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MULTI-DIMENSIONAL DATA ANALYSIS AND PROCESSING IN ELECTRON-INDUCED MICROANALYSIS

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Abstract

The new facilities offered by computer controlled data capturing devices allow one to open the field of data acquisition from one or two-dimensional spaces to multi-dimensional ones. The methods used for analysing and processing such data sets have to move in parallel towards multi-dimensionality. Multivariate Statistical Analysis is one of the tools which appear to be promising in : data analysis, data reduction, data processing (multivariate noise filtering), data interpolation and extrapolation. Illustrations of these different possibilities are given in the fields of spatially resolved spectroscopy, time-dependent spectroscopy and elemental mapping from Electron Energy Loss Spectroscopy.

Key Words: Multivariate statistics, time and space series, elemental mapping, data processing, microanalysis

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Introduction

Due to the increasing facilities offered by computer controlled data capturing devices, microanalysts and microscopists are now allowed to open the field of data acquisition, moving from a one-dimensional space (e.g. spectrum : $I(E)$) or a two-dimensional space (e.g. image: $I(x, y)$) to higher dimensional spaces. This is the case, for example, for time-dependent spectroscopy ($I(E, t)$) or for the recording of image sequences either for studying dynamic processes ($I(x, y, t)$) or the location of a chemical species in a specimen ($I(x, y, E)$). Even more sophisticated procedures can be expected in the near future (time dependent energy filtered series, three-dimensional chemical mapping). In conventional microscopy also, three-dimensional data may be recorded, either for performing 3D-reconstruction (confocal microscopy, electron tomography, X-ray microtomography) or for studying dynamic events.

Facing such a large amount of data, the question about the most appropriate tools for analysis and processing arises. Besides the extension of "standard" methods developed for mono-dimensional data, some tools specifically developed for multi-dimensional data sets can be valuable.

One such tool is Multivariate Statistical Analysis (MSA). This technique was developed at the beginning of the century to help to interpret data sets in the fields of Sociology and Econometry. It was introduced in the seventies for applications in chemistry (Malinowski and Howery (1980)) (mass spectrometry, chromatography, spectrophotometry, etc.), and in the eighties for applications in Auger spectroscopy (Garenström (1981, 1986), Browning (1987),

Prutton et al. (1987, 1990), Kenny et al.(1992)), in X-Ray spectroscopic imaging (King et al.(1989), Paque et al.(1990)) and in high resolution electron microscopy (Van Heel and Frank (1980, 1981), Frank and Van Heel (1982), Savoji and Burge(1983)) where it has mainly been used for analysing a data set made of similar (but not completely equivalent) views of a given object and for the automatic partitioning of this complex data set into several homogeneous subsets. It was later suggested that this technique could also be well suited to the processing of energy filtered image sequences used for elemental mapping (Hannequin and Bonnet (1988), Bonnet and Hannequin (1989), Trebbia and Bonnet (1990), Trebbia and Mory (1990)).

It was shown that MSA could be useful for performing several different tasks : data analysis, data processing (filtering) and also data interpolation and extrapolation. These different possibilities are briefly described in the next subsection.

MSA : Basics and Possibilities

Although it may appear to be some "magical speculation" to non-specialists, MSA is based on a solid mathematical background and relies on a very simple idea which is summarized hereafter.

Let us suppose that one has recorded several measurements pertaining to a single experiment : for example, a collection of N EDX spectra obtained at different locations on a given specimen. If no elemental concentration variation between these different sampling areas on the specimen exists, then all these spectra should exhibit the same quantitative features (peak locations, peak/background ratios). In other words, they should be proportional to each other (the only varying parameter being the acquisition time) and, from a mathematical point of view, they are fully dependent : from any given spectrum of that collection, one can build any other one (within statistical error) provided that one knows the arbitrary multiplicative coefficient (integrated intensity ratio) to be used as a scaling factor. The situation is identical to a collection of parallel vectors with different norms : all these vectors have the same basis, that we shall refer to later as a factorial axis, but different scaling factors containing the information on the magnitude. Each one of these scaling factors is the coordinate of the relevant vector on the factorial axis.

On the other hand, if any concentration variation between two probed locations exists, the two related spectra are not proportional and this situation is similar to two independent vectors generating a vectorial space of dimension two.

MSA benefits from such a property. Each measurement (i.e. a spectrum of 1024 channels) is considered as a single vector (with 1024 components), the whole data set, the N spectra, being a collection of N vectors. These N vectors are gathered in a single matrix (N by 1024 in our example) and MSA merely finds the characteristics of the vectorial space generated by this matrix : looking for the eigenvectors (the so-called factorial axes) enables one to find whether some information is redundant (any couple of proportional spectra would pertain to the same eigenvector, thus reducing the dimension of the vectorial space generated by the whole data set) and to classify hierarchically the non-proportionality between spectra (peak variations, noise fluctuations, ...) by looking at the eigenvalue associated to each eigenvector.

The details of the calculations performed by MSA can be found elsewhere (Trebbia and Bonnet (1990)) and we would like to point out some comments here:

1) MSA is an analysis procedure.

a) It gives the number N' of factorial axes. If $N' < N$, then some measurements are redundant and convey no special information, but the fact that some kind of stationarity has been observed.

b) Provided that the original matrix of data has been properly set, the eigenvalue associated with each eigenvector is a direct measure of the relative importance of the specific information carried by this factorial axis.

c) MSA gives the coefficient of the linear combination needed to build, from the original data set, the eigenvector set. In other words, one gets the coordinates, also called weights, on the factorial axes of each one of the original spectra. These coordinates are nothing but the scaling factors discussed above. Note that, in the general case, these coordinates may be positive or negative, depending on the location, in the N' - dimensional vectorial space, of the point taken as origin.

2) Looking at these results (eigenvalue for each eigenvector and coordinates of each measurement), the user has to face the interpretation of the results and to give a

physical meaning to the information conveyed by the factorial axes. It may be of use to look at the projections of the whole data set on each factorial axis: a close inspection of which channels in the spectra are linked to a specific factorial axis is of great value for making a decision.

