Mathematical topographical correction of XPS images using multivariate statistical methods

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For rough heterogeneous samples, the contrast observed in XPS images may result from both changes in elemental or chemical composition and sample topography. Background image acquisition and subtraction are frequently utilized to minimize topographical effects so that images represent concentration variations in the sample. This procedure may significantly increase the data acquisition time. Multivariate statistical methods can assist in resolving topographical and chemical information from multispectral XPS images. Principal component analysis (PCA) is one method for identification of the highest correlation/variation between the images. Topography, which is common to all of the images, will be resolved in the first most significant component. The score of this component contains spatial information about the topography of the surface, whereas the loading is a quantitative representation of the topography contribution to each elemental/chemical image. The simple-to-use self-modelling mixture analysis (Simplisma) method is a pure variable method that searches for the source of most differences in the data and therefore has the potential to distinguish between chemical and topographical phases in images. The mathematical background correction scheme is developed and validated by comparing results to the experimental background correction for samples with differing degrees of topography. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: XPS; photoelectron imaging; topographical background correction; multivariate image analysis; PCA; Simplisma; multicomponent rough sample; polymer blend

INTRODUCTION

Surface analysis of materials of practical interest using imaging techniques often represents a challenge because the analytical signal yields depend not only on the surface composition but also upon the local topography. The contrast in images acquired in XPS may result from changes in elemental or chemical composition and sample topography. Topography may cause shadowing of x-rays, preventing or decreasing photoelectron emission. Photoelectron intensities will be low if images or spectra are acquired from regions that are shadowed. Analysis of multicomponent samples with multiple chemical phases, each represented by a combination of different elements, is a complicated task even for flat samples. Image intensity variations resulting from topographic contrast may be misinterpreted as evidence of chemical heterogeneity. Identification of chemical phases in multicomponent samples therefore requires differentiating between topographical and chemical contrast.

The use of imaging techniques in the chemical characterization of rough samples can require extra attention from the analyst and extra time in data acquisition. Images from samples with significant topography may contain areas that are outside of the depth of focus, because the current photoelectron spectrometers have a smaller focal depth of field in image acquisition mode than in spectroscopy mode. Intensities will be unusually high or low in areas of the image that are not in focus. A comparison of images acquired at several different binding energies (for different elements or chemical states) and/or the acquisition of small-area spectra can be utilized to distinguish intensity changes resulting from artifacts from those indicative of changes in chemistry. Background correction can be utilized to correct for topographical artifacts. One of the most common approaches to background image correction for surface analysis methods such as XPS and AES requires acquiring background images at slightly lower and/or higher binding energies than the binding energy of interest. Background-corrected images result from subtracting a background energy image, or the average of images acquired at energies above and below the energy of interest, from the image acquired at the peak energy. By this means, the effects of topography are minimized and image intensity variations reflect concentration differences across the sample. The additional image acquisition can, however, increase the analysis time significantly.

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Multivariate statistical analysis (MSA) methods are increasingly utilized in surface spectroscopic and imaging techniques to aid the analyst in interpreting the vast amount of information resulting from multi-dimensional data set acquisitions. The goal of MSA methods is to extract significant information from an image data set while reducing the dimensionality of the data. Principal component analysis (PCA) divides information into orthogonal components by transforming multivariate images into a number of principal component images. The objective is to identify images that are globally correlated or anti-correlated. Topographic contrast should be common to all elemental or chemical images acquired from the same area on the sample, so it is reasonable to expect that this information will be extracted as a separate principal component.

A variety of different methods have been developed as an extension of PCA to solve rotational ambiguity in the data analysis in order to extract positive, and potentially more chemically meaningful, components. One such method is a pure variable method—the simple to use self-modeling mixture analysis called Simplisma. Simplisma finds the pure variables (a variable at which only one of the compounds is present in the system) in the dataset and uses the intensities of the pure variables to estimate the concentration profiles. Non-negative loadings are obtained, which make them more useful for chemical phase identification. Simplisma searches for the source of the greatest differences in the data, and therefore has the potential to distinguish between chemical and topographical phases in images.

