

Getting more from XPS imaging: multivariate analysis for spectromicroscopy

Keywords

parallel imaging, spherical mirror analyser (SMA), multivariate analysis, multi-spectral imaging

Application Note MO328(1)

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Overview

The spherical mirror analyser (SMA) is used to acquire fast XPS images from specimen surfaces with high lateral and energy resolution. Here we review the properties of the SMA including spatial and energy resolution and provide examples of the capabilities of such an imaging analyser. In the last few years the combination of the SMA with a two-dimensional, pulse counting electron detector has again increased the level of information available for surface characterisation. The delay-line detector (DLD) represents the next generation of photoelectron detection for XPS imaging and has allowed the realisation of quantitative surface chemical state microscopy by X-ray photoelectron spectroscopy. To generate such information requires the acquisition of multi-spectral datasets comprising a series of images incremented in energy so that each pixel contains photoelectron intensity as a function of energy. The datasets generated by this method contain >65,500 spectra and are therefore ideally suited to multivariate analysis to analyse the information content of the dataset and as a tool for noise reduction in individual images or spectra.

The spherical mirror analyser

The SMA has been successfully incorporated into a commercially available X-ray photoelectron spectrometer, as described by Page[1], where the outer hemisphere of the classical hemispherical sector (HSA) acts as the inner hemisphere of the SMA. In imaging mode the electrons pass through the HSA into the SMA before returning to the image plane of the HSA.

A 2-dimensional detector positioned at the image plane of the analyser will detect energy and spatially resolved photoelectrons. The delay-line detector (DLD) is a genuine electron pulse counting detector which is used to acquire x,y coordinates for each electron event. Integration of the signal over several seconds allows the generation of a truly quantitative elemental or chemical state image of the surface over a 256x256 pixel array. In the highest magnification mode the spatial resolution at the surface is <1 μm .

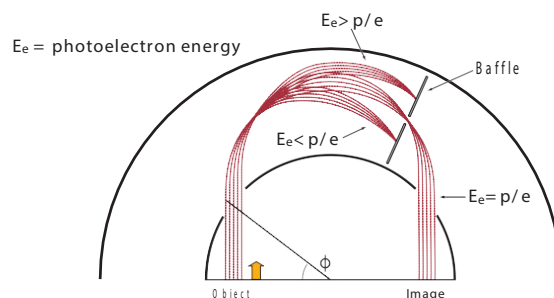


Figure 1: Electron trajectories through the SMA

It has been established that a modern imaging XPS instrument is capable of acquiring data that is both spatially and energetically resolved. Typically XPS images are acquired at a single energy, corresponding to a core level transition and corrected by subtracting a background image from a lower binding energy. In many cases this approach is sufficient to characterise the distribution of elements at the surface, however, the energy chosen for the photoemission peak may not be representative of the surface chemistry across the entire field of view. Furthermore the choice of a single energy may not be capable of resolving overlapping peaks due to small chemical shifts and cannot be quantified as accurately as is the case for spectroscopic analysis. These limitations may be avoided by acquiring a set of images incremented in energy resulting in a three-dimensional dataset containing a spectrum at each pixel of the image, shown schematically in figure 2.

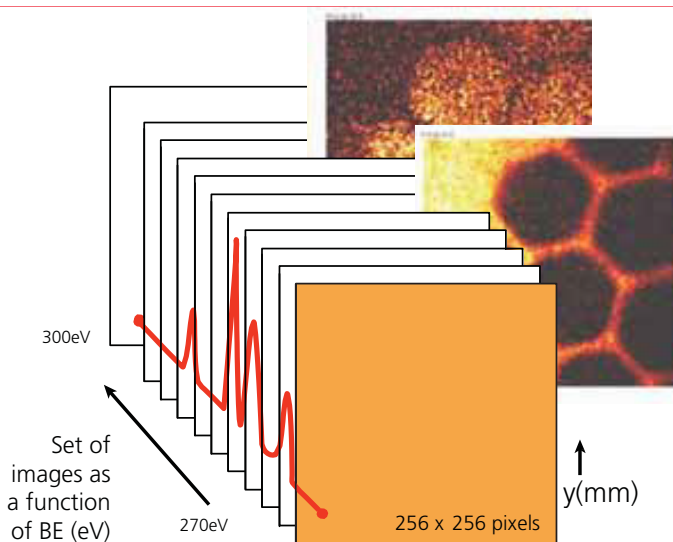


Figure 2: Schematic diagram of spectra from images dataset

By generating such spectra at a pixel, accepted spectroscopic data processing techniques may be applied including genuine background subtraction and curve fitting routines for each spectrum.