3) Once the interpretation of MSA results has been made, one may go to the next step : the processing of the original data. For example,

a) if one wants to discard a peculiar kind of information which has been interpreted as noise or artefact, one has merely to reduce the dimension of the vectorial space, removing any unneeded factorial axis. Each measurement is then restored in this sub-space. This process is analogous to applying a specific filter, the type of filter being determined by the number, the importance and the physical meaning of the factorial axes which are taken into account. Examples of such a process (reconstitution with a reduced number of factorial axes) can be found in (Bretaudière and Frank (1986)).

b) discarding a part of information which has been evaluated as being of less-importance can also be seen as data compression. Let us suppose, for example, that a collection of N measurements gives rise to only N' "significant" factorial axes, the word "significant" being determined through the interpretation step 2) above. Then, the reconstruction of the whole data set with only these N' "useful" factorial axes would lead to a compressed data set from which any "useless" information has been removed.

c) one can build a scatter diagram (Jeanguillaume(1985), El Gomati et al.(1987)). It consists in representing an element (pixel, energy channel) by a point in the N'-dimensional vectorial space (generally, N' is restricted to 2 or 3). The observation of this scatter diagram can be of great help in the interpretation of data : the gathering of data within restricted space volumes would lead to automatic classification algorithms. MSA is thus able to discriminate among all the data which pertain to a specific space volume, a cloud, sharing the same specific properties, this specificity being determined by the coordinates of the gravity center of the cloud.

d) in the same way, one may look at this scatter diagram and try to find some trends between selected data (linear evolution of their coordinates along a specific axis, for example). Therefore, such an analysis enables

one to find an appropriate model describing as closely as possible the observed trends, and to use this model for the estimation of the coordinates of an intermediate point. This "interpolation" facility, leading to the construction of a fictitious (i.e. not actually recorded) measurement only requires two assumptions : i) the validity of the model and ii) the continuity of the model in the unexplored area of the diagram.

e) the "extrapolation" facility, that is the construction of a fictitious image beyond the limits of the actual diagram, is obviously a little bit more hazardous since the two previous assumptions, which must also be fulfilled, are more speculative : there is no way, with MSA, of confidently predicting that there is no fatal break in the model at the frontiers of the diagram. This point will be discussed in more detail in the section devoted to the zero-dose extrapolation.

To conclude this subsection, we would like to emphasize that the efficiency of MSA, when compared to other monovariate procedures, precisely relies on the fact that the analysis is performed on the complete data set, constructed as a whole. The validity of the analysis is therefore more established if many measurements are taken into account. The higher the number of measurements (N in our example), the greater is our knowledge on the possible links between them, and, for example, the more accurate the model used for interpolation.

But one must never forget that MSA is mainly an analysis tool, the validity of the processing tasks being highly dependent on the extra-assumptions needed by the process.

MSA in Microanalysis: Some Possible Applications

In the present paper, we would like to investigate some possible applications in the field of electron induced microanalysis, i.e., electron induced spectroscopies (energy dispersive X-ray microanalysis, EDX; Auger electron spectroscopy, AES; electron energy loss spectroscopy, EELS; etc.) and elemental mapping.

Spectroscopy: Classical spectroscopy consists of recording the signal induced by a physical event as a function of energy (or wavelength). Improved spectroscopic techniques consist of repeating several such

experiments for different values of another parameter (time, space location, emergence angle, etc.) leading to the following (non exhaustive) classification :

Time dependent spectroscopy is a method which is beginning to be used in several laboratories where it benefits from the possibilities offered by parallel detection spectrometers. Its goal is to study dynamic phenomena such as the diffusion of ions under the electron beam, the nucleation process of precipitates in materials (see for instance Ellis et al.(1985)). Such experiments have already been performed by Craven et al. (1989) and Tence et al. (1990) for instance. Though the data sets produced by time-resolved spectroscopy can be processed by techniques developed in classical spectroscopy (background modelling and subtraction, peak area estimation), we believe that many tasks can be solved much more conveniently by processing the whole data set at once with MSA. A preliminary investigation of the possible applications of MSA to time-dependent spectroscopy was reported (Bonnet et al. (1991)). A difficult but exciting challenge opened by MSA is the possible extrapolation to zero-dose (Bonnet and Hannequin (1988)). We will show that, in favorable situations, MSA seems to be one appropriate method to perform this task.

Spatially (or angular) resolved spectroscopy is also beginning to be applied in several labs. The space parameter can be the depth in the specimen or a lateral dimension (Disko et al.(1991) for instance). In the former case, one speaks of depth profiling, a technique which is sometimes used in Auger spectroscopy, in addition to SIMS, in order to get estimations of the concentration of a given element as a function of depth. The latter case concerns studies of concentration variations along an interface for instance. Here again, the spectrum sequence could probably be processed more efficiently by multivariate methods than by a univariate method applied sequentially to each individual spectrum. As an example, we will show how the concentration variations of one or several elements can be estimated without any need to model the background or the characteristic peaks, provided that some additional information is available concerning the spectra of pure elements.

Imaging : Image sequences are also used in the field of microanalysis. Two different kinds of image sequences are in fact recorded in the

context of elemental mapping. The first one consists of the several images required to build a single elemental map, when using electron energy-filtered images for instance. It is well-known that one single image, recorded at the energy-loss characteristic of a given element, cannot be considered as representative of the true concentration of that element. The reason is that the characteristic ionization signal (which is proportional to the true concentration) is superimposed on a large background which is non characteristic but depends on several phenomena (specimen thickness, presence of other species). It is also widely accepted that even two images (one recorded below the characteristic energy-loss edge and one recorded above the edge) are not sufficient. Therefore, image sequences made of several images (below and above the edge) are required in order to compute an elemental map. The standard method used to perform this computation is based on a modelling of the background (below the edge) and a subtraction of the extrapolated background (above the edge) (Jeanguillaume et al. (1978), Bonnet et al.(1988)). Since this method sometimes suffers from drawbacks, the possible applications of MSA to these image sequences were investigated over the last three years. A first method consisted of submitting the whole data set to MSA. A new alternative is to only process the images below the edge and then, by extrapolation in the factorial space, to compute a "fictitious" background for energy losses above the edge. These possibilities will be described in the last section.

