CMA4CH 2008, Mediterraneum Meeting

Multivariate Analysis and Chemometry Applied to Environment and Cultural Heritage
2nd ed., Ventotene Island, Italy, Europe, 1-4 June 2008

Chemometrics and Laser Induced Breakdown Spectroscopy (LIBS) Analyses for Identification of Wall Paintings Pigments

<u>S. Duchêne</u>[1], R. Bruder[2], J.B. Sirven[2], V. Detalle[1]

[1]LRMH, 29 rue de Paris, 77420 Champs-sur-Marne, France
[2]DEN/DANS/DPC/SCP, CEA Saclay, 91191 Gif-sur-Yvette, France

Abstract

Laser Induced Breakdown Spectroscopy (LIBS) can be successfully used for cultural heritage applications, such as pigment and stone identification or archaeological metal characterisation. In this work we focus on the study of wall painting pigments. Two methods of signal analysis are tested. The first one is based on spectral lines identification in order to detect characteristic chemical elements. In the second one, we apply chemometrics models (SIMCA and PLS-DA) to a pigment reference database. Results show the improvement of pigments identification obtained with the multivariate analyses approach. This work includes laboratory study and on site validation.

Introduction

LIBS principle relies on the focalisation of a laser on the surface of a sample that induces a plasma. The spectral emission of the plasma is collected and allows identifying the elemental identification of the material. In the conservation field, it can be used as an in situ, rapid, micro-destructive approach for pigment identifications. Different studies demonstrate that it can be performed with a basic observation of the specific emission lines in the spectra to detect characteristic chemical elements, which is a classical spectroscopic approach. The pigments can be identified by taking into account detected and non-detected elements. This method can also be assisted by multivariate treatments.

Materials & Methods

The portable instrumentation was composed of a 1064 nm Nd-YAG laser (Continuum, USA, Minilite II Q-Switched) and the detection system is based on 3 integrated spectrometers (Ocean Optics, USA, HR2000) working from 200 to 940 nm. Samples consisted in air-entrained concrete plates, covered with 2 layers for frescoes: a render made of coarse sand and lime and a finishing layer made of fine sand and lime tired up and flattened. Pigments were diluted in water and applied on wet coating. For the *a secco* technique a third layer with the medium and pigment was applied on the dry plaster.

A specific database was built-up using 26 different pigments (azurite, lead white, titanium dioxide, prussian blue, charcoal, cinnabar, indigo, lead-tin yellow, lapis, red lake, lithopone, malachite, massicot, red lead, manganese dioxide, bone black, yellow ochre, red ochre, orpiment, ultramarine, extrafine smalt, standard smalt, green earth, vermilion, copper resinate, chrome oxide green) and 3 mixes prepared by a restorer using different painting techniques (*fresco*, animal glue for all the pigments and casein, egg tempera and oil for only 3 pigments, i.e. azurite, cinnabar and yellow ochre). 30 spectra per pigment and per technique were acquired. 25 spectra constituted the reference database and the 5 remaining ones, considered as unknown spectra, were used for the validation step. Classical spectroscopic analