Image Quantification Property Page

One of the advantages of parallel imaging XPS instruments is the ability to rapidly acquire images at specific binding energies. This is in contrast to probe based XPS imaging, where the probe only acquires data one pixel at a time and therefore image acquisition is a relatively slow operation compared to parallel XPS imaging, where data are collected simultaneously across the imaged surface. Ideally, a sample would be analysed by collecting images at increments in the binding energy and then constructing data sets consisting of spectroscopic information at each pixel in an image, thus providing chemical state information about the sample. The cost of the more complete analysis, which can be performed by both parallel and probe based instruments with multiple detectors, is time and therefore possible sample damage, and data analysis complexity. The benefit of spectra at pixel data-sets, however, is a superior understanding of the sample chemistry combined with spatial information. Fortunately, a quick look at the sample using a limited number of peak and background images is sufficient for many applications. The Image Quantification property page shown in Figure 1 contains a section headed "Region of Interest, ROI Quantification" which primarily supports the analysis of peak and background data sets.
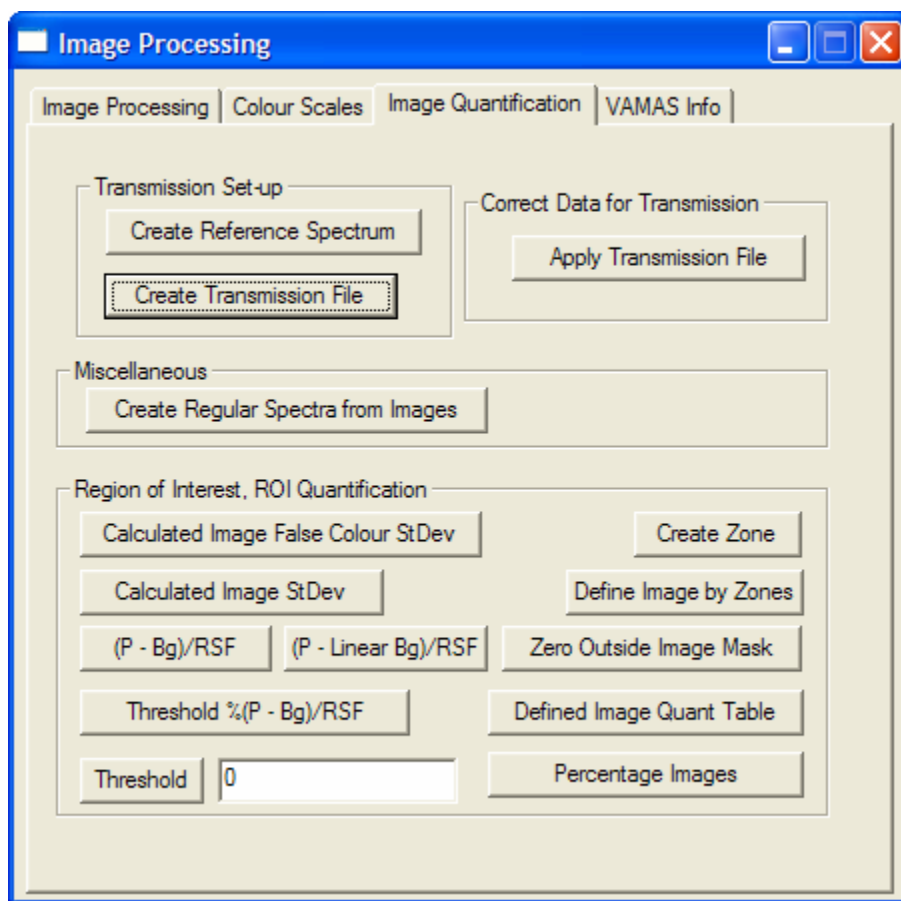