The other kind of image sequences encountered in the field of elemental mapping consists of several maps (for different elements) of the same specimen region. This situation can be found for any kind of spectroscopy: X-Ray imaging, Auger mapping, EELS mapping. In this case, the different images (especially those of low concentration elements) are often rather noisy. It is of course possible to improve the signal-to-noise ratio by applying standard processing techniques (Fourier filtering, etc.) to each image separately. But this procedure cannot take the often important correlations which exist between the different maps into account. Here again, MSA is an appropriate method for performing such a task, but this point will not be considered any more in this paper.

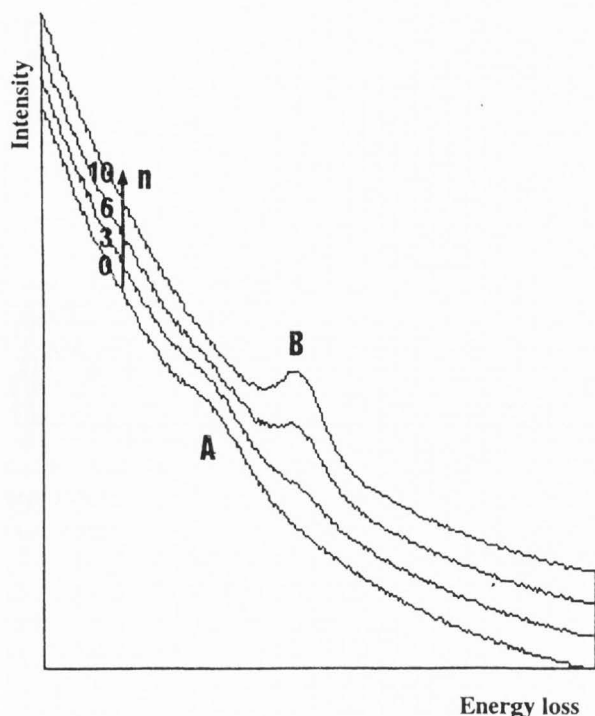


Fig. 1 : Four of the spectra which compose a simulated spatially resolved spectrum series. The concentrations in element A (lower characteristic energy loss) and in element B are supposed to be anti-correlated, as it would be the case for a compound $A_x B_{1-x}$ for instance, where x is a spatially-varying parameter. The four spectra are supposed to correspond to the compounds $A_1 B_0$ ($n=0$), $A_{0.79} B_{0.21}$ ($n=3$), $A_{0.35} B_{0.65}$ ($n=6$) and $A_0 B_1$ ($n=10$).

Quantification of Concentration Variations in Spatially Resolved Spectroscopy

As stated in the introduction, this technique provides data sets composed of a series of spectra $I(E)$ obtained at different locations in the specimen. Generally, the specimen sites explored are along a vertical direction (depth profiling) or along a lateral direction, normal to an interface for instance. Quantifying the concentrations of the different elements by "standard" techniques would rely on background removal, peak area estimation... The problem becomes more difficult when several elements give rise to overlapping peaks since in this situation, deconvolution or modelling must be performed. In this section, we would like to show that MSA applied to the whole spectrum series could help in understanding and

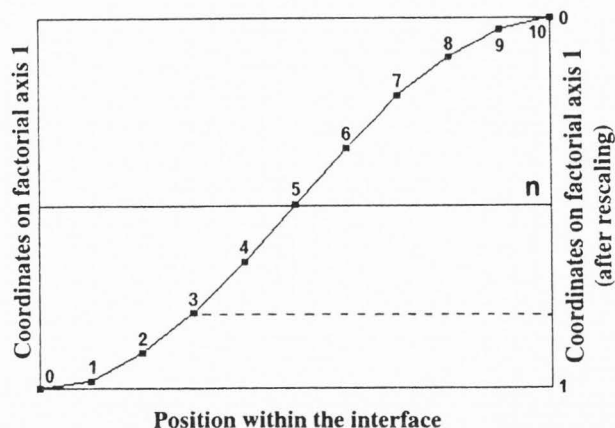


Fig. 2 : Coordinates of the different spectra of the simulated series (see Fig. 1) on the first factorial axis, after MSA. In this favorable situation, this graph plots directly the law of evolution of the concentration parameter x as a function of the spatial parameter (here a cosinusoidal shape). Furthermore, the concentration in element A can be directly read as its coordinate on axis 1 provided that this axis has been previously scaled from 0 (spectrum without element A) to 1 (spectrum corresponding to pure element A). For instance, the coordinate of spectrum number 3 is 0.79, which corresponds to the simulated value : $0.5(1 + \cos 3\pi/10)$.

quantifying the concentration variations. For this purpose, we have built two simulated spectrum sequences, each spectrum being composed of a decreasing background, two overlapping Gaussian peaks and Poisson noise. First simulation : perfectly correlated concentrations.

We suppose that we are facing a binary compound $A_x B_{1-x}$, with x varying across an interface from $x=1$ to $x=0$, according to a cosinusoidal law for instance. Eleven spectra ($n=0$ to 10) are simulated and four of them (corresponding to $A_1 B_0$, $A_{0.79} B_{0.21}$, $A_{0.35} B_{0.65}$ and $A_0 B_1$) are shown in Fig. 1. The MSA results can be summarized as follows :

- only one factorial axis is significant, due to the fact that the concentration variation for elements A and B are perfectly anticorrelated,
- the coordinates of the spectra on the main factorial axis (number 1) display the shape of the model which describes the concentration variations, here a cosinusoidal model (see Fig. 2),

- the concentration in element A (or B) can be directly obtained from this figure, provided that concentrations are known for at least two experimental spectra. (In this situation, the acquisition of two spectra far away from the zone of variation gives these references): the factorial axis has only to be calibrated (in concentration units) and then the ordinate of any spectrum immediatly gives the concentration.

