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Combining spectroscopic data in the forensic analysis of paint: Application of a multiblock technique as chemometric tool

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ABSTRACT

A study (Muehlethaler et al. [9]) has demonstrated the application of chemometrics for the analysis of domestic red paints. The paints have been analyzed with IR and Raman spectroscopies. As a result of these analyses, exploratory techniques, such as principal component analysis (PCA) and hierarchical clusters analysis (HCA) have been applied to both IR and Raman spectra. This allowed to observe the structure of the data among those red paints, and infer potential groups among them and to propose a classification model based on their chemical composition. IR spectroscopy showed group patterns related mainly to the binder and extender composition of the paints, whereas Raman spectroscopy data were mainly related to the pigment composition.

The aim of the present study is to evaluate the potential of a Multiblock algorithm applied to the same data set. The concept of Multiblock, as a chemometric tool, is to combine data from several different analytical techniques in order to visualize most of the information at once. IR and Raman spectroscopy are then considered as "blocks" of data of the same dataset. One algorithm called common component and specific weight analysis (CCSWA) has been used in order to produce independent PCAs for each block, and the combined (common) information in a score plot. The results of this study showed group patterns of the analyzed paints, related to both binder and pigment compositions in one single score plot. Moreover, the number of groups observed with the multiblock representation (20 groups) is higher than independent PCAs projections (12 and 7 groups for IR and Raman respectively). This new application of chemometrics showed a great potential in forensic science, as practitioners often use a combination of several analytical techniques in order to characterize samples. This could be helpful when multiple and complementary analytical techniques are used in order to characterize and compare paint samples.

1. Introduction

The analysis of paint samples in criminal cases involve the characterization of multiple compounds present in the paint mixture analyzed. From the binder to pigments, through extender materials and additives, the forensic scientist will deploy a variety of analytical techniques in order to characterize as completely as possible the mixture of those constituents.

The analytical sequence is thus following well-known forensic principles: from general to specific techniques, and from non-destructive to destructive techniques. Indeed, analyses allowing the general description of samples will be applied before the more advanced ones, which will describe the smallest constituents of paints. Likewise, methods which are less destructive will be preferred to destructive ones, in order to preserve the sample from unnecessary damages [1]. An agreed complete sequence in the field of paint analysis demonstrates the significant number of analytical techniques available to a paint examiner [2]. Among those, spectroscopic techniques, and especially Fourier-transform infrared (FTIR) and Raman spectroscopies are widespread in the characterization of paint components. Raman and FTIR are particularly appreciable for their complementarity, as they are both measuring vibrational transitions of molecular bonds in the paint mixture. Based on selection rules for determining Raman and/or IR active molecular bonds, the use of both techniques allow better characterization and possibly further

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discrimination between samples. FTIR provide information mostly about binder type [3–6], where Raman is predominantly related to pigments that are present in the paint samples [5,7,8].

In a complete analytical sequence (e.g. comprising optical examination and chemical analyses), results of the different analyses of the sequence have to be interpreted. Independent evaluations of comparisons are thus often made. In the particular case of mentioned spectroscopies, the great amount of data produced can be treated with chemometric tools, which allows the visualization and classification of complex data matrices related to chemical composition. Those tools allow extraction of data structure and useful information in the characterization of chemical compounds, as well as discrimination among samples. Nevertheless, the combination of information provided by different analytical results can be tedious and complicated. The results can be indeed interpreted separately for every analytical technique, and then combined in a single characterization, as it has been done by Muehlethaler et al. [9] with domestic red paints analyzed with both Raman and IR spectroscopies. The idea developed through the application of multiblock technique, is to combine the results of both spectroscopies together, in order to make the interpretation step easier.

In order to illustrate the difficulty of combining different kind of information, a simple example is represented in Fig. 1. Let an unknown sample constituted of a wine glass containing a red liquid to be analyzed and characterized with two different analytical techniques. The shape of the glass can be analyzed on one side (block1), while the color of the contained liquid can be analyzed on the other side (block2). Chemometric tools can be applied separately on every analytical technique, in order to characterize the unknown sample by the comparison with known samples. Considered separately, those tools allow the association of the unknown sample with one class (for shape and color), each of which containing several objects. The combination of both information at the same time, illustrated in the left side of Fig. 1, can lead to a better discriminating power, limiting the undifferentiated known samples as shown with the only red wineglass represented. Moreover, this simple example try to demonstrate the easier representation of the data structure when both information are considered at the same time.