This work reports on the use of multivariate statistical methods in the resolution of topographical and chemical information from multispectral XPS images without experimental background acquisition. The mathematical topographical correction scheme is developed and validated by comparing multivariate analysis results to topographic correction based on background image acquisition for two samples with differing degrees of topography. The first sample is a rough fossilized carbonate rock and the second sample is a flat polymer blend from which multispectral images are acquired. No a priori knowledge of topographic influence on image intensity variation is required in order to utilize MSA correction methods.

**EXPERIMENTAL**

**Sample preparation**

Two samples are used to illustrate this method. The first is a fossilized rock sample collected from carbonate structures found on the shores of Lake Alchichica in Mexico. The carbonates at this lake form white mounds typically meters in diameter. The lake is situated in a volcanic crater and is an alkaline lake rich in Mg. This location is considered to be an analog for places like ‘White Rock’ on Mars.

The second sample is a polymer blend of poly(vinyl chloride) (PVC, MW 77.3 kDa) and poly(methyl methacrylate) (PMMA, MW 100 kDa) obtained from Scientific Polymer Products, Inc. As-received materials were used in 2% w/v solutions of PVC and PMMA in HPLC-grade tetrahydrofuran (THF). Solutions containing a 50:50 mixture of the two polymers were allowed to sit for 24 h before deposition onto Teflon watch-glasses using pipettes. The resulting films were air-dried for 24–48 h. The films were peeled from the Teflon substrate before analysis by XPS. The air-facing side of the samples was analyzed by XPS.

**Instrumentation for XPS**

The XPS spectra and images were acquired on a Kratos AXIS Ultra photoelectron spectrometer using a monochromatic Al Kα source operating at 300 W. The base pressure was 2 × 10⁻¹⁰ Torr and the operating pressure was 2 × 10⁻⁹ Torr. Charge compensation was accomplished using low-energy electrons. Standard operating conditions for good charge compensation are −2.8 V bias voltage, −1.0 V filament voltage and a filament current of 2.1 A.

**Data acquisition**

Eight areas on the rock sample were chosen for analysis. Large-area survey and high-resolution spectra were acquired at 80 eV pass energy for 2 min and at 20 eV for 2–5 min, respectively, for all areas in order to obtain a complete characterization of the rock composition as a function of the rock’s color.

For area 1 in Fig. 1, medium magnification (350 × 350 μm) peak images and two background images were acquired for all elements and for two types of carbon at 285 eV and 290 eV, referred to as C285 and C290, respectively, throughout the article. Small-area (27 μm diameter) survey spectra were acquired from several areas selected from the images.

For the polymer blend sample, medium magnification (350 × 350 μm) O 1s, Cl 2p and C 1s images were acquired for 3 min each at a pass energy of 80 eV. An images-to-spectra dataset was acquired from the same area. In this experiment, images are acquired as a function of binding energy (BE) across the range of interest, i.e. the C 1s peak. For the dataset utilized in this study, medium magnification images were acquired from 289 eV to 279 eV with a 0.2 eV step. This corresponds to a binding energy range of 291–281 eV after charge correction. A pass energy of 80 eV and an acquisition time of 2 min per image were employed. This experiment creates a multispectral dataset consisting of 50 images with a dataset size of 256 × 256 × 50.

**Figure 1.** Fossilized rock sample with visible white, brown and green areas. The size of the photo is 1.4 × 2 cm. Images were acquired from area 1 within the green part of the sample.
Programs used
All image data files were transferred from the KRATOS format to a format supported by MATLAB® and ENVI.11 MATLAB utilizes ASCII files, whereas a generalized raster data format consisting of a simple ‘flat binary file’ and a small associated ASCII (text) header file was utilized for ENVI.