Second simulation : partly correlated concentrations.

If we suppose that the concentration variations of the two (or more) elements to be considered are no longer perfectly anti-correlated, the situation becomes slightly more complex because we have to work in a two-(or more) dimensional space. This is illustrated through another simulation. Crossing an "interface", the concentration of element A is supposed to decrease exponentially as $e^{-0.5n}$ ($n=0$ to 10) and the concentration of element B is supposed to increase linearly as $n/10$. As in the previous simulation, the characteristic peaks related to each element are supposed to be overlapping Gaussians with different widths. Now, MSA results can be summarized as :

- two factorial axes are significant because the concentration variations are no longer exactly anti-correlated. These two main axes explain 99% of the total variance observed between the eleven spectra. The nine remaining axes have been stated as non significant. Factorial axis 1 is representative of the anti-correlated part of the variations whereas factorial axis 2 represents the correlated part. This can be confirmed by the observation of the factorial components, i.e. of the coordinates of the energy channels on the factorial axes (see Fig. 3).

- The coordinates of the spectra must be observed in a two-dimensional factorial space (axes 1 and 2) (see Fig. 4).

- However, the coordinates of the different spectra in this representation space are not directly proportional to the concentrations in elements A and B. The reason is that the decomposition of the data set into orthogonal components has no direct physical meaning (in other words, axis 1 and 2 are not directly connected to elements A and B). Furthermore, the point used as the origin of the factorial space has no reason to correspond to a physical situation where the concentration in elements A and B are nil ($C_A = C_B = 0$).

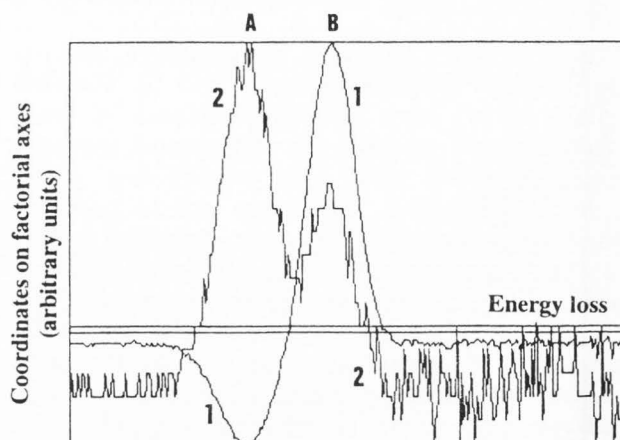


Fig. 3 : Eigen-spectra corresponding to a simulation of spatially resolved spectroscopy where the concentrations of two elements (A and B) are not exactly anti-correlated. In this case, the first eigen-spectrum (i.e. the component connected to the first eigen-value in the matrix decomposition) corresponds to the anti-correlated part of the concentration variations and the second eigenspectrum corresponds to the correlated part.

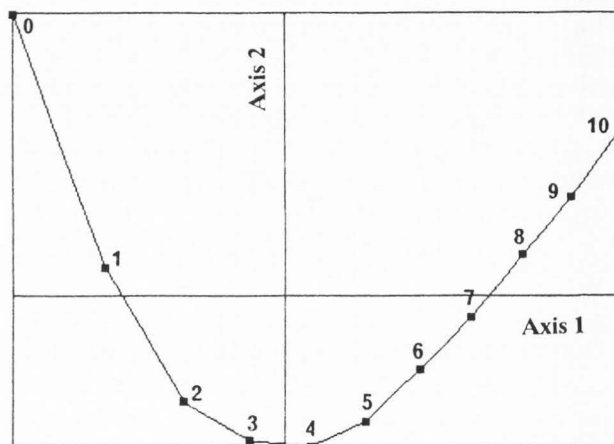


Fig. 4 : Coordinates of the different spectra (second simulation) in the factorial subspace generated by axes 1 and 2.

- The situation can be greatly improved if one is able to add to the data set submitted to MSA a spectrum corresponding to such a situation. In real world experiments, this should be done either by the acquisition of such a spectrum, if there exists in the specimen regions where neither element A nor element B are present. Or, more probably, this could be done by modelling the background in the experimental spectrum sequence. In the present simulation,

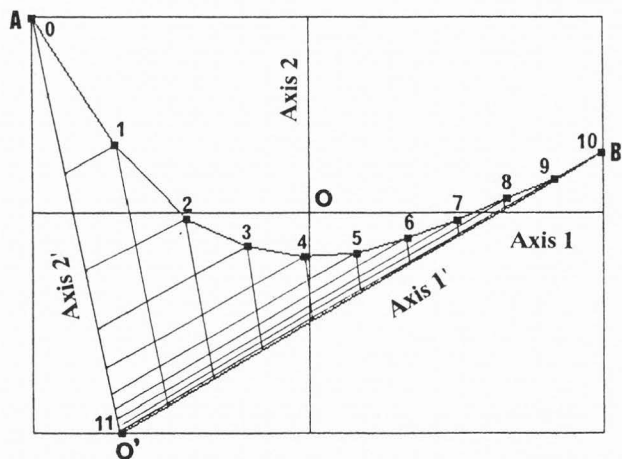


Fig. 5 : Coordinates of the different spectra in the new factorial subspace (axes 1 and 2) when one spectrum (without any characteristic peak corresponding to element A or B) has been added to the previous series. This additional spectrum (number 11) defines the origin O' of coordinates in a new (oblique) factorial space (axes 1' and 2') which can then be used, after scaling, to read directly the concentrations in elements A and B. For instance, the relative coordinates of spectrum number 1 are 0.09 and 0.63 on axes 1' and 2' respectively. These values agree closely with the simulated values (0.10 and 0.61 respectively).

it was of course easy to add a simulated background in the data set.