Figure 1: Image Quantification Property Page

The objective, when imaging a sample, is to obtain a set of images corresponding to each element and/or chemical state resolved by XPS such that the images are representative of the surface chemistry. Individual images acquired at specific binding energies are a combination of chemically significant electrons, scattered electrons and instrumental artifacts, thus a typical image acquired at a given binding energy is not easy to interpret. Similarly in spectroscopy, the intensity of a single peak on its own is of limited significance. The procedure used in quantification of XPS spectra is to define a background to the measured peaks, integrate the signal from the background subtracted intensity, apply intensity corrections to the measured intensity and normalize the resulting intensities to the total corrected signal for each peak used in the analysis. The process for quantifying spectra is aimed at reducing the influence of the background and the measurement mechanism from the resulting quantification values. The same logic applies to the image data, that is, the images measures at the peak positions are adjusted using the background images, scaled using relative sensitivity factors (RSF) and normalized to the total image intensity, with the view to providing representative images of the sample composition.
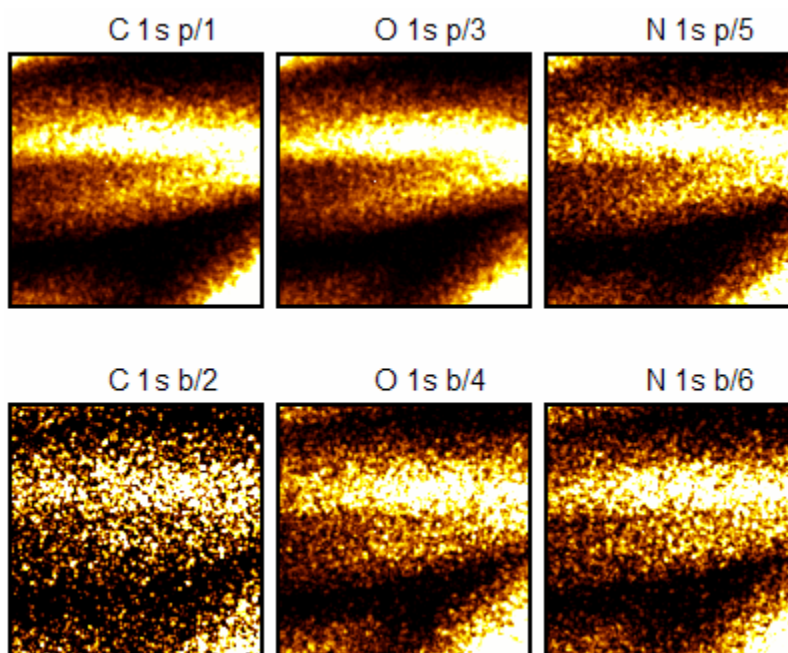

Figure 2: Images taken from natural fibers.

For an image data set, the signal is measured at the peak maximum for each transition of interest, accompanied by at least one background image for each peak image. The difference images are scaled using RSFs, possibly allowing for the fact that the height of a peak relative to another is dependent on the width of the peaks too, before normalizing the images to the total intensity image. The final step is sometime problematic in that images may not have genuine signal at all points of the imaged surface. Figure 2 is a case

in point, where the images are acquired from a sample consisting of natural fibers and therefore the measurement only reveals meaningful intensities for fibers within the focal depth of the lens system. That is to say, zones within the images in Figure 2 should produce zero counts; however due to noise this is not necessarily true, the consequence of which is that normalization to the total intensity image can result in the promotion of noise to the same or greater significance than genuine signal in the quantified images.

C 1s p/1 %At Conc   O 1s p/3 %At Conc   N 1s p/5 %At Conc
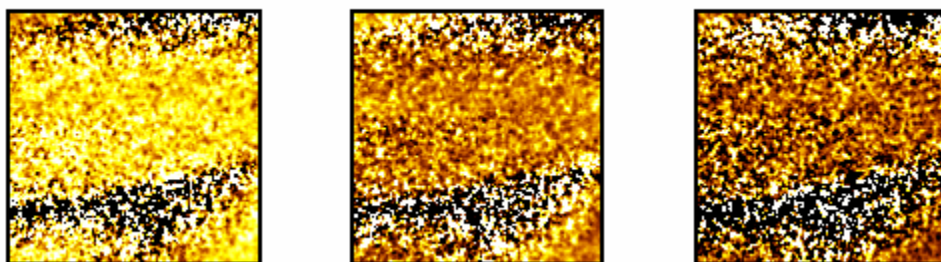
Figure 3: Normalized peak-minus-background images generated from the data in Figure 2 without any preprocessing of the images.