A typical multi-spectral imaging experiment over a core level transition takes in the order of 75 minutes of data acquisition (30 eV energy range, 0.2 eV steps, 30 sec per image). Whilst this seems like a relatively long acquisition time for the entire experiment, on a spectrum-at-pixel basis the acquisition time for the stated example is only 68 msec. Such short acquisition times lead to very poor signal to noise ratios for a spectrum from a single pixel. However, as previously stated the large datasets generated by the experiment are suitable for multivariate analysis which can be used to gain significant improvement in signal to noise.

Multivariate analysis of multi-spectra imaging data

Principal component analysis (PCA) assumes that any dataset can be described by a linear combination of one or more pure components. As described in the paper by Walton[2], when the data matrix is multiplied by its transpose, a covariance matrix is formed which can then be decomposed into an orthogonal dataset, using singular value decomposition (SVD) sort. From this the maximum variation in the data is partitioned into abstract components with the largest eigenvalues. The abstract factors without any obvious features can be attributed to noise. If the original dataset is reconstructed from only those abstract factors containing significant information, the result is a new dataset where the influence of the noise is reduced in magnitude.

One limitation of the PCA approach to noise reduction is the significant computation time required. A substantial decrease can be achieved by operating on a subset of images at a time. In the example shown in figure 3, the dataset of 256 images is processed in groups of 16 images such that the SVD is applied to adjacent images and then stepped through the dataset instead of being applied to the entire dataset at once. The result is to move the vector containing the most information to the top of the dataset. Repeating this for a number of different components moves the most significant vectors to the top of the dataset. As the number of components in XPS is significantly less than the number of vectors that describe the entire dataset this results in a significant reduction in computational time. A PCA is then applied to the sorted vectors only. This approach has been termed SVD sort/reduced PCA and is discussed more rigorously by Fairley[3].

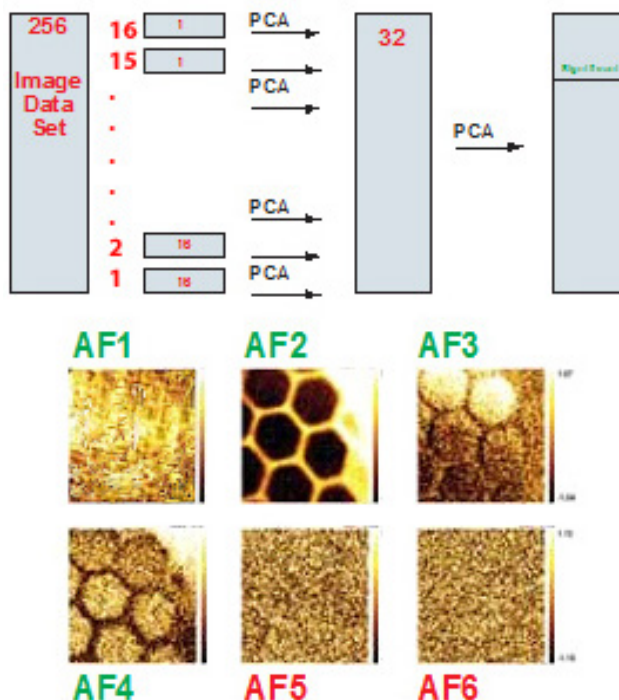


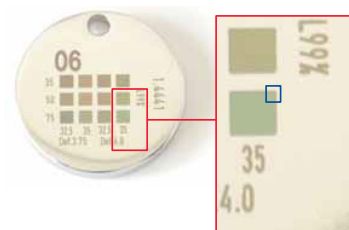
Figure 3 : SVD sort / reduced PCA processing of spectra from image dataset