The weights (or coordinates) of the spectra on the two new main factorial axes after introducing the "reference" spectrum 11 (concentrations of A and B nil) are displayed in Fig. 5.

The additional point O' in the factorial space can then be used as an origin for a new set of modified factorial axes ($O'B$, $O'A$), where A is the point representative of $C_A = 1$; $C_B = 0$ and B corresponds to $C_A = 0$; $C_B = 1$. (This procedure is a particular realization of the so-called "oblique analysis" described by Hannequin and Bonnet (1988)).

Now, it is possible to obtain the concentrations for any spectrum by determining the coordinates of the different representative points on the new factorial axes ($O'B$, $O'A$). This is illustrated in Fig. 5. Note : Though the procedure described above for the quantification of mixed elements spectra appears very fascinating at first sight, it must be stressed that several requirements must be

fulfilled for its use in experimental situations. These requirements are the need to define precisely the locations of the representative points O' , A and B in the factorial space. Fixing points A and B implies that there are regions in the specimen where element A (respectively B) can be found alone. Furthermore, the fact that the quantification can be performed without taking into account the background comes from the hypothesis that the background does not change from one spectrum to another, including the "reference" spectrum (number 11 in our simulation). There is no doubt that in many experimental situations, one or several of these requirements cannot be fulfilled and that the application of such a technique would be more questionable than in these simulations.

Extrapolation to Zero-Dose in Time-Resolved Spectroscopy

In a previous paper (Bonnet et al. 1991), we tried to define the possible applications of MSA to time-resolved spectroscopic data, i.e., to spectrum sequences recorded as a function of time: $I(E,t)$. We have found that the first goal of applying a global multivariate technique is to carefully analyse the data set. Indeed, the more sophisticated the acquisition procedure, the more important the risks of artefacts. But we have shown that MSA is able to check the consistency of a data set and to depict artefacts such as primary current modification (see also Barkshire et al. (1991)), spectrometer drift... We have also shown that, for consistent data, MSA is able to plot the evolution of the sequence, to find the number of information components.

After analyzing the content of the data set, MSA can be used to process it by filtering the information components and reconstituting the data set with only the desired components.

Besides reconstituting the data set with its true weighting coefficients on the factorial axes, it is also possible to perform the reconstitution with other (interpolated or extrapolated) coefficients, thus leading to "fictitious" spectra. This idea is at the origin of the extrapolation to zero-dose in spectroscopy (Bonnet and Hannequin (1988)).

We must say that this idea did not lead to much experimental verification up to now, maybe because it is not completely mature. In the present paper, we would like to check by a simulation an idea suggested by Cazaux (LASSI,

Reims; personal communication) in order to increase the chances of success of such an extrapolation to zero-dose.

The problem is that, even if MSA may help in determining a model for the evolution of an element in a time - resolved experiment, the extrapolation of the model outside the experimental domain (in forecasting as well as exploring towards the past) requires the introduction of hypotheses, the weakest of which being the hypothesis of continuity. In order to avoid the use of strong (and maybe unjustified) hypotheses, it would be interesting to get not only one evolution model but several models supposed to converge towards a unique origin.

To perform time-resolved spectroscopy means the realization of several experiments (on several equivalent specimen regions) at different dose rates and the submission of the whole data set to the analysis. If the different dose rates lead to different evolution models, then these models could have a common origin at a point which represents the zero-dose situation.

In order to illustrate this possibility and the ability of MSA to process such data, we performed the following simulation :

Three groups (a,b,c) of five spectra are computed. Each one is made of a decreasing background and a Gaussian characteristic peak. Poisson noise is also simulated. The amplitude of the peak decreases as a function of time but the law which describes the amplitude decrease is different for the three spectrum sequences : $(1-n/10)$, $(1-n/10)^2$ and $(1-n/10)^{1/2}$, where n is the spectrum number in the series ($n=1$ to 5).

The fifteen spectra are submitted together to MSA. Only one factorial axis is significant (77% of the total variance). The weights of the different spectra on this axis are displayed in Fig. 6. One can see that the three groups corresponding to three different dose rates are characterized by three different traces in the (time - axis 1) space. These three traces can be mathematically modelled and the representative point corresponding to the zero-dose can be obtained at the intersection of the three traces, giving the weight of the fictitious spectrum on axis 1. This weighting coefficient can then be used to build the fictitious spectrum, taking into account the eigenfactors resulting from the analysis of the initial data set. The result of this

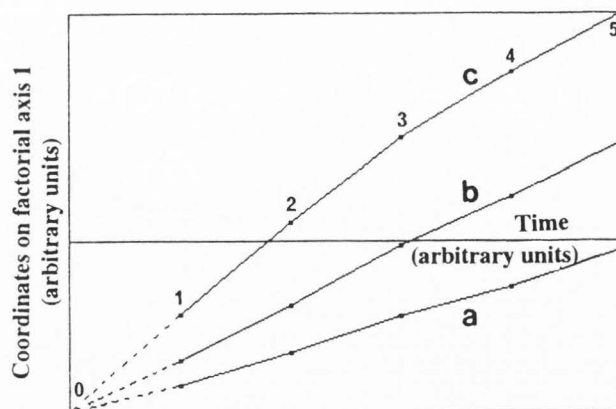


Fig. 6 : Coordinates on the factorial axis 1 of the 15 spectra simulating an experiment in time-dependent spectroscopy. The horizontal axis represents the time parameter. The three spectrum sets (a,b,c) correspond to three different dose rates: a) the amplitude decreases following the model $(1-n/10)^2$, where n is the spectrum number in the sequence, b) model $(1-n/10)$, c) model $(1-n/10)^{1/2}$. In this simulation, the dose effects were supposed to be proportional to the dose (without any threshold effects introducing discontinuities). Therefore, the three data sets converge towards one single point at zero-dose. The coordinate of this unique point on axis 1 can be used to compute the fictitious zero-dose spectrum.

reconstitution is very close to the corresponding simulated spectrum at $n = 0$ (see Fig. 6c in Bonnet et al. (1991) for a similar result).