Image analysis was performed using both MATLAB and ENVI. Multivariate image analysis utilized ENVI. The image PCA routine in the PLS_Toolbox12 in MATLAB is used to extract spectral or intensity profiles/loadings from images-to-spectra and degradation datasets, respectively. A Simplisma routine by Windig was used for the data analysis.8

RESULTS AND DISCUSSION
Introduction to mathematical correction procedure
Principal component analysis uses a mathematical procedure that transforms a number of correlated variables into a smaller number of uncorrelated variables called principal component images (scores). The objective is to identify images that are globally correlated or anti-correlated. This information is displayed as the loading of the different images that are responsible for correlation. Scores show the relationship between pixels that contribute the most to a principal component, resulting in a principal component image. The first principal component accounts for the source of largest correlation in the data, or for the pixels common to all or some of the image dataset.

Ideally, photoelectron images contain concentration information at any single pixel in the image, thus reflecting spatial differences in concentration. Images from samples with significant topography may contain areas that are shadowed or outside of the depth of focus. These areas will show intensity variations unrelated to chemical composition. Thus, not only differences in concentration of a particular element but also topographical heterogeneity will contribute to the total image contrast.

Image intensity variations resulting from topographic effects should be the same in the background and peak images. In a series of images the relationship between absolute pixel intensity and relative image contrast resulting from topography is a complicated phenomenon. As shown in Fig. 2, the position of each pixel within the image is fixed, therefore the same pixels within all images will be responsible for intensity variations resulting from topography. The absolute intensity in those pixels, however, will be different for each photoelectron image, resulting in different relative contrast within the images. The intensity will depend on both the binding energy (e.g. inelastic scattering increases with increasing binding energy) and shadowing or out-of-focus topographic effects (Fig. 2).

The topographical background is thus common to all elemental or chemical images, although the magnitude of the correction required will differ. Thus, if topographical heterogeneities are present within the analysis area, the first principal component will extract quantitative (loadings) and qualitative (scores) information with respect to topographic contrast variations, whereas all other components will contain chemical information from the image data. The mathematical representation of the topographical background for all images can be obtained from the first score and loadings. For the i-th image, the scorei must be multiplied by the value of load1 for the ith image

\[ \text{Math}_{\text{back, top}} = \text{score}_1 \times \text{load}_1(i) \] (1)

Moreover, exclusion of the first principal component during reproduction of the data from the loadings and scores should produce images that will contain only chemical information, thereby correcting the original data for topographic intensity variations. Inspection of mathematically corrected images will allow the analyst to evaluate the contrast in the original images without experimental background acquisition.

The following procedure of background subtraction is thus proposed:

1. Apply PCA to the multivariate image dataset consisting of N chemical/elemental images to obtain scores and loadings for all components. No scaling is applied to the data at this stage in order to keep the relative intensities of the original images.
2. Evaluate whether the first principal component represents topography or chemistry. The discussion below describes the characteristics of principal component loadings that can be used to distinguish between these two possibilities.
3a) If the first principal component represents topography, reproduce images Im with all but the first component

\[ \text{Im}_i = \text{score}_2 \times \text{load}_2(i) + \ldots + \text{score}_N \times \text{load}_N(i) \] (2)

3b) If the first principal component represents chemistry, then there is no topographical influence on image appearance and no correction is necessary.

In the second step of the proposed background correction procedure, the question of how to characterize the information captured in the first principal component arises. Several

![Figure 2. Topographical contrast vs. intensity, where the position of each pixel in each image is fixed. In a series of images the same pixels within each image will be affected by topographical contrast, whereas the intensities of the same pixels in different images will differ, thus complicating the identification of topographical effects.](Image 1 (BE 1) Image 2 (BE 2) Image 3 (BE 3) Image 4 (BE 4)
Topographical correction of XPS images

Plate 1. Photoelectron $350 \times 350 \mu m$ images for nine elements and two types of carbon acquired from area 1 (shown in Fig. 1): (a) original, (b) background; (c) background-corrected. Background subtraction causes more obvious spatial structure for some images (i.e. Mg, O, Cl, Na) and reveals chemical contrast in other images (i.e. K, F, S, N).

Plate 2. Principal component analysis results applied to the original (a) and background (b) images shown in Plate 1. The first principal component image for both datasets is the same, representing the topographical background component of the images. Note the equal contribution of all elements to the loading of the first component. For the original data (a) the second principal component is representative of Na/Cl images overlaying Mg/O/Ca images and the third is C285 overlaying Mg/Ca images. For background images (b) the second principal component is a chemical part of background combination of Mg/O and both types of C.

