Image Arithmetic and Quantification of Difficult Data

Not all image data arrives in a form open to immediate quantification. Overlapping of peaks sometimes requires manipulation of the data before moving to the quantification step. For this reason, an image calculator has been added to the Image Processing dialog window on the Image Quantification property page. The image calculator permits image data to be combined using arithmetic expressions.

Introduction to the Issues

Consider the imaging problem set by a sample prepared from gold deposited on a hafnium oxide layer covering a silicon substrate, where the gold and hafnium oxide are selectively removed from the original sample using a focused ion beam. The spectrum in Figure 1 illustrates the relative positions of the gold and silicon photoelectric lines, where it can be seen that Si images will be influenced by the Au 4f doublet via the background resulting from inelastic scattering of the Au 4f electrons.

Printed using CasaXPS
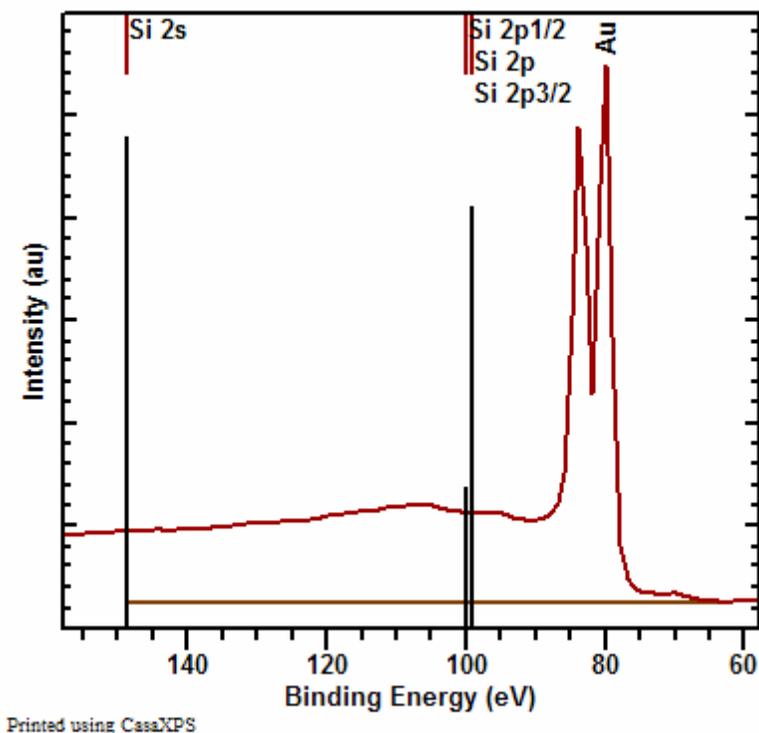
Figure 1: Spectrum showing the positions of the Si 2s and Si 2p lines relative to the Au 4f lines.

In an attempt to mitigate the influences of the Au 4f electrons on a Si 2s image, a background image measured at binding energy 129.91 eV is acquired as well as the Si peak image at 147.91 eV. The problem with such a pair of Si images is that for any region of the sample where gold is present, the background image corresponding to the Si

peak may well be more intense than the peak itself. Figure 2 illustrates this point, where the scale bars show the background image b) contains higher counts than the peak image a).
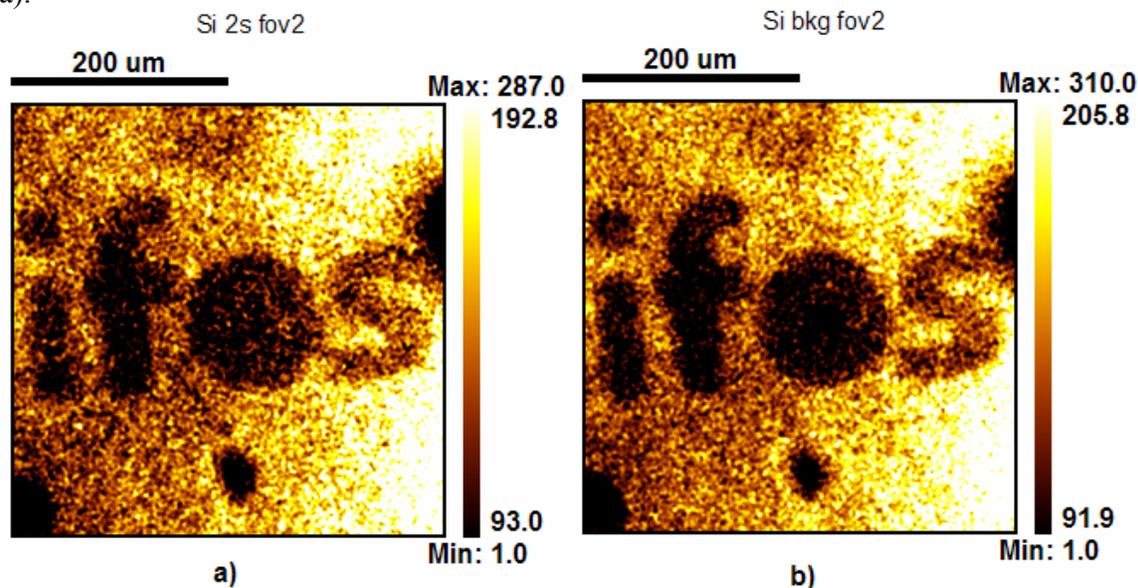
Figure 2: a) Peak image for the Si 2s transition. b) Background image for the Si 2s transition.

