figure 3. The two bands of images are displayed using the same 10%/90% threshold rule used in Figure 2, where the images are taken from the energy interval around the maximum for the Cu 3p and Al 2p Oxide peak positions. While it is true that images of similar definition can be obtained by summing the appropriate raw data, the real advantage of the procedure lies in the ability to perform proper quantification at each pixel within the image and therefore obtain quantifiable results for features with size related to the spatial dimensions of the pixels in the image set.



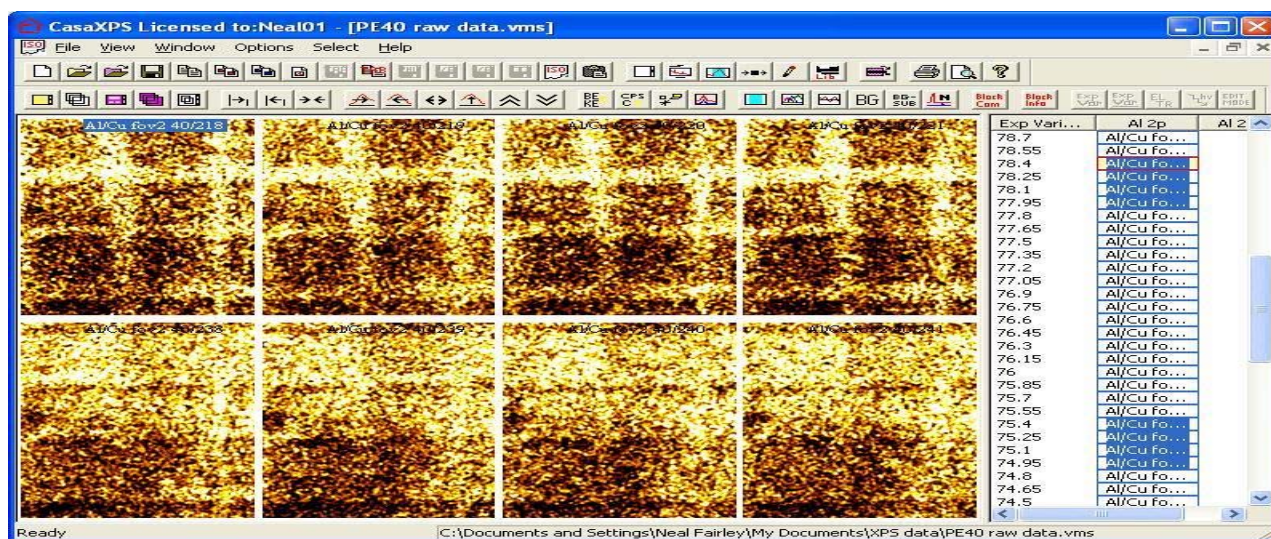


Figure 3: Unprocessed images near the peak maximum for the Cu 3p and Al 2p Oxide transitions.

Data Reduction Steps in CasaXPS v2.2.36

1. Acquire a set of maps at fix energy steps. PHI Multipak .map files or Kratos Axis Ultra/Nova instruments with DL detectors both offer pulse counted quantifiable images in this format.
2. Copy the images into the same Experiment Frame by selecting the VAMAS block in the right-hand-side and then right-clicking the mouse over the selected VAMAS blocks. This will provide a set of images suitable for TFA Prediction (see below).
3. For each energy-stepped image sequence, overlay the images in the Active Tile. Only the first three will be visibly overlaid but the entire selected set of images will be marked in the right-hand-side as being managed by the Active Tile.
4. Using the PCA property page on the Processing Dialog window, press the PCA Apply button (Figure 4). The time required by the PCA will depend on the size of the image set used and can take several minutes. Once the PCA has completed, the first three abstract factors will appear overlaid in the Active Tile.
5. Determine the number of abstract factors for which spatial information is present. The abstract factors containing noise are typically uniform in appearance, however if relative peak intensities are large, the non-linear counting statistics can introduce structure in lower order abstract factors as a consequence of the variation in noise between genuine chemical state information. Therefore low intensity abstract factors with spatial structure may still be attributed to noise. Trial and error may be required to determine the appropriate number of abstract factors for use with the TFA Predict step.
6. Load one of the abstract factors into the Active Tile and enter the required number of abstract factors for use in the TFA Predict step into the field labeled Factor (Figure 4) and select the set of images previously copied before the PCA was performed. Press the **TFA Predict** pushbutton.
7. The set of images will have been transformed at this point into a set of smoothed images. Overlay all these images into the Active Tile. The Options menu now includes an **Image Processing** menu item, from which the Image Processing dialog window is invoked (Figure 5). By pressing the **Convert Images to Spectra** pushbutton, the data overlaid in the Active Tile is transformed into an equivalent new Experiment Frame containing the spectra at each pixel. Again, these data sets can be large so each operation may take a significant amount of time. A PC with large swap space and RAM would be advisable. The spectra appear as one column of VAMAS blocks in the right-side of the Experiment Frame; however each VAMAS block includes a corresponding variable for each row of pixels and therefore effectively is a line scan of spectra. Ctrl PageUp/PageDown/Home/End allows additional corresponding variable data to be displayed in the Active Tile.