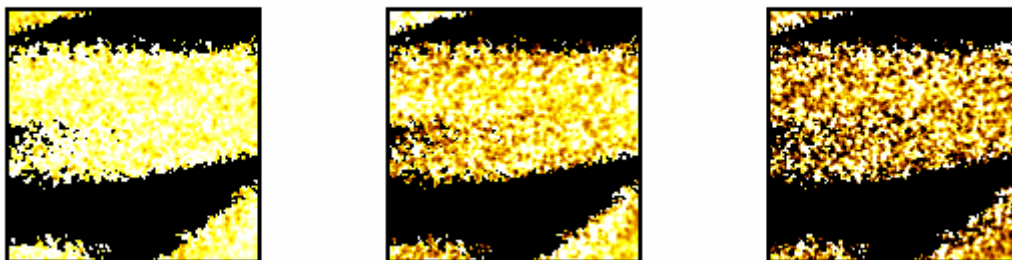C 1s p/1 %At Conc   O 1s p/3 %At Conc   N 1s p/5 %At Conc

Figure 4: Peak minus background images where pixels below a threshold of 4.5 counts in the total intensity image are set to zero before normalization is performed.

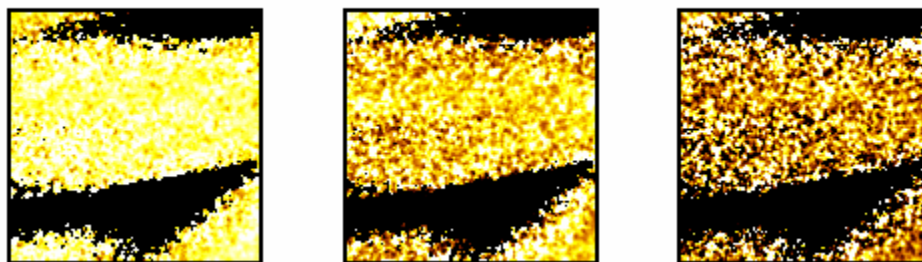C 1s p/1 %At Conc   O 1s p/3 %At Conc   N 1s p/5 %At Conc

Figure 5: Peak minus background images where pixels below a threshold of 2 counts in the total intensity image are set to zero before normalization is performed.

Figure 3 illustrates the issues with lack of signal in the raw images; regions with very little counts in the raw images (Figure 2) result in normalized images containing adjacent pixels with concentrations near 100% and 0%. Clearly the appearance of large concentrations next to very small concentrations is an artifact of the calculation. The

problem is reduced by identifying the zones for which the count rate is low and setting all pixels below a threshold to zero prior to normalizing the image set. Figure 4 and Figure 5 show the same data after a mask has been applied to the background subtracted images before normalization to the total intensity image. The higher threshold used to create the mask in Figure 4 compared to Figure 5 eliminates signal close to the limits of the focal depth for the lens system, therefore the attenuation of the image as a fiber changes in depth influences the resulting images, particularly the C 1s image. Reducing the threshold allows more pixels to be included into the computation producing the fuller appearance of the C 1s image seen in Figure 5.

The images in Figures 3, 4 and 5 are computed from the background subtracted images in Figure 6. The objective in creating the normalized image sets is to remove the intensity variation not due to elemental spatial variation. The trick is to set the threshold to include useful image information without loosing too much of the image.
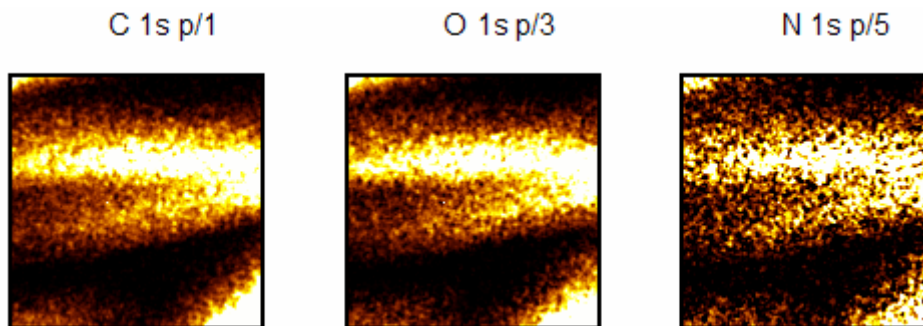

Figure 6: Background subtracted images corresponding to the peak and background images in Figure 2.

The processing steps performed on the image data set will now be described.