In an ideal world, the experiment would be repeated using two background images, one below and one above the Si 2s peak so that the peak-height image can be measured relative to a linear background approximation. In the real world, it is not always possible to rerun an experiment for a variety of reasons: due to time, instrument/sample availability or financial constraints. Since the data cannot, in this case, be measured a second time, an alternative strategy based on the available data might be required to get the best information from the existing data.

The following describes one possible enhancement of the results based on the use of the Image Calculator. The approach involves attempting to remove the influence of the Au 4f peak background from the Si 2s image by using the Au 4f image. It should be pointed out that the objective in using this example is to show the potential for manipulating images rather than providing a recommended route to analysing these specific images. The motivation for including the image calculator was provided by image data in which overlapping peaks prevented a direct quantification, that is, some images were a combination of the response to the presence of more than one element on the sample. Quantification of XPS images requires elemental peak-minus-background images before sensitivity factors can be applied to produce the atomic concentration images; therefore the image calculator is key to generating independent elemental images. The advantage of considering the manipulation of the Si 2s image using the Au 4f data is that the consequences of these actions can be understood in the context of easily characterised image data.

An Alternative Solution to the Si 2s Problem

The approach to analysing the Si 2s peak image shown in Figure 2 is to avoid using the Si 2s background image, also shown in Figure 2, by subtracting a proportion of the Au 4f image from the Si 2s peak image, where for both images, the intensities used in the calculation are measured relative to the Au 4f background image acquired at a binding energy of 64.91 eV. The assumption is that the background to the Au 4f peak at higher binding energies to the Au 4f peak varies in proportion to the height of the Au 4f peak. For a clean gold surface such an assumption is plausible. If the gold surface is contaminated by a non-uniform layer of carbon, say, then the assumption would be doubtful. The potential problem is that the computed image includes a component of a thickness image for the over layer material due to increased scattering of the Au 4f electrons with increased thickness of the over layer. Nevertheless, the analysis of these images will proceed using the assumption that the Au 4f signal can be used to measure the background to the Si 2s peak image.

The first step is to create a set of peak minus background images without any scaling of the intensities by sensitivity factors. The data, as acquired, is logically ordered in CasaXPS as seen in Figure 3. Each image must be assigned as either a peak or a background image and each element must have both a peak and background image. While the data in Figure 3 includes a background image for the Si 2s image, the approach described above requires the removal of the Si 2s background image from the peak minus background calculation, on the basis that the Si 2s and the Au 4f peak images are measured relative to the image representing the background to the Au 4f peak. That is, the background to both Si 2s and Au 4f is assumed to be the background shown on the spectrum in Figure 1.
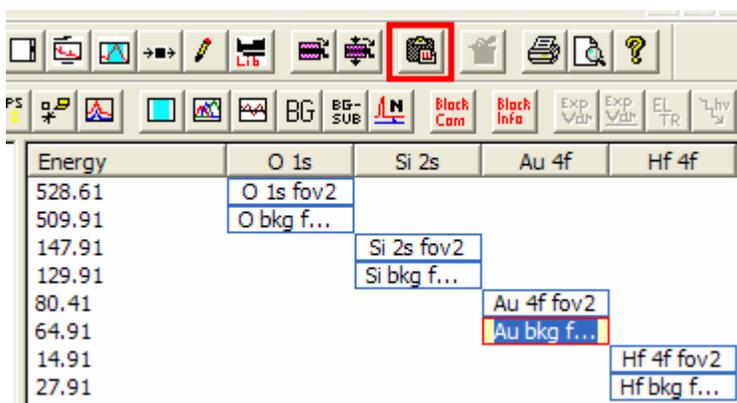
Figure 3: Original Data Set of Peak and Background Images.