Surface characterisation of laser marked implant quality stainless steel

Stainless implant materials according to ASTM F 138 are widely used for the production of implants for bone surgery. The corrosion resistance of these materials is obtained by a combined surface treatment including (electro) polishing and passivation. The necessary process of laser marking these materials for labelling and traceability was found to be detrimental to pitting resistance in some stainless steels. Here a disc shape specimen of ASTM F 138 stainless steel, shown in figure 4 was machined, electropolished and laser marked.

Electrochemical investigations revealed a good corrosion resistance of the non-lasered surface on the steel with the lasered surface found to build up a strongly oxidised surface layer.

Figure 4 : ASTM F 138 stainless steel laser marked disc. Area outlined in blue indicates the approximate area imaged by XPS



Experimental

XPS data were acquired from an AXIS Nova using monochromatic Al K α radiation. Images were acquired at 160 eV pass energy from a 400x400 μm^2 area with 256x256 pixels. Multi-spectral images were acquired from the Fe 2p region (698-720 eV) and the Cr 2p region (583-570 eV) at 0.5 eV steps with each image acquired for 30 sec respectively. Computation times for SVD sort/reduced PCA followed by background subtraction and fitting of components are typically 6-10 minutes on a standard PC.

Results

Figure 5 shows images taken from specific energy channels across the Fe 2p spectrum. Here the Fe 2p spectrum is generated by summing the spectra at each of the 256x256 pixels of the image. The single energy channel images are equivalent to images that would be acquired in a conventional imaging experiment. In the more conventional imaging experiment the background image would normally be subtracted from each single energy image to enhance image contrast at the expense of total intensity with the compromise that this type of background removal is highly simplistic.

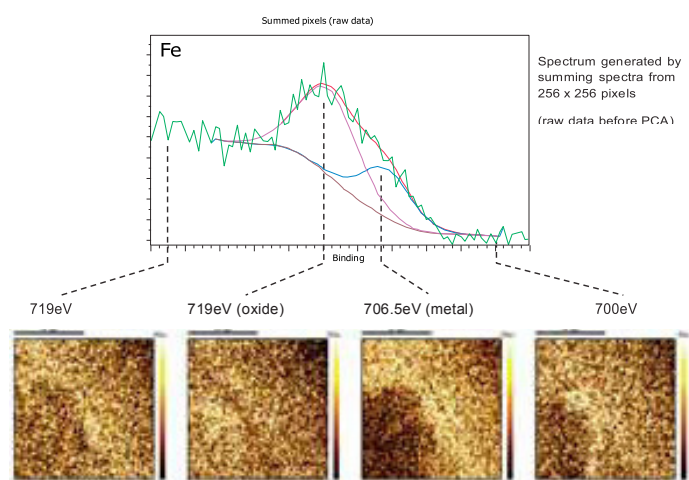


Figure 5: The average Fe 2p spectrum (generated by summing the spectra from each pixel in the image) and representative single energy channel images from the multi-spectral image dataset

After acquiring the multi-spectral images CasaXPS [3] processing software was used to perform an SVD sort/reduced PCA with the data being reconstructed from the first two components of the Fe 2p and Cr 2p datasets.

The quantified images shown in figure 6 can be contrasted directly with those shown in figure 5. It can be seen that there is significant enhancement of image quality through the combination of noise reduction, removal of X-ray/detector inhomogeneities and the application of proper background removal.

The overlay of the Cr and Fe images indicates that there is higher concentration of Cr at the edge of the laser marked part of the surface. This is likely to be significant in the corrosion behaviour of this material.