Plate 3. Background-corrected images achieved by mathematical correction through PCA. Similar results are obtained from mathematical correction and experimental background subtraction (Plate 1(c)), especially for images in which topography was a dominating factor in the original images (i.e. K, N, S, and F). No experimental background acquisition is necessary to distinguish topographical and chemical contrast by PCA.
methods can be used to investigate this. One approach is to acquire one additional image at a binding energy at which no chemical species are present, for a comparison with score image 1. A similarity between them indicates that the first component is indeed topography. Additional confirmation can be obtained by analyzing the shape of the loadings for the first component. Topography, as the component common to all of the images, will result in approximately equal contributions of all the variables to the first loading. Variations resulting from elemental or chemical changes will not result in such a correlation between all components. If one element or phase rises in concentrations, one or more element or chemical phase concentrations must decrease. Loadings resulting from changes in chemistry therefore will have a larger spread of variance (negative and positive) for different variables. Barkshire et al. have demonstrated a similar point. Their work shows that, in PCA results from Auger images, surface topography is one explanation for principal components that contain approximately equal contributions of variables.

Application to sample with significant topography

Spectroscopic and imaging analysis of the sample

Spectroscopic analysis of multiple areas on the fossilized rock sample distinguishes major regions with differing compositions. Table 1 shows quantitative results from survey spectra of areas chosen on the colored (1–4) and white parts (5–8) of the rock.

Areas on the white part of the sample are enriched in O, Mg and Ca and depleted in C and N, whereas areas on the colored part of the sample have higher concentrations of N and C. There are some areas on both white and colored regions on the sample that are enriched in Na and Cl. The biplot of scores and loadings for two principal components extracted from the data in Table 1 (Fig. 3) shows separation of the white and colored areas on the sample resulting primarily from differences in C and O concentrations.

Eleven elemental and chemical images were acquired from area 1, located in the green part of the sample in Fig. 1. From spectroscopic analysis, it is evident that this area is depleted in O, Mg, Ca and enriched in C and N. Plate 1 shows original, background and background-corrected images from this area. A visual analysis of the image provides significant information. The original Mg, O and Ca images are similar to each other. The Cl and Na images are also apparent. The K and F images are similar to each other and have intense features combining bright areas from both the O and Cl images. The image at C290 is similar to the Cl and Na images, whereas the C 285 image shows bright areas different from that in the C290 image. The N and S images are less intense and are similar to the Mg image. There are dark parts in all of the images. Small-area (27 µm diameter) survey spectra acquired from several selected areas of interest show that no elements are present in these dark areas, demonstrating that they are either shadowed or below the focal point. Small-area spectra acquired from intense areas within F, K and S images show homogeneous distribution of low concentrations of these elements, indicating the possibility that contrast and intensity in the original images may be due to topographical artifacts.

The background images (Plate 1(b)) for all of the elements and Cl images is also apparent. The K and F images are similar to each other and have intense features combining bright areas from both the O and Cl images. The image at C290 is similar to the Cl and Na images, whereas the C 285 image shows bright areas different from that in the C290 image. The N and S images are less intense and are similar to the Mg image. There are dark parts in all of the images. Small-area (27 µm diameter) survey spectra acquired from several selected areas of interest show that no elements are present in these dark areas, demonstrating that they are either shadowed or below the focal point. Small-area spectra acquired from intense areas within F, K and S images show homogeneous distribution of low concentrations of these elements, indicating the possibility that contrast and intensity in the original images may be due to topographical artifacts.

The background images (Plate 1(b)) for all of the elements are similar and, additionally, they resemble the original F and K images. The intensity in the background images increases with increasing BE, as is evident in the most intense background for the F image.