The peak minus background operation is performed using the information in a quantification region defined on each image specifying the relationship between the images in terms of peak and background. Images are linked as peak and background pairs using the name field of these regions, while the background images must each have the string *bg* entered into the TAG fields in the regions. Since each peak image requires a

3

corresponding background image and the background to the Au 4f image at 64.91 eV must be applied to both peak images, a copy of the Au 4f background image must be made for use with the Si 2s peak image:

1. Select the Au 4f background image as shown in Figure 3.
2. Press the toolbar button marked with the red box in Figure 3.
3. Add or modify the region defined on the new Au 4f background image so that the region name matches the region name used on the Si 2s peak image and ensure the TAG field is set to *bg*. The peak minus background calculation uses the region name to link the Si 2s peak image with the Au 4f background image, hence the region names used for both these images must match exactly.

Figure 4 shows the shape of the VAMAS blocks in the right-hand-side of the experiment frame following the copying of the Au 4f background image. Note that the Au 4f background image has been moved from the Au 4f column to the Si 2s column by adjusting the element/transition fields in the VAMAS block. The element/transition fields can be changed using the ⊡ toolbar button:

1. Select the copy of the Au 4f background block in the right-hand-side of the Experiment Frame.
2. Press the ⊡ toolbar button to invoke a dialog window.
3. Set the Element/Species and Transition fields to match the Si 2s peak column header.

Once the OK button is pressed on the dialog window, the display will rearrange to that shown in Figure 4.

Energy	O 1s	Si 2s	Au 4f	Hf 4f
528.61	O 1s fov2			
509.91	O bkg f...			
147.91		Si 2s fov2		
129.91		Si bkg f...		
80.41			Au 4f fov2	
64.91		Au bkg f...	Au bkg f...	
14.91				Hf 4f fov2
27.91				Hf bkg f...

Figure 4: Logical structure of the VAMAS file following the copying of the Au 4f background image.

Creating the set of peak minus background images suitable for use in the image calculator involves overlaying in the active tile all the peak and background images to be included in the calculation. Figure 5 shows the right-hand-side of the Experiment Frame after selecting the appropriate VAMAS blocks and pressing the ⊡ overlay toolbar button. The red boxes around the selected VAMAS blocks indicated the data are loaded into the Active Tile in the left-hand-side of the Experiment Frame. Note that the original Si 2s background image has been excluded from the selection in Figure 5.

4

Figure 5: Selection of VAMAS blocks used to create the background subtracted images.

When the (P – Bg) button is pressed, a new Experiment Frame is created from the images in the Active Tile (the *(P – Bg)* button is indicated on the Image Quantification property page in Figure 6). If no new Experiment Frame appears, then either the images in the active tile are not in peak and background pairs or the regions are not appropriately defined.
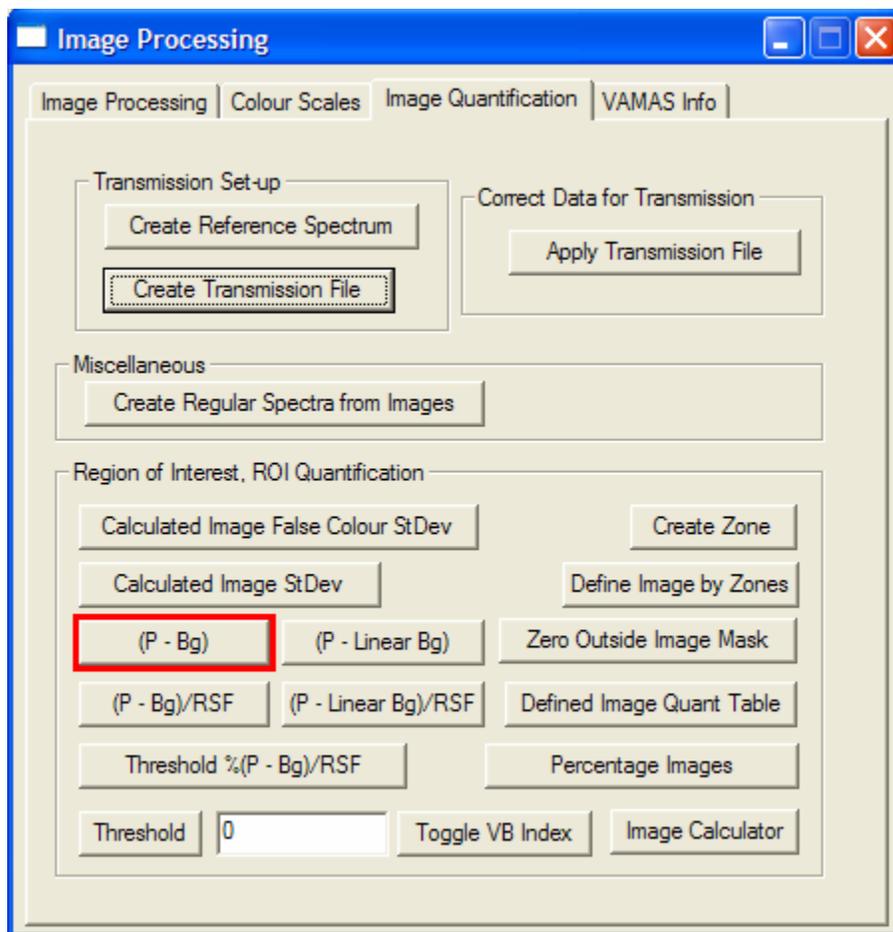
Figure 6: Image Quantification property page indicating the position of the peak minus background button.