Quantification of Peak and Background Images

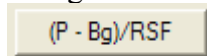### Quantification using a Peak and One Background Image

The VAMAS file containing the images displayed in Figure 2 appears as a set of VAMAS blocks as depicted in Figure 7. The experimental variable for each of the images is the binding energy at which the image was acquired and for each element a peak and background image appears in the file.
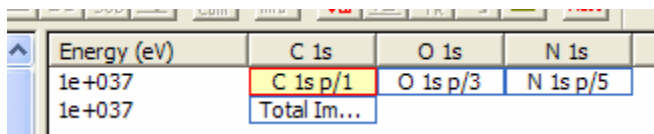

Figure 7

Quantification of the data requires the specification of a relative sensitivity factor and the definition of each image as either a peak or background image. The means of making these assignments relies on the creation of quantification regions for each of the images. Quantification regions are defined using the Regions property page on the Quantification Parameter dialog window, available from the Quantify option on the Options menu. Each image used in the quantification process is assigned a region name, an RSF and a TAG string. The region name given to each image links the images together as far as the peak and background are concerned, while the images corresponding to the backgrounds are designated using the TAG string which must be specified as **bg**. For images used as peak signal, provided the TAG string is different from **bg** the TAG string is of no consequence. An RSF can be assigned using the RSF text-field in the region defined on the peak images consistent with the required quantification. Once the image data are prepared with quantification regions, the first step in the analysis can be performed, namely, the creation of the background subtracted images as shown in Figure 6.

After the images have been prepared as described above, the set of images, both peak and background images, must be overlaid in the active tile before pressing the (P - Bg)/RSF button on the Image Quantification property page shown in Figure 1. The result of pressing the button is the creation of a new experiment frame containing the set of background subtracted images plus an image representing the sum of all the background subtracted images as illustrated in Figure 8. The data presented in the form of background subtracted images are scaled using the RSFs defined by the quantification regions and provides an intermediate step en route to the quantified images. The total intensity image offers a means of examining the image used to normalize the background subtracted images and therefore an opportunity to identify those pixels for which the signal-to-noise level is insufficient for use in the normalization step.
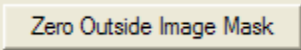
Energy (eV)	C 1s	O 1s	N 1s
1e+037	C 1s p/1	O 1s p/3	N 1s p/5
1e+037	Total Im...		

Figure 8: Experiment frame generated by pressing the (P-Bg)/RSF button.

Before moving to the atomic concentration images, which involves dividing each image by the total intensity image, a mask image can be prepared from the total intensity image to represent those pixels suitable for use in the atomic concentration calculation. Using the total intensity image, a false colour mask is prepared, where the intensity-range representative of pixels with sufficient counts in the total intensity image for computing the atomic concentration is assigned a false colour. For the purposes of preparing a mask, a false colour is defined for those pixels above a given threshold in the total intensity image and below the maximum for pixels within the image. The image in Figure 9 displays all pixels with intensity above 2 using the red colour. The method for defining false colour scales is described elsewhere.

The false colour image in Figure 9 is used to define a mask image. The mask is established by pressing the "Define Image from F/C" button on the Image Processing

property page. Once a mask image is defined, the button labeled "Zero Outside Image Mask" shown in Figure 1 can be applied to the background subtracted data. The set of background subtracted images must be overlaid in the active tile before pressing the

Zero Outside Image Mask button on the Image Quantification Property page. A new experiment frame is created containing the normalized images shown in Figure 5. Only those pixels corresponding to the red pixels in the false-colour image will have non-zero entries in the final set of quantified images.
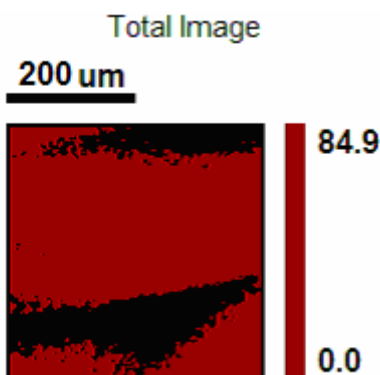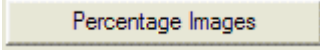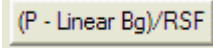

Figure 9: False Colour image defining those pixels containing signal of sufficient significance to the normalization step in calculating atomic concentrations.

The background subtracted images, after the mask has been applied to zero spurious pixel intensities, appear in a new experiment frame. The final step in obtaining the atomic concentration images in Figures 3, 4 and 5 involve overlaying the masked background

subtracted images in the active tile and pressing the Percentage Images button shown in Figure 1.