Table 1. Large-area quantification results from eight areas on the fossilized sample (shown in Fig. 1)

<table>
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<tr>
<th>Area</th>
<th>O 1s</th>
<th>Mg 2p</th>
<th>K 2s</th>
<th>Ca 2p</th>
<th>Na 1s</th>
<th>Cl 2p</th>
<th>C 1s</th>
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After experimental background correction (Plate 1(c)), additional details in spatial structure are apparent. The Mg, O and Ca images are similar to the original images, but removal of the imaging artifacts decreases intensity in some parts of the images. The similarity between the C285 image and N is noticeable after background removal. Parts of the C290 image are similar to the Ca, Mg and O images, which might be due to a mixed phase of metal oxides and carbonates. The K, F and S images are low-intensity, low-contrast images showing that indeed only small amounts of these elements are present, and that the contrast and intensity in the original images come from the topographical heterogeneities and not from differences in chemistry. Visual inspection of the original images can readily lead to inappropriate conclusions on the composition of chemical phases existing within this sample. The combination of background subtraction and small-area analysis from multiple areas on the sample is time-intensive, but allows for the understanding of sample composition.

Principal component analysis applied to original imaging data sets
As the number of images increases and the spatial arrangement of chemical phases becomes less obvious, it becomes easier to miss areas of correlation and anti-correlation within image datasets. The MSA methods can be applied to imaging datasets to assist in discovering chemical phases within the sample. Principal component analysis was applied to all three datasets shown in Plate 1, using autoscaling as a scaling option. Autoscaling weights all images equally, so that images with low intensities (S and K) are given the same importance as images with high intensities (Mg and O).

There are three principal components in the PCA model obtained from the original data (Plate 2(a)). The first component image is identical to the F image. The loading for this component has equal contributions from all elements, confirming that this component is a representation of topographical effects contributing to the images. Fluorine, which is the element at the highest BE, has the highest background and the highest contribution to the first loading. The first principal component therefore is identified as the background image representing topography of the analysis area. This is confirmed by the principal components extracted from the background images as described below. The second principal component image is similar to the Cl or Na images overlaying the inverse of the O and Mg images. The loading of this component shows the highest positive contribution from Na, Cl and C290 and the negative contributions from the Mg, N and O images. The third principal component image and loading are representative of C285 overlaid with the inverse of the Ca and Mg images. Principal component analysis applied to the original data thus extracts one topographical and two chemical components. Two principal components contain positive and negative contributions from different chemical phases, i.e. NaCl salt, Mg and Ca oxide/carbonates and the C285 phase. Chemical phases are extracted from original images without background subtraction but the resolution is not very clear, as will be evident from the phases extracted from background-corrected data below.

A two-component model is extracted from the background images (Plate 2(b)). The first component image is identical to the first component image extracted from the original images (Plate 2(a)). This confirms identification of the first principal component extracted from the original data as a representation of topography. Visually, the second component image has a contribution from the bright areas on the O, Mg and C285 images and the score shows the highest contributions from these elements.

Figure 4 plots loadings for the first principal component obtained from original images in comparison with intensity values obtained from background images. For this comparison, the ‘no scaling’ option for PCA was chosen in order to utilize original intensity values. The relative contributions of the elements to the first principal component loading and the experimental background are very similar. This is another confirmation that the first principal component extracted from the original dataset represents the topographical background.

Figure 5 shows three principal components extracted from the background-corrected images shown in Plate 1(c). The first principal component image is very similar to the O and Mg images. The loading has the highest contributions from O, Mg, Ca and C290, allowing for identification of the first component as Mg and Ca carbonates. The second component image is similar to the inverse of the Cl and Na images and the loading shows the highest negative contribution from Cl and Na. The third principal component image is similar to the image of C285 overlaid on the inverse of the Mg and Ca images. The highest contribution to this component comes from an organic phase (C285 and N) and a Ca/Mg oxide phase. This oxide phase was resolved from the carbonates only after background subtraction. Components representing four distinct chemical phases—Ca and Mg carbonates, Ca and Mg oxides, sodium chloride
Figure 5. Principal component analysis results applied to background-corrected images. No topographical component is extracted. The first principal component is a chemical phase of Mg/Ca carbonates/oxides, the second is an NaCl phase and the third is an organic phase (C285/N) overlaying the Mg/Ca oxide phase. Resolution of the chemical phases is improved after background subtraction compared with the original data (Plate 2(a)).