The Experiment Frame in Figure 7 shows the images resulting from applying the (P-Bg) button in Figure 6 to the data prepared in Figure 5. The overlay in Figure 7 of the Si 2s

and Au 4f background subtracted images are almost identical in appearance, although variation must exist between these two images for the current approach to be valid or even useful.

The image calculator is invoked by pressing the [Image Calculator] button shown in Figure 6. The resulting dialog window offers a text-edit window in which each line of the text-edit window represents an expression in terms of VAMAS block indices and each expression results in an image in the new Experiment Frame. The expressions are defined in terms of the VAMAS blocks using strings of the form: vb0, vb1, vb2, … where the index number relates to the order of the images in the underlying VAMAS file. The VAMAS block index strings can be displayed as part of the strings labelling the data in the right-hand-side of the Experiment Frame. The *vb* labels are toggled on/off by pressing the [Toggle VB Index] button on the Image Quantification property page or using the menu item on the View menu on the CasaXPS main window.
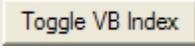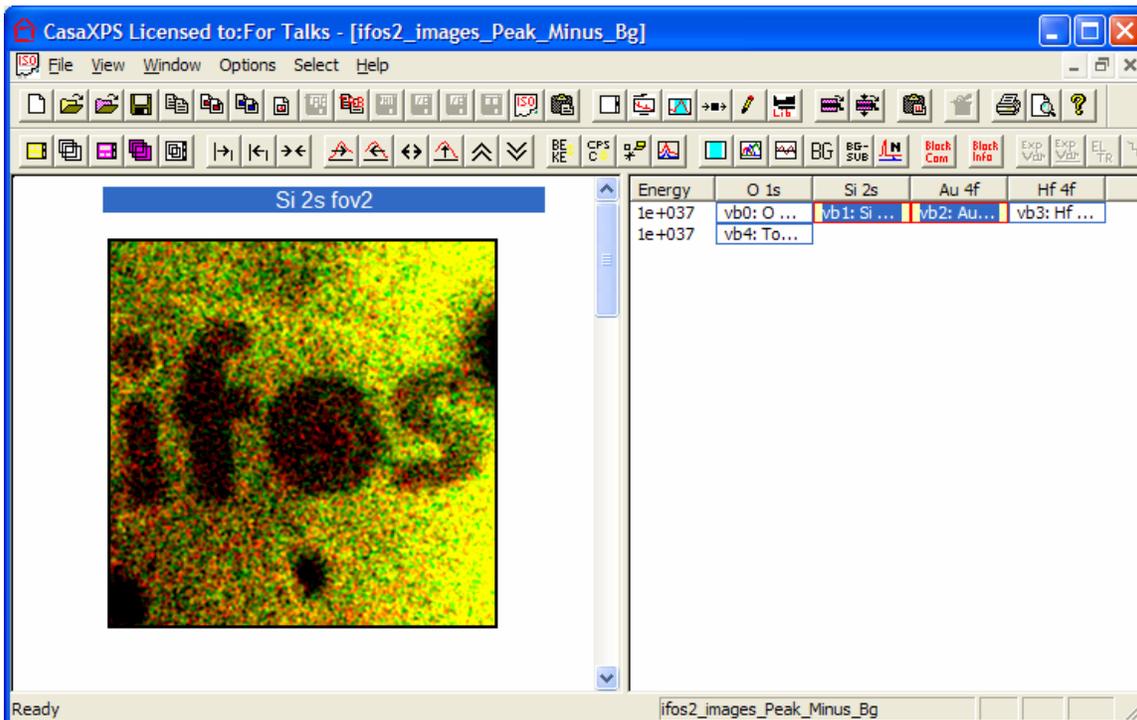
Figure 7 Background subtracted images generated from the data in Figure 5.