The use of these steps to produce the atomic concentration images is required because the images contain pixels for which the signal to noise is insufficient. For images where the counts are adequate across the entire image, the process is simplified using the ***Quantify Peak – BG*** button on the Image Processing property page (see below and elsewhere).

Peak and Two Background Quantification

Image quantification is also possible where two background images are used to estimate the intensity of the peak image above the background signal. The button (P - Linear Bg)/RSF requires the experimental variable for both the peak and the two background images to be assigned with the binding energy or kinetic energy at which the images were acquired. These energy values are used to interpolate a linear background using the two background images, from which the height of the background below the peak image is estimated. The procedure for using two background images is identical to that of using a single background image described above, other than the need for three images per

transition and the correct assignment of the experimental variable to the energy at which the images are acquired.

Examining XPS Images using Peak and Background

Some of the difficulties with simply considering raw XPS images can be investigated using a well understood sample. The following example is Hf oxide on a Si wafer covered by Au, which is then etched with the IFOS logo (Kaiserslautern, Germany) using a focused ion beam. The images shown in Figure 10 are unprocessed; nevertheless the action of the focused ion beam is apparent for each pair of peak and background images, regardless of the transition. For example, the action of the ion gun in etching the characters IFOS is more obvious in the O 1s background image than the O 1s peak image. Similar confusion exits for the Si 2s images, since both peak and background appear to offer the same information, somewhat contrary to the belief that the etching of the ion gun was sufficient to expose Si at the centre of the O in IFOS.
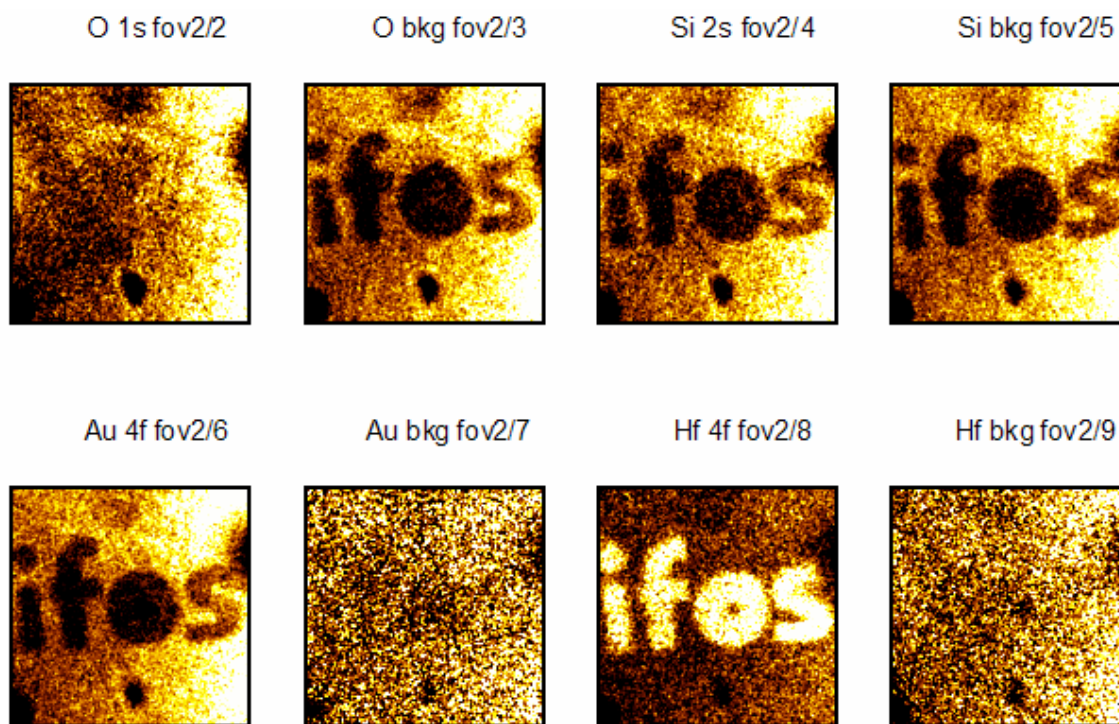