8. Define Regions and/or Components on the spectra from each VAMAS block in the Experiment Frame. To create images from the spectra, overlay the spectra in the Active Tile and use either of the buttons: **Convert Regions to Images** or **Convert Components to Images** shown in Figure 5. Fitting complex peak models to spectra throughout an image set can take many minutes. It is therefore advisable to check your model on smaller selections of Spectral line-scans (i.e. VAMAS Blocks) and apply as many constraints as appropriate within the peak models.
9. Once images have been generated for each chemical state, these maps can be copied into a new Experiment Frame, overlaid and quantified using the **Quantify Images** button on the Image Processing dialog window (Figure 5).

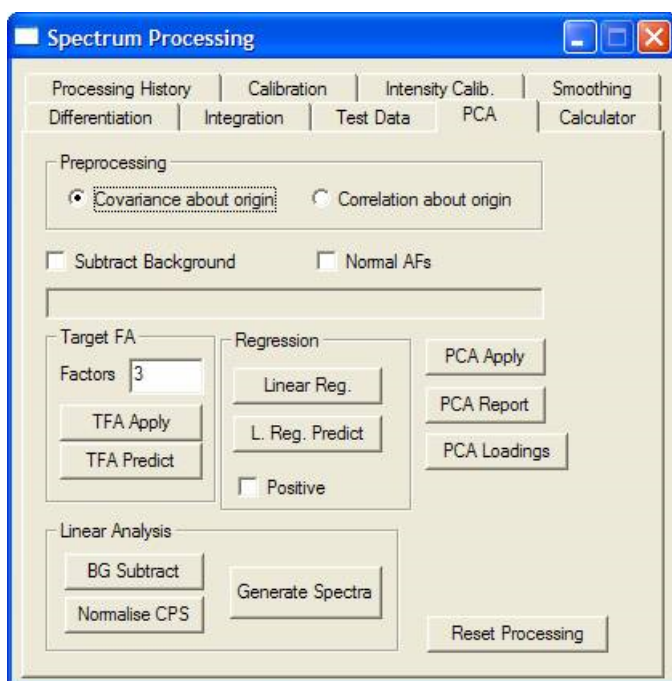


Figure 4 Image PCA is performed on the Spectrum Processing Dialog Window.

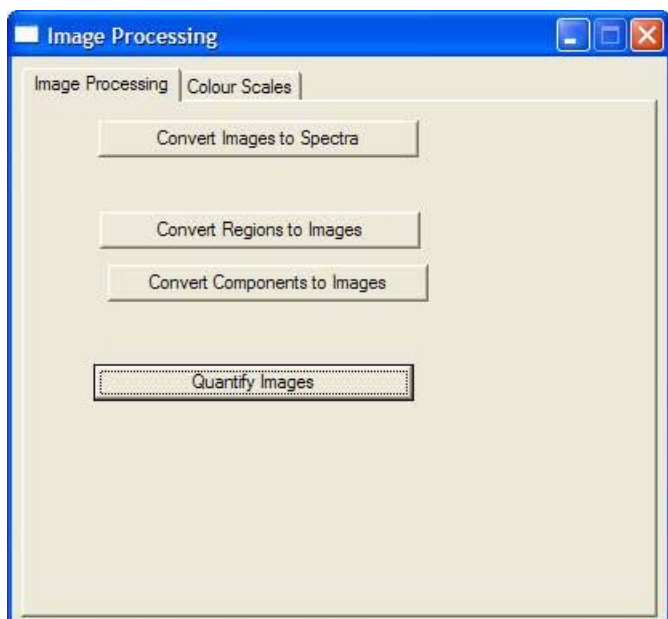


Figure 5: Image Processing dialog window (available from the Options menu)

[1] D. E. Peebles *et al*, Multivariate statistical analysis for XPS spectral imaging: effect of analyzer resolution, submitted JVST (2003).