This kind of data combination can be achieved with so-called multiblock techniques. There exist numerous multiblock algorithms, such as Sum-PCA [10–12], CPCA [13], HPCA [13,14] and CCSWA [15–18]. The common idea in those algorithms is to highlight potential links between different data sets [14]. Variations within and between-blocks are highlighted by the determination of latent variables, or principal component, which are common within data blocks. A block is a data matrix with a number of columns related with measured variables, and a number of lines corresponding to the different samples/analyses. Different configurations between blocks and their dimensions are possible [14]. Among those, the present study will focus on the configuration defined by blocks having different variables for the same objects/analyses considered, as illustrated in Fig. 2. This configuration corresponds to the situation of analyzing the same paint samples through the two considered spectroscopic techniques (Raman and FTIR) described in the paint analysis sequence earlier.

The aim of the present study is thus to evaluate the application of a multiblock technique, CCSWA (common component and specific weight analysis), on spectroscopic data sets from domestic red paint analyses. The potential of this algorithm will be demonstrated in the particular field of forensic paint analysis, and compared with independent chemometric methods already published [9]. The interpretation of the results in a combined representation will also be highlighted.

2. Materials and methods

2.1. Samples

The spectroscopic raw data consist of Raman and FTIR spectra coming from the analysis of 34 red household paint samples from a precedent study [9]. They possess the same color code (RAL 3000) and have been purchased in the Swiss market. Details about the paint samples can be found in the precedent publication [9]. They have been considered as an ideal dataset, as they have not been

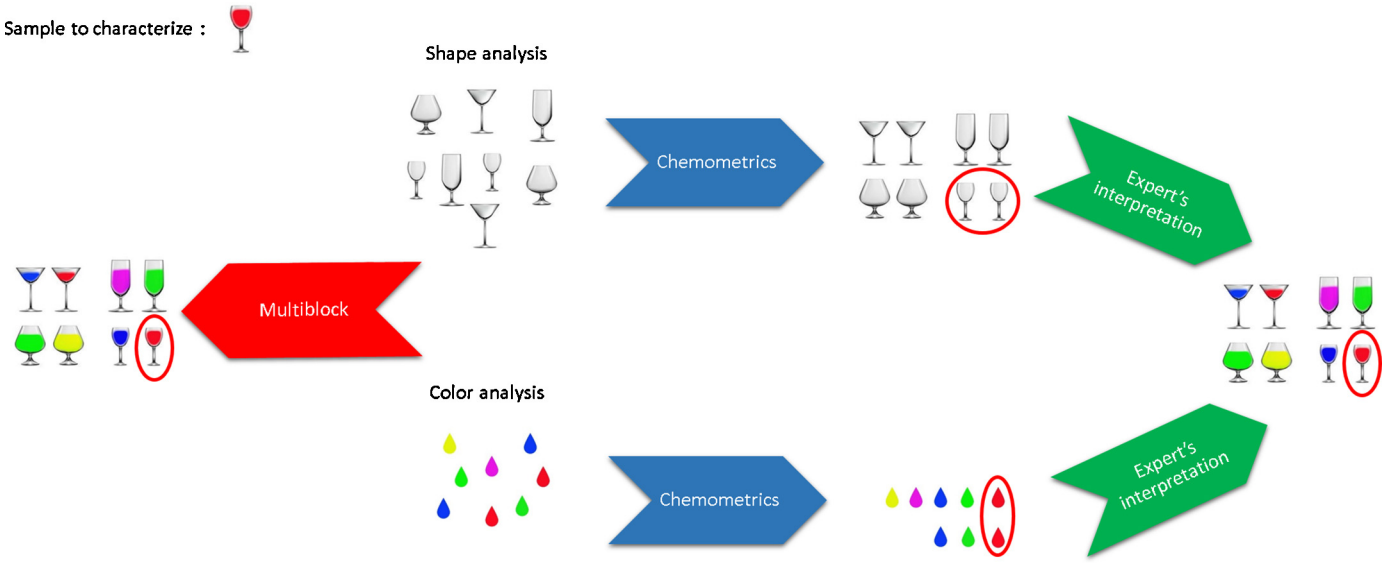

Fig. 1. Scheme of a simple application of multiblock technique. The sample to analyze is illustrated by a glass, which could be characterized by its shape (wineglass) and the color of its content (red). Analysis of shape and color are the analytical techniques available and applied to the unknown sample, in order to compare it with known samples. Chemometric tools (such as PCA) allow the visualization of the considered sample population depending of classes, and are illustrated in the center of the figure with blue arrows. The classes undifferentiated from the unknown sample are highlighted with red circles. On the left side of the figure, the combination of both kind of information by a multiblock tool is illustrated. On the right end side of the figure, the results of independent chemometrics have to be interpreted by the expert in order to combine both information. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)