

Micro-Raman and X-ray fluorescence spectroscopy data fusion for the classification of ochre pigments

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Abstract

Two different data-fusion strategies are evaluated for the combination of the outputs of combined Raman/X-Ray fluorescence instrument. The studied application deals with the classification of ochre pigments investigated in the field of cultural heritage. The two fusion strategies are: (1) first level fusion: combines raw signals obtained from each technique and (2) second level fusion: combines extracted features provided individually by each technique. Classification tool is partial least squares-discriminant analysis (PLS-DA). Classification results obtained performing different data-fusion strategies are compared with those results obtained performing a single classification model for each data source. The results show that the combination of signal features is the most suitable for a rapid and unique processing of both types of spectra. Benefits and drawbacks of each strategy are also discussed.

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1. Introduction

It is well known that micro-Raman (Raman) and micro X-ray fluorescence (XRF) spectroscopy are particularly amenable to cultural heritage field [1–3]. Raman spectroscopy provides information regarding the molecular structure of the material under investigation. It provides a measure of molecular and crystal lattice vibrations and hence is sensitive to the composition, chemical environment and crystalline structure of the art material analysed [4]. By contrast, XRF is a technique that enables qualitative and quantitative elemental analysis [5–7].

Their increasing contribution to the study of art-works is partly due to the recent major improvements in instrument configuration [1,5,8], where the development of portable instruments that are capable for undertaking *in situ* measurements and collecting suitable information in a non-destructive way has played a significant role. Indeed, since the turn of the century,

a new generation of analytical instruments has been developed in the art diagnosis field. Among which, a rather promising is a prototype instrument (PRAXIS prototype) that combines both Raman and XRF techniques, with all the respective attributes. This instrument has been already tested [1] and is currently being applied in art and archaeological studies.

Thanks to this analytical instrumentation, we can now obtain micro-Raman and micro-XRF spectra from the same spot on a given sample. A novel perspective of data processing is therefore needed in order to find tools for processing large amounts of data from several sources (complementary techniques) rapidly and effortlessly and, by means of data fusion, obtain a distinct and reliable result. Data fusion is a formal framework in which the means and tools for combining data from several sources are expressed. It has been widely applied to robotics, remote sensing, image analysis and analytical chemistry [9,11–13].

The aim of this paper is to introduce an improved method for classification of pigments belonging to the cultural heritage field. The method is based on the evaluation of the spectroscopic data (Raman and XRF) both collected by the PRAXIS prototype from the same spot using different data-fusion strategies. The data-

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fusion strategies are tested on experimental data obtained from reference and test samples of ochre pigments. More specifically, an evaluation of their predictions related to the classification of these pigments is considered.

This specific classification is selected as ochre differentiation is a rather complicated problem. All ochre pigments are natural and contain iron oxide(III) (Fe_2O_3) as their main component. They are therefore distinguished by investigating the presence of minor components. Natural ochre pigments present a wide range of colours, from yellow to orange, red and violet. In some cases, it is not possible to distinguish them just by visual inspection. And it is really difficult when we are dealing with trace analysis, for instance, in restoration studies, identification of ancient works, etc. Their colour is given away by the ferric oxide (Fe_2O_3) or ferric oxide monohydrate ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$). The various shades are determined by several factors: the average size of crystallites and the corresponding dispersion; their proportion with respect to the presence of other chemical components such as aluminosilicate materials (kaolinite, quartz, manganese oxide, etc.) and other minor components (calcite, gypsum, etc.). Also, the presence of magnetite (Fe_3O_4) may also contribute to the material's shade.

The identification of ochre pigments is rather complicated and implies the characterization of the specific iron oxide or hydroxide material, as well as the designation of the minor components existing in the natural material. Data from different techniques is usually required and combination of the results leads to the final identification of the ochre pigment [10–13]. One of the works that clearly demonstrated this issue is the one of Bikiaris et al. [10] in which Raman spectroscopy (that enables one to differentiate between the various iron oxides and hydroxides) is combined with energy dispersive spectroscopy analysis from scanning electron microscopy (that enables elemental composition of the minor components) or Fourier transform infrared spectroscopy (that enables the identification of kaolinite and quartz).

In the current work we try to observe whether data obtained from Raman and X-ray fluorescence from the same spot on ochre pigments (which are related to structure and elemental composition respectively) can be properly handled using data-fusion strategies and classification can thus be accomplished.

2. Theory

2.1. Signal processing

An initial signal process, previous to the fusion strategy, is necessary to focus on the deterministic information present in the data. Dealing with spectroscopic data, allocate the spectra properly implies smoothing and de-noising procedures, background correction and normalization. In Raman and XRF data-fusion, this stage is highly required due to the presence of noise and background signal components in the raw spectra. In this work the wavelet transform was applied for noise suppression and multipoint baseline correction for background suppression in spectra.

Data alignment is also necessary to achieve a common spatial reference. When data to be fused come from different techniques, they might be in different scales, so before applying the fusion process they have to be formatted into a common form and aligned in the time domain. In this work, normalization was applied to achieve this. It is also an attempt to correct the systematic bias in data and permits to balance data before it enters the data-fusion system.

2.2. Data fusion

Data fusion combines information from several sources to produce a single model or decision. Hall and Llinas [14] propose different techniques for multisensor data fusion and define a group of strategies. Two of them are suitable to be used with spectral data: (1) data level fusion or low-level fusion and (2) feature level fusion or mid-level fusion. Fig. 1 shows both strategies in which the spectra coming from Raman and XRF measurements are fused.

In low-level fusion, the raw data is fused. In our particular case the raw Raman and XRF spectra are just fused. For the raw data fusion it has to be considered that data must be commensurate and must be properly associated. Thus, for example, if the same spectroscopic technique is used, the spectra must be able to be co-aligned on the same scale. If different spectroscopic techniques are used, the spectra need to be balanced in order to perform a correct data sensor association. Once the raw data is

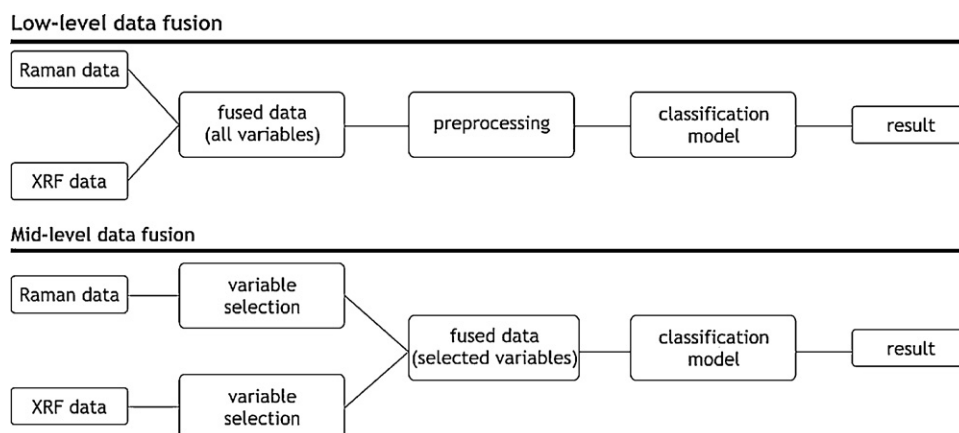


Fig. 1. Two data-fusion architectures: low-level and mid-level.

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