Expressions are any arithmetic expression involving the set of *vb* strings in the current file, these include an expression involving a single *vb* string or a more complicated expression such as *vb1 – vb2 * 0.3*, say. The simple expression *vb0*, for example, would effectively copy the first VAMAS block through into a new Experiment Frame. The first *vb* string encountered reading left-to-right in an expression is the basis for the computation. That is, element/transition, VAMAS block identifier etc are based on the first *vb* string encountered in an expression. Figure 8 provides an example of an image calculation applied to the data in Figure 7, the result of which appears in Figure 9. The

function ZERO (), applied to the second expression, has the effect of setting all negative intensities resulting from the computation to zero.

The sample used in this example was prepared by etching the letters IFOS into the gold and hafnium oxide layers. Additional etching was directed at the centre of the character O in the IFOS logo with the intention of exposing the silicon substrate. The peak-minus-background images overlaid in Figure 7 represent the Si 2s and the Au 4f data before manipulation with the image calculator. These images show little sign of increased silicon at the centre of the O, however following the correction for the Si 2s background using the expressions in Figure 8, the equivalent images displayed in Figure 9 clearly show an enhanced silicon signal in the expected location.
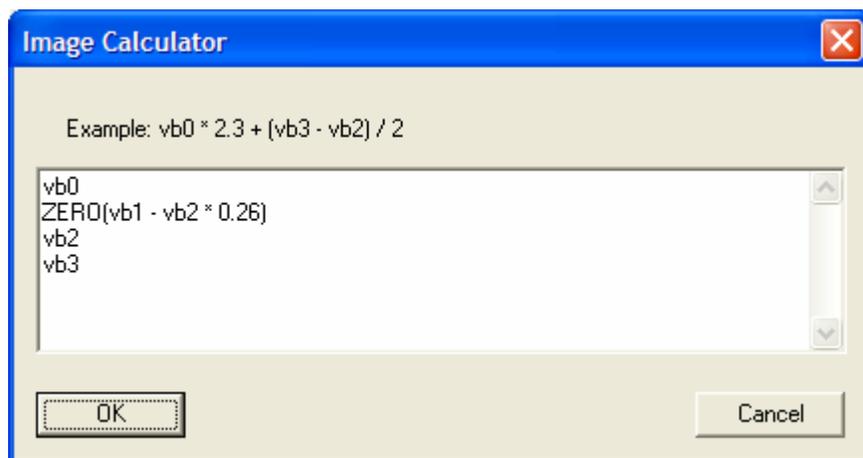
Figure 8 Dialog window offered by the Image Calculator button showing the expressions used to calculate the images in Figure 9.

The final processing step is to convert the elemental images into atomic concentration images. Using the [Threshold %(P - Bg)/RSF] button applied to the data in Figure 9 results in the images in Figure 10, where each image is normalized to the total intensity image computed from the four RSF scaled images and expressed as a percentage of the total intensity at each pixel. A threshold can be entered into the text-field below the button, which ensures all pixels below the threshold value in the total intensity image are set to zero.