Here again, the actual realization of such an experiment could obviously be more disappointing than this crude simulation. There is no guarantee of obtaining traces with different slopes, nor of obtaining several traces intersecting at the same location. But the idea is that, even if such an experiment does not allow attainment of the ultimate goal, which is to get information about the state of the specimen at zero-dose, at least such an analysis seems to be a useful tool to understand the effects of the dose. For instance, if the intersecting point (even roughly approximated) seems to be far away from the experimental points in the factorial space, this means that large effects occurred before the first measurement, thus rendering hazardous any extrapolation to zero-dose. If

instead of the continuous traces observed in this simulation, one obtains trace discontinuities, this militates against any extrapolation but, at the same time, brings new insight into largely unknown phenomena.

Application in Electron Energy Loss Elemental Mapping

As described in the introduction, image sequences are necessary to perform elemental mapping by electron energy loss and Auger spectroscopy. They are made of several energy-filtered images below the characteristic edge of the element that one wants to map and one or several energy-filtered images above this edge. In many situations, a pixel to pixel image processing of the whole sequence allows one to obtain a meaningful result. Such a process consists, for each pixel of the sequence, of a modelling of the signal variation below the energy-loss edge, an extrapolation of the model to energy-losses above the edge and a subtraction of these extrapolated values from the experimental signal intensities recorded for these energy-loss values, the final result being considered as the net signal produced by the atomic species.

But, in some situations, this procedure is not convenient, for several reasons :

- one has to define an a-priori model ($I = A \cdot E^{-R}$ is the most commonly used, where E is the energy-loss and A, R two adjustable parameters). When the chosen model does not match the experimental variation, the modelling, and thus the extrapolation, will be defective.

- the computation being done for each pixel, the statistical confidence in the resulting parameters is rather weak, especially for situations where one must take care of the electron dose received by the specimen,

- the apparatus and acquisition procedures for recording the image sequences involved in this kind of experiment are very sophisticated (see for instance Tence (1987)). Therefore, there is no guarantee that the data sets are free from artefacts, such as primary electron beam current or spectrometer drifts, specimen shifts, etc. Therefore, it is of primary importance to check the consistency of the whole data set submitted to the process.

For these different reasons, it seems useful to use several methods for the processing of

data and to cross-correlate the different results obtained.

Since MSA seems particularly suitable for processing image sequences as well as single data sequences or spectrum sequences, its potential possibilities were investigated.

First method investigated.

This consists of submitting the whole image sequence (energy-filtered images below and above the characteristic energy-loss) to some variant of MSA (Correspondence Analysis or Principal Component Analysis). The possibilities of the procedure are data analysis, data compression, data processing.

Data analysis: the consistency of the data set can be checked through the visualization of the weights of the different images and the weights of the different pixels in the factorial space. The interpretation of these projections can help in understanding the data set precisely, depicting eventual acquisition artefacts. Examples of this possibility have been described by Trebbia and Mory (1990).

Data compression : at any time, the original image sequences can be reconstituted from its decomposition into factorial images. Since a small number of these factors contain significant information, a large number of images can be replaced by a small number of factorial images, thus leading to an important data reduction. Though this point is not fundamental at the present state of the routine acquisition procedure, where the number of images in the sequence is less than ten, it could become really useful with new acquisition procedures: the "spectrum imaging" procedure for instance, where one complete energy spectrum is recorded for every pixel (Jeanguillaume and Colliex (1989), Thomas et al. (1990), Balossier et al.(1991)).

Data processing : Since one or several factorial images can be discarded during the reconstitution process, there is a way to filter the data set. Keeping or rejecting one of the different factors is, of course, the responsibility of the user and must rely on a careful interpretation of the meaning of this factor (or axis). One interesting possibility is to improve the signal-to-noise ratio of the image sequence (in low dose experiments). This is possible because an important part of the noise is rejected in the low order factorial axes, especially when the noise components are orthogonal to the useful information components. The hypothesis that a factorial

axis is mainly representative of noise can be ascertained by observing that the factorial image does not contain organized information but displays a random contrast. Therefore, discarding these factors which mainly contain noise results in a reconstituted sequence with a higher signal-to-noise ratio. Applying the standard processing procedure to such a noise-filtered sequence provides better quality results.

Second method investigated

The method previously described can only be considered as a pre-processing method since it does not lead directly to the desired elemental map. It only performs data analysis, checking and data processing (noise filtering). A more ambitious task would be to obtain the map without returning to the standard procedure, which needs to define an a-priori model for the pixel intensity evolution as a function of the energy-loss.

For this purpose, a second method has undergone preliminary investigation (Bonnet et al. (1992)). It consists of submitting to MSA only the images below the characteristic edge. Then, after data analysis and check for consistency, the extrapolation procedure in the factorial space, described in the previous sections, is applied in order to get the "fictitious" images of the background for the energy-losses of interest (above the edge). Then, these "fictitious" images of the background are subtracted from the experimental images recorded at these energy losses, providing the desired elemental map.

Though this procedure was successfully applied to an experimental sequence of a metal cobalt catalyst on a CeO_2 layer (Bonnet et al. (1992)), numerous other tests have to be performed before we can claim that it is really superior to the standard procedure. Among them, we studied once again the image sequence of uranium clusters (decorating a DNA on a thin carbon film) previously investigated by Trebbia and Mory (1990). This sequence has the advantage that the different images are duplicated (i.e. twice recorded), giving an opportunity to study the consistency of the different processing steps (see Mory et al. (1988)).