Figure 10: Raw XPS images

The processed data shown in Figure 11 clearly shows the data in the light expected from the sample preparation. The processing proceeds as follows. The data in Figure 10 are assigned quantification regions where the name fields link the peak and background images for each element, the TAG field identifies the background image for each pair and the RSF is assigned an appropriate value for the different peak height intensities. Overlaying both the peak and background images in the active tile, and since the images are well populated with counts and therefore all pixels are appropriate for the quantification step, the **_Quantify Peak – BG_** button on the Image Processing property

page can be applied. The resulting images are shown in Figure 11. What is most gratifying is that the processed images are entirely consistent with the knowledge of the sample, namely, a coating of gold over Hf Oxide on top of Si wafer. The O 1s and Hf 4f images in Figure 11 show similar structure within the characters expected from the Hf Oxide layer, gold is predominantly surrounding the IFOS characters and the Si signal is clearly enhanced at the centre of the O in IFOS.
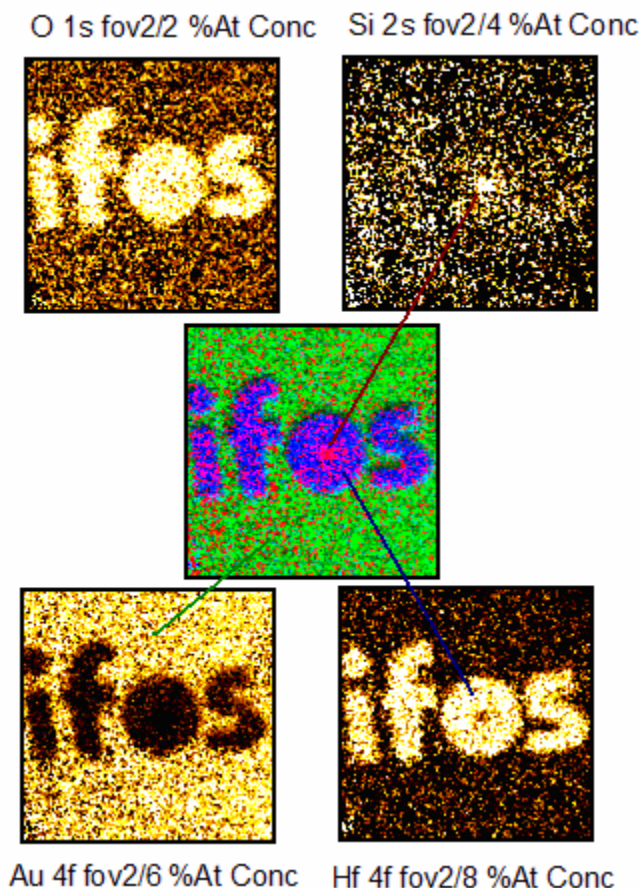

Figure 11: Quantified Peak minus background images calculated from those images in Figure 10.