Mathematical background correction

The PCA analysis of the original images allows the analyst to differentiate topography from chemical information. Loadings for the chemical components provide information about the distributions of elemental/chemical species and contributions to particular chemical phases. This information, though, can be resolved better and visualized by removing the first principal component from the original images through the procedure of mathematical background correction described above. The original data were reproduced using score images and loadings from principal components 2–11. Plate 3 shows 11 images obtained through mathematical correction. The mathematically corrected images are closer to the experimentally corrected images (Plate 1(c)) than they are to the original images (Plate 1(a)) because they have the same distribution of features for the different elements. The most important information resulting from the mathematical correction is for the elements present at low concentrations, i.e. K, S and F. It is critical to know if the contrast observed in these images results from chemistry or topography. As Plate 3 shows, both the experimentally and the mathematically corrected K, F and S images confirm that the sources of the contrast and intensity in the original images are the topographical artifacts. This information is thus obtainable from the original data without acquiring additional background images and small-area spectra.

Simplisma analysis

The Simplisma method was also applied to the original and experimentally corrected datasets (Fig. 6). Simplisma extracts four pure images from the original dataset (Fig. 6(a)), three of which are chemical phases and the fourth represents the topographical background. It is interesting to note that the background was extracted not as the first pure image but as the last or least pure. Simplisma searches for the source of maximum variability among the dataset and not for the source of commonality as with PCA. The first and most distinct chemical phase is the sodium chloride phase, the second phase is a combination of Ca and Mg oxides and carbonates and the third is an organic phase of C285 and N. It is only after removing these three sources of chemical variability that Simplisma extracts the fourth component. This fourth component has the highest relative contribution from F and S, which have the highest contribution from topography in the corresponding original images. No background correction is required for distinguishing between the chemical phases in this multivariate analysis. The quality of the resolution of pure images from the original dataset is very similar to that obtained by PCA applied to the dataset after experimental background correction (Fig. 5). Pure spectra accompanying each pure image carry the necessary quantitative information on chemical phases. Both S and K, for example, have low contributions to the first three pure images, confirming that the source of the high intensity and contrast in the original images of these elements is not from chemistry but rather from topography. It is interesting to note that F has a high significance in all four pure images owing to the high background in the F image.

After experimental background correction, Simplisma extracts five pure components (Fig. 6(b)). Three of them (3–5) resemble the three chemical phases extracted from the original dataset, and instead of a topographical background phase the first and second pure components are exclusively due to K and F, respectively. Pure images of these two components are relatively featureless. These components reflect the changes introduced by experimental background subtraction. Errors resulting from over- or under-subtraction of intensity will be the most noticeable in images of elements present at the lowest concentrations (K and F in this example).
Figure 6. Simplisma applied to original (a) and background-corrected (b) images. Three chemical and one topographical pure component are extracted. No background subtraction is necessary for Simplisma to resolve the chemical phases. Note that F has a high contribution to all four pure components owing to the high background. Five pure components are extracted from the background-corrected data (b): three are the same chemical phases that are extracted from the original data and two result from the contribution of topography to the K and F images.

Figure 7. Simplisma applied to the mathematically corrected images. Good resolution of chemical phases is achieved. The three pure components are identical to the first three obtained from the original data (Fig. 6(a)). No components due to topography or image subtraction artifacts are resolved.

These results demonstrate the sensitivity of Simplisma to artifacts introduced into images. The quality of the mathematical background correction therefore can be tested by applying Simplisma to mathematically reproduced data from all but the first principal component (Plate 3). Figure 7 shows three pure components resolved after this test. These three components represent the three chemical phases discussed above. No components due to topographical background or background subtraction artifacts are resolved, meaning that the proposed correction scheme shows promise.