Fig. 7 displays the results obtained with the various procedures described here above for odd numbered and even numbered images. Fig. 7 a,b display the results obtained by the standard procedure. In Fig. 7 c,d are shown the results

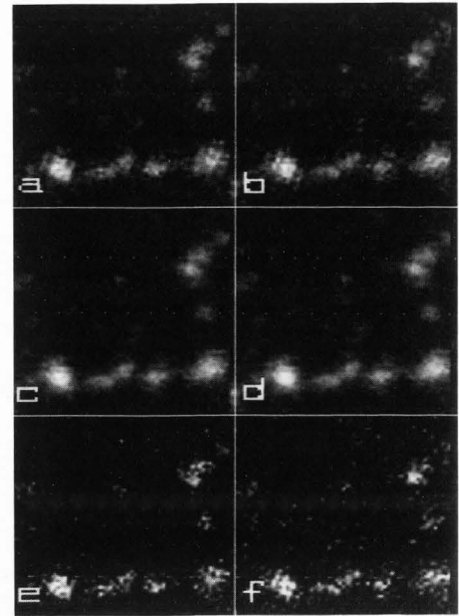


Fig. 7 : Gallery of two uranium maps computed from a series of 10 electron energy filtered images. These 10 images were recorded at 5 different energy losses and duplicated. a, b) elemental map produced with the standard procedure consisting in background modelling and subtraction from energy filtered images above the characteristic edge. c, d) In each case, the 5 experimental images were submitted to MSA and then reconstituted after keeping only the first factorial component, thus discarding a large part of noise and other artefacts (50 Hz ripples). The 5 reconstituted images were then submitted to the standard procedure. e, f) In each case, the 4 experimental images below the characteristic edge were submitted to MSA. From the coordinates of these images in the factorial space, the coordinate of the fictitious (i.e. not attainable experimentally) background image was then computed and subtracted from the fifth experimental image above the edge.

obtained by the multivariate procedure 1 (standard procedure applied to a reconstituted sequence obtained by retaining only axis 1, which represents 70% of the total variance for odd as well as even images). Fig. 7 e,f display the results obtained with the second multivariate procedure. The weights of the different images on axis 1 (which carries 43 % and 45 % of the total variance for odd and even

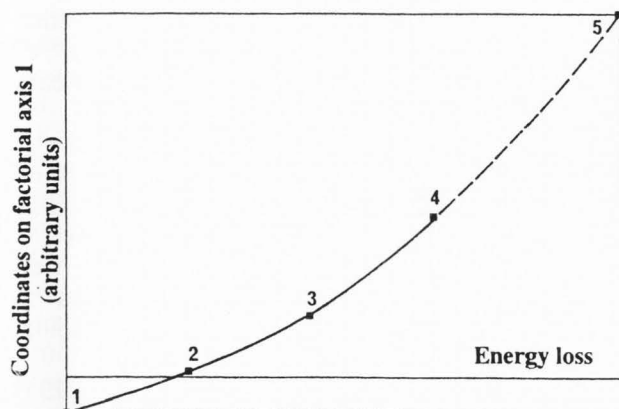


Fig. 8 : Coordinates of the odd numbered images on the factorial axis 1 (as a function of the energy loss) and the extrapolated value for the fictitious background at 112 eV (above the uranium 045 excitation threshold).

images) are shown on Fig. 8. From these weights, the weight of the fictitious background image is extrapolated (extrapolated value is shown) and the corresponding images are built.

The results obtained from the three procedures are consistent from a qualitative point of view. However, there are some points which deserve further attention :

- the different methods provide slightly different quantitative results,
- though they are supposed to be equivalent (apart from statistical noise), the image pairs have not exactly the same coordinates on the main factorial axis, thus leading to two different extrapolated back-ground images. We have not been able to explain this difference, either by looking at the odd and even factorial images, or by looking at some intermediate parameters (such as R) in the standard procedure (modelling).

In conclusion, it seems to us that the new procedure merits further studies before being adopted as a safe technique. It is clear that its application would be rendered easier by recording more than three or four images below the edge, as it was the case in the experimental sequences used so far. This will evidently be the case with the new spectral imaging procedure.

It should also be stressed that if the extrapolation process could be replaced by an interpolation process, the task would be much more easy. This can be done in the favorable situation where background images can be

recorded on both sides of the characteristic edge (see Fig. 4 in Colliex (1986)).

Conclusions

The goal of this paper is to take stock of the possibilities offered by Multivariate Statistical Analysis for the analysis and processing of various multivariate data sets which can be recorded in the field of electron-induced microanalysis. The basic idea is that applying repetitively a monovariate procedure on individual data seems less satisfactory than applying a multivariate procedure on the whole data set since it allows one to understand and process all the correlations between these data at once. MSA is not the only multivariate procedure available. Geostatistics for instance (Daly et al.(1992)) offers another option. However, we concentrated on this technique which can be implemented easily and already offers several possibilities : data analysis, data reduction, data processing, data interpolation and extrapolation.

We have considered three possible applications. In the context of spatially resolved spectroscopy, we have shown that concentration variations can be quantitatively estimated from some simple computations in the factorial space, without performing any data processing (such as background subtraction, peak area estimation) in the space of the experiment (i.e. $I(E)$).

In applications related to time-resolved spectroscopy, MSA can probably be useful to understand the evolution (as a function of time, or dose) of several element features. In this paper, we have focused our attention on the perspective of extrapolating such experimental data towards the zero dose limit. Though we are fully aware that this task is quite difficult, we tried to show that specific experiments and multivariate processing of the recorded data could help in understanding the phenomena which take place at the very beginning of the irradiation.

In the field of elemental mapping by energy-loss spectroscopic technique, we have shown that two procedures relying on MSA can be used in conjunction with the standard technique based on a modelling of the intensity of every pixel. These complementary methods can help in understanding the data set, in depicting eventual acquisition artefacts, in performing data reduction when very large sequences are

recorded, in filtering noise and (for the latter method) in producing a fictitious background image. This image can then be subtracted from the experimental images recorded at an energy above the characteristic energy loss in order to produce the element map.