The difficulties in interpreting the raw images in Figure 10 can be explained in terms of the survey spectrum in Figure 12 acquired from the same sample. The fact that the peak and background images for the Si 2s transition both have the character of the Au coating is not surprising given the position of the Si 2s region with respect to the Au 4f doublet. Variations in the background due to the Au 4f cause the greatest variations across the Si images in Figure 10, hence the similar appearance of the Si images to the Au 4f image. Indeed, the background variations are a key reason why XPS imaging has in the past been viewed with mistrust. The survey spectrum in Figure 12 shows that XPS may even achieve better results using two background images either side of the peaks or even by collecting sets of images across the peaks and working with spectra-at-pixels to define full quantification regions from which atomic concentrations can be computed. Both these options offer the prospect of increased quality in the final sample analysis.
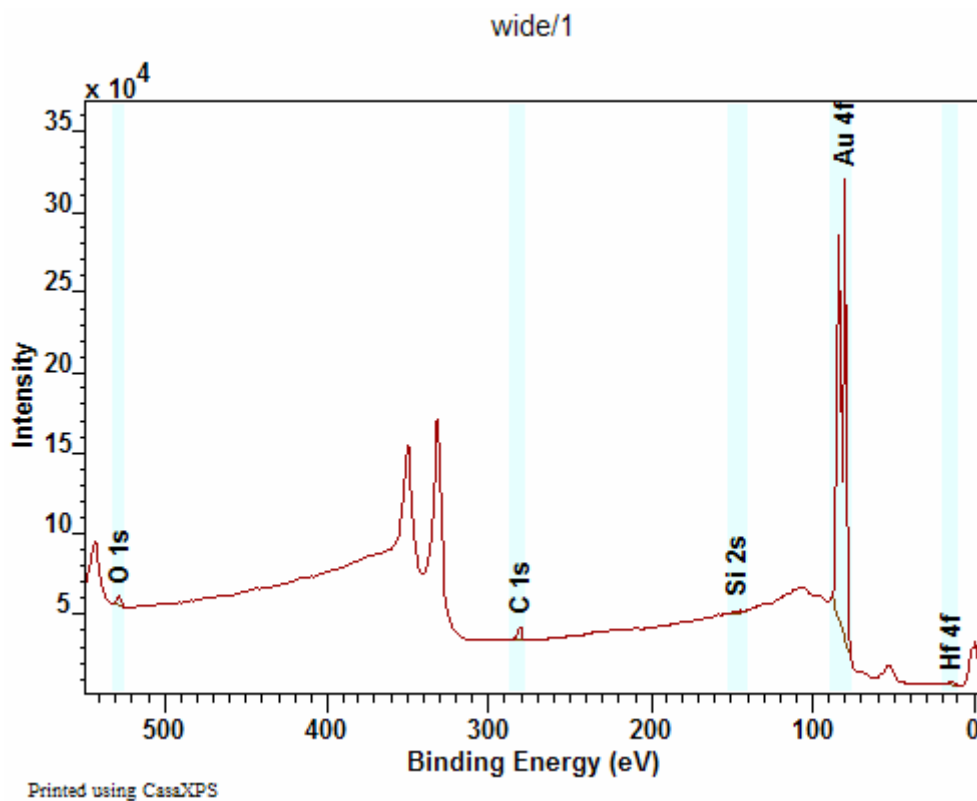
Figure 12: Survey spectrum showing the influence of the background on the raw image data.

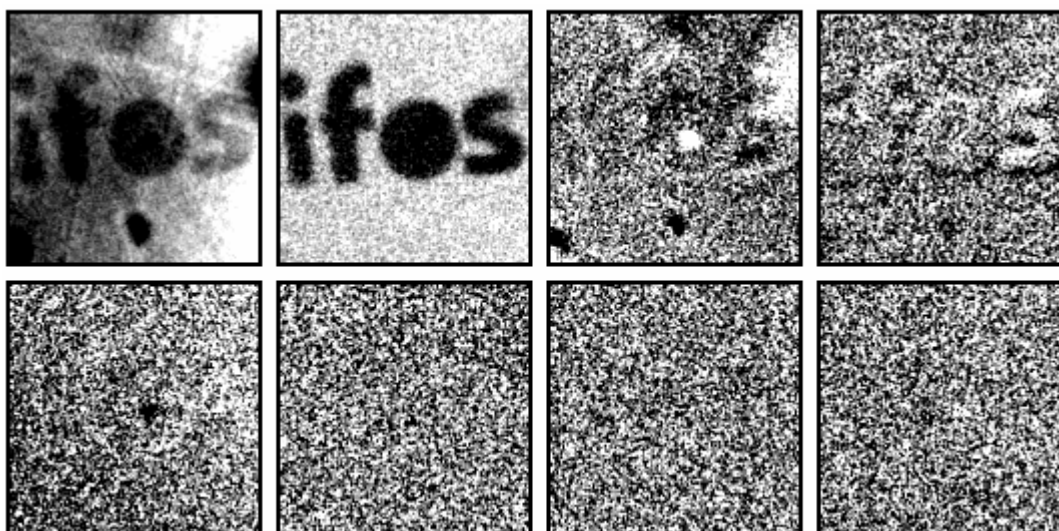## Peak and Background Images using PCA Noise Reduction

Figure 13: Abstract Factors computed from the eight images in Figure 10 using a square-root transformation applied to each image before performing a PCA to the data set.