Key Points

- The peak-minus-background buttons convert the image data to counts per second.
- All computations involving the Image Calculator are performed using the raw intensities; therefore timing information may need to be included explicitly.
- A set of mathematical functions are available within the image calculator, eg SQRT, ZERO, SIN, EXP, LN and ABS. Note, the calculator is case sensitive.
- Spaces are important in expressions: *vb0-0.5*vb1* is not a valid expression, but *vb0 - 0.5*vb1* is valid. The following are also equivalent and valid expressions *vb0+-0.5*vb1* or *vb0+vb1*-0.5*.
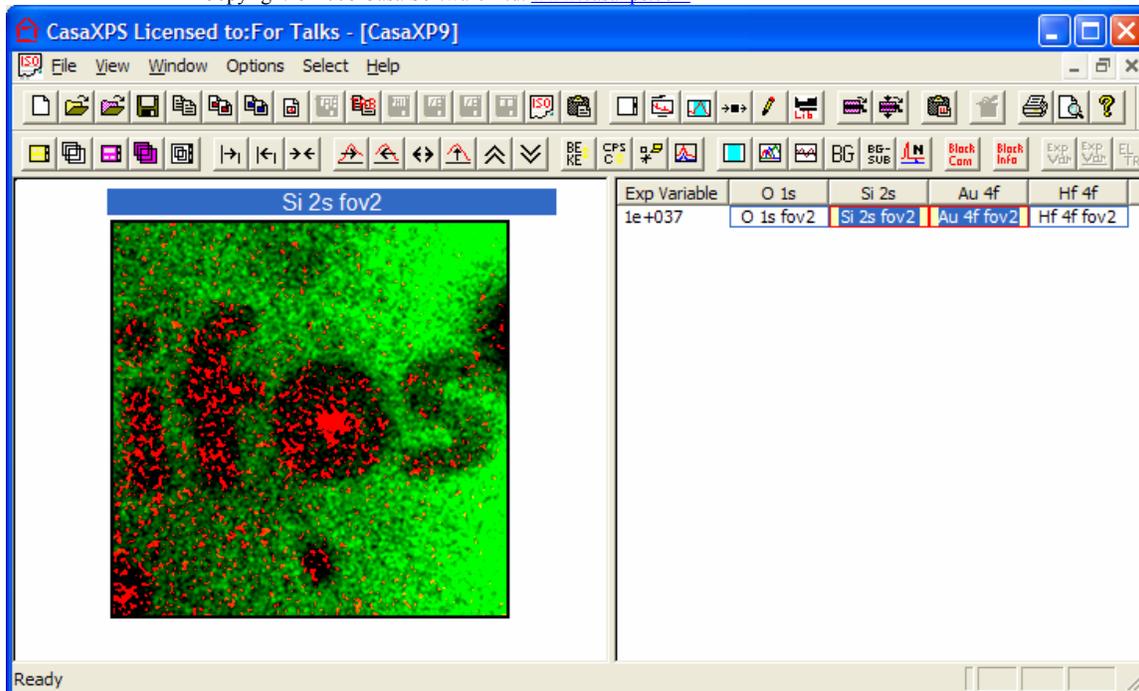
Figure 9: Images calculated from the background subtracted images in Figure 7 using the expressions in Figure 8.
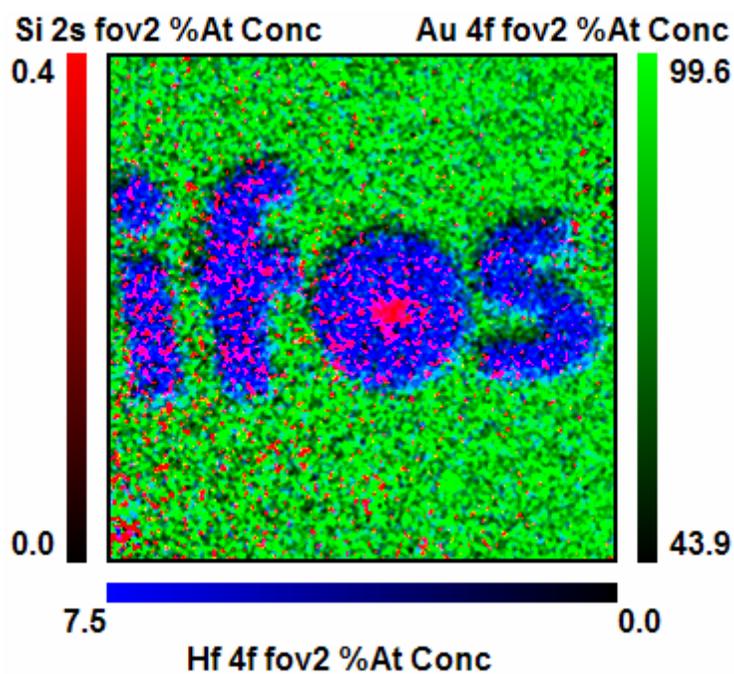
Figure 10: Overlay of the Si, Au and Hf images after normalization to the total intensity image.