Application to a sample with insignificant topography

For the polymer blend sample, an images-to-spectra dataset was acquired as described in the Experimental section. Selected images from this experiment are displayed in Fig. 8(a). The first and last images in this set, which are acquired at BEs in the featureless parts of the C 1s spectrum, can be considered as background images. These images do not have significant contrast or intensity, confirming the flatness of the sample. Spectra reconstructed from two
different areas are shown in Fig. 8(b). One is representative of the PVC-enriched phase of the polymer blend, whereas the other is a PMMA-enriched area of the polymer blend.

Principal component analysis applied to these data results in the two components shown in Fig. 9. The first loading has a spectrum-like shape, meaning that different binding energies make different contributions to this component. This result is one indication that the component is not a topographical phase but rather a chemical phase.

An image of the experimental background (the first and last images in the images-to-spectra experiment) is different from the first principal component score image, confirming this conclusion. Principal component analysis applied to the original data gives only chemical components, meaning that there is no significant topography present. The topographical background correction is thus not necessary for the data acquired from this sample. A loading of the first component can be curve-fitted with PVC and PMMA spectral shapes, so we can identify it as a polymer blend phase. The second loading has negative components. Peaks around binding energies corresponding to O–C=O and hydrocarbon (HC) species have the largest contribution to this component. This component can be identified as a product of PVC degradation in the blend under x-ray exposure.5

Simplisma applied to the same dataset resolves two chemical components with positive values in loadings (Fig. 10). This pure variable approach allows for a more chemically reasonable resolution. Pure component images are inversely correlated. A curve-fit of pure component spectra using PVC and PMMA standard spectral shapes allows the identification of both components, the first as a PVC-enriched phase of the polymer blend and the second as a PMMA-enriched phase of the polymer blend. Hydrocarbon (HC), a product of PVC degradation, is present in a larger amount in the PVC-enriched phase than in the PMMA-enriched phase.

Figure 8. (a) Selected C 1s 350 × 350 µm images from an images-to-spectra dataset acquired from the PVC/PMMA blend sample. Fifty images were acquired in the C 1s spectral range. The first and last images can be considered to be background images. (b) Spectra reproduced from the areas of interest. The spectrum on the left is PVC-enriched and, the spectrum on the right is PMMA-enriched.

Figure 9. Principal component analysis applied to images-to-spectra data from the polymer blend. The first principal component is a chemical component, based on the spectrum-like shape of the loading and the different spatial structure of the principal component image compared with the experimental background image. This component is identified as a PVC/PMMA blend. The second component is a product of PVC degradation within the blend. No topographical correction is necessary for this sample.

For this flat sample both MVA methods extract chemical phases and no topographical information, confirming the absence of topographical influence on the image appearance.
CONCLUSIONS

This work suggests that multivariate statistical methods can assist in resolving topographical and chemical information from multispectral XPS images without experimental background acquisition. The mathematical background correction scheme is developed and validated by comparing results with the experimental background correction for samples with differing degrees of topography.

For a rough sample with significant topographical influence on the original image appearance, PCA extracts topography (which is common to all of the images) as the first most significant component. The score of this component contains spatial information about the topography of the surface, whereas the loading is a quantitative representation of the topography contribution to each elemental/chemical image. Original data are corrected by reproducing each image with all but the first principal component. Mathematical background correction results in images similar to those obtained by the experimental correction scheme. Visual inspection of mathematically corrected images allows the analyst to make conclusions on the source of contrast in photoelectron images. No background correction is required for distinguishing between chemical phases.

For a flat polymer blend sample, PCA applied to the original data extracts only chemical components, confirming that there is no topography present and thus background correction is not necessary for the data acquired from this sample. No prior knowledge of topography influence on the original images is necessary for the PCA-based correction to be utilized.

Simplisma appears to be more effective than PCA in resolving chemical and topographical phases from original images. Instead of mixtures of chemical phases appearing in a single chemical component, pure chemical phases are resolved as separate components. The resolution of pure images from the original dataset is similar to that obtained by PCA applied to the same dataset after experimental background correction.

The results presented herein demonstrate that if data acquisition time is limited, or questions of interpretation arise after the acquisition of image datasets, multivariate methods can provide significant assistance in distinguishing between topographical and chemical contrast in photoelectron images.

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