9

While best suited to large numbers of images with similar appearance, PCA noise reduction can be applied to data such as the limited number of images in Figure 10 with some success. The objective is to find a set of abstract factor images representative of all the useful image information in the data set with the view to excluding noise, if possible. The abstract factor images in Figure 13 show structure in the first five abstract factors, while the last three abstract factors are uniform with the general appearance of noise. Therefore, a first attempt at noise reduction might include the first five abstract factors to reconstruct the images. The enhanced images in Figure 14 should be compared to those in Figure 11, where the most notable changing is in the Si 2s image. The images in both Figure 11 and Figure 14 have been displayed using the default contrast adjustment in CasaXPS, however using the Colour Scale property page on the Image Processing dialog window allows the structure for the Si 2s image to be examined in more detail. Figure 15 shows the result for the Si 2s image in Figure 14, where the limits for the colour-scale have been adjusted to enhance the contrast across the IFOS characters. It can be seen in Figure 15 that the signal is more intense at the centre of the O in IFOS, which is consistent with the result from Figure 11; however the difference lies in the ability of the PCA procedure to highlight the Si 2s signal within the craters bottom formed by the ion beam etching.
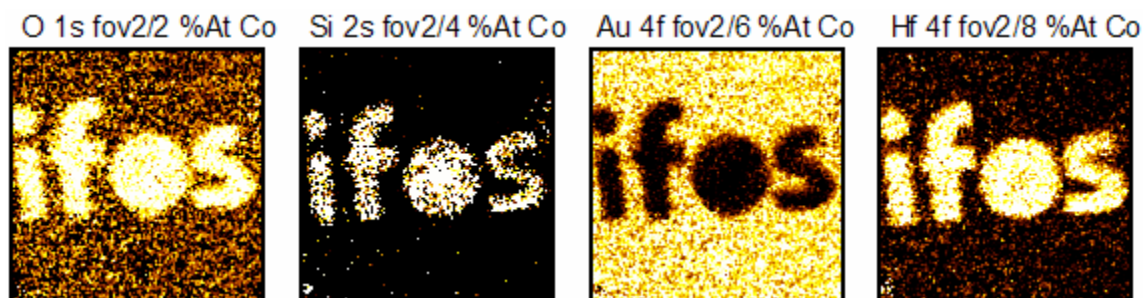

Figure 14: Reconstruction using five abstract factors.
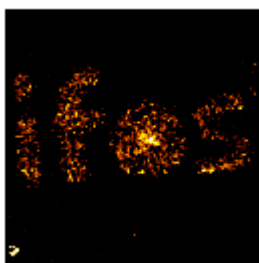

Figure 15: Contrast Adjustment for the Si 2s image.

The use of five abstract factors to reproduce the images in preparation for quantification is not a unique solution. It is possible to perform the analysis using between one and eight abstract factors to represent the images. The Si 2s images computed with a range of abstract factors in the reconstruction step are shown in Figure 16. It is clear there is a trade-off between the noise in the image and revealing hidden structure within the data. The sequence of images in Figure 16 show how the number of abstract factors alters the

emphasis of the image in the sense that if few abstract factors are used in the analysis then the emphasis is placed on the larger structure within the Si 2s image, namely the IFOS logo; while as more and more abstract factors are added the emphasis moves towards the smaller feature, namely the centre of the O in IFOS. The same sample analysed using a PHI Auger instrument also supports the conclusions of the PCA analysis in Figure 14. The AES image in Figure 17 shows an enhanced Si signal at the centre of the O in IFOS and also suggests Si is detectable across the bottom of the crater.
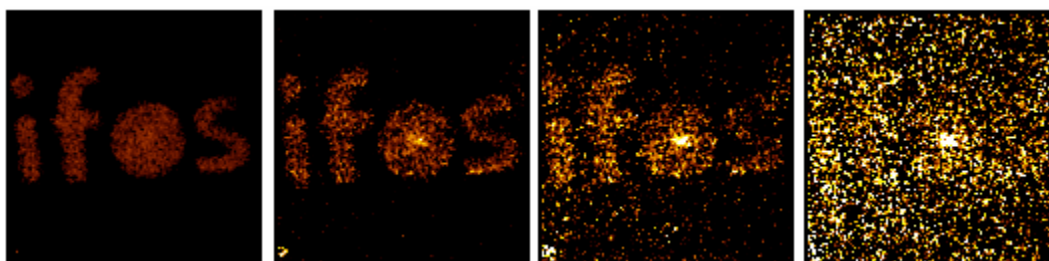

Figure 16: Si 2s image computed using 2, 5, 7 and 8 Abstract Factors, respectively.

Figure 17: AES image of sample shown in Figure 16.

PCA noise reduction should be viewed as a tool for providing a different perspective of the data and therefore offers a means of better understanding the possibilities before the analyst.