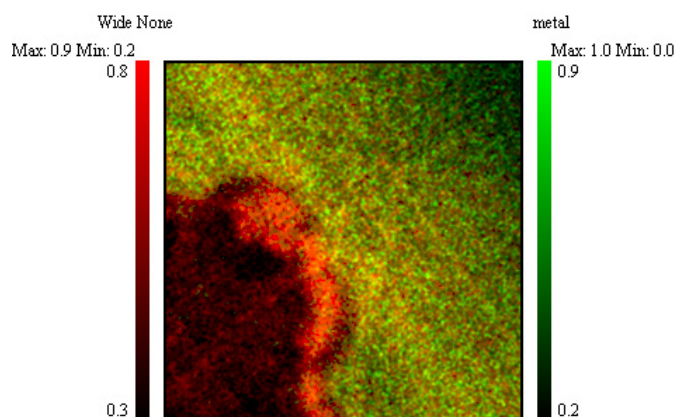


Figure 6: Overlay of Cr (red) and Fe (green) images reconstructed after SVD sort/reduced PCA of the multispectral datasets

Chemical state information

Following the multivariate analysis spectra were constructed from a 3x3 group of pixels which allowed subtraction of a genuine Shirley background followed by fitting of components to the Fe 2p_{3/2} envelope for the oxide and element. The spectra from the metallic and oxide regions are shown in figure 7a. Small variations in peak position were allowed to compensate for any lateral differential charging. The fitting of chemical components to the spectra at each pixel allows genuine chemical state images to be generated corresponding to Fe metal and Fe oxide as shown in figure 7b.

The surface ratio of Cr oxide to Fe oxide was clearly higher on the untreated compared to the laser marked surface areas.

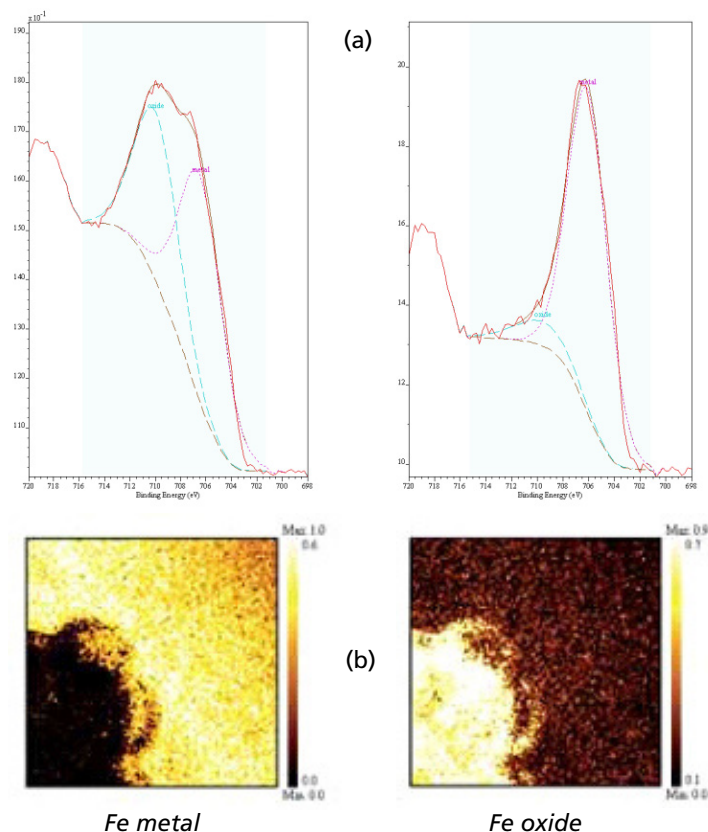


Figure 7 : (a) Fe 2p_{3/2} spectra generated by summing pixels from the metallic (left) and oxide (right) regions of the sample identified in the parallel images (b) XPS image of relative concentration of Fe metal (left) and Fe oxide (right) generated after fitting components to the Fe 2p_{3/2} spectrum.


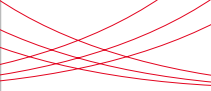

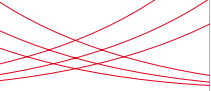
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- 2 Walton J., Fairley N. J. Electron Spec. and Rel. Phenomena 148 (2005) 29-40
- 3 Fairley, N. <http://www.casaxps.com>

Acknowledgements

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