The techniques described in this paper were mainly illustrated through numerical simulations. When applied on real data given by experiments which are now in progress, they will show whether these assumptions are reasonable or not.

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Discussion with Reviewers

R. Browning: I'm not sure that $(1-n/10)^{1/2}$ can be a physically realistic process. Doesn't $n^{1/2}$ imply the surface has pre-knowledge of the coming events. It is the same for any sublinear dependence. I would expect the linear dependence of a decaying feature to be :

$$R_t = R_0 e^{-kt}$$

Authors: We agree with the comment that the models used for the amplitude dependence as a function of dose could be physically unrealistic. However, to our knowledge, there is no theoretical or experimental evidence for any model which can describe the effect of dose on microanalytical data of diffusible elements. We are not even sure that this effect can be described by continuous models. Therefore, we chose these models for testing a data processing method rather than for checking a physical hypothesis. However, as you suggested, we have undergone new simulations with a model of the type $R_n = R_0 e^{-kn}$, with different values of k (0.1, 0.2 and 0.3). The qualitative results are comparable to those of Fig. 6 (results available from the authors), indicating that the principle

underlined in section 2 holds for any model, provided the hypothesis of continuity is fulfilled.

P. Statham: The essence of MSA is to reduce the dimensionality of a problem to something comprehensible. A key stage in this process is the elimination of "insignificant" eigenvectors. In Fourier transform spectroscopy, it is often possible to estimate the expected variance in magnitude of Fourier components caused by statistical noise in the raw data. Are the authors aware of any techniques in MSA for estimating the expected variance in eigenvalues caused by statistics so that objective significance tests could be used to eliminate eigenvectors ?

Authors: We agree with the idea that the question concerning the number of "useful" eigenvectors (i.e. the number of factors which really represent information and the number of factors which are essentially due to noise) is often very important for the different applications of MSA. This question was often considered in the different fields of application of MSA. Here is a list of different answers reported in the literature :

- drop of the eigenvalues : there is sometimes a gap between the eigenvalues associated with the "useful" eigenvectors and those associated with noise.
- this qualitative observation was quantified by Malinowski (1977) through several indexes which can be used to estimate the real number of factors. Some of these indexes need an estimate of the root mean square error in the data submitted to factor analysis.
- likelihood ratio test : a reconstitution of the series is undergone by including an increasing number of factors. When there is no longer a change (this being asserted by a statistical test), the new factor is "useless" (Hannequin et al., 1989).
- methods for choosing factors useful for a given purpose appeared recently in the field of pattern recognition (for an application in electron microscopy and relevant references, see Harauz and Chiu, 1991).

A systematic comparison of these different methods in different situations would be necessary before drawing conclusions concerning their actual usefulness.

P. Statham: Whereas random "high frequency" spatial intensity variations are instantly recognisable as "noise", statistical fluctuations in the original data will also have "low frequency" components which could in principle be misinterpreted as undulations in the background. If the data set is not very large, is it possible that this could introduce the sort of variation in results that the authors have noticed in the Uranium maps example (Fig. 7) ?

Authors: There are two aspects to your question which we would like to address separately. The first one concerns the "high frequency/low frequency" considerations. We think that this concept cannot be handled by MSA, which considers every pixel of the series independantly of its neighbors. From this point of view, filtering by MSA is rather different from frequency filtering.

The second aspect concerns the size of the data set. We are aware of the fact that MSA was developed in order to process large data sets (many individuals and many variables) and that we are applying it to data sets which are large in one dimension (pixels or energy channels) but small in the other dimension (images or spectra). This may have some consequences concerning the noise rejection. For instance, if we have only three images, we can only define two factorial axes in Correspondence Analysis. If these three images contain two real information components ("background" and "object" for instance), these two components are going to define (more or less) the two factorial axes and there is no more factorial axis available for the noise. In this situation (which we encounter in processing color - RGB - images for instance), the noise is constrained to occupy also the two available factorial axes and no noise rejection is possible.

Returning to your question, it is possible that these kinds of effects are responsible for the (small) variations observed in the results reported in Fig. 7.

P. Statham: Since the authors are making a case for MSA as a more efficient and convenient approach than conventional spectrum modelling techniques, I would have liked to see more of an objective appraisal of the various approaches to the Uranium map example in Fig. 7. Without the authors' help, I cannot see why the reader should automatically

see any way of ranking the solutions given by Fig. 7.

Authors: Our purpose is not to make an efficiency rank between different methods of data analysis. We agree that it would be difficult for the reader to decide from Fig. 7 which process is best suited for extracting the useful information. This can only be done with simulations or by computing some objective criteria, such as the signal to noise ratio for instance.

The purpose of Fig. 7 is only to show that different methods can lead to "a result", not to decide which one is the best.

Obviously, if one has good reasons for assuming that a given model is well adapted for the description of background and/or noise, then such an a priori model must be used for data reduction.

But in the case where no a priori information is available, then, provided that the data set is large enough, MSA is even an ultimate resort for extracting the different components of this data set, filtering and exploiting them. Therefore, we consider that MSA is not a more efficient and convenient approach than modelling techniques, but an alternative method when no model is available.

M. Prutton: In the second simulation considering quantification of concentration variations in spatially resolved spectroscopy the components A and B have different functional variations with respect to position across an interface. A and B are concentrations and cannot add up to 100% as the simulation is set up. This means, presumably, that at least one element is present or some property of the details of the measurement technique cause A and B not to be perfectly anti-correlated in an apparently binary system. If the analyst has other evidence that a real piece of material is binary then such absence of perfect anti-correlation is teaching him that there may an artefact introduced by the measurement technique. If there is no such evidence then perhaps the analyst should seek elements other than A and B which may be localised at the interface. Would you agree with this kind of interpretation?

Authors: Yes, we totally agree with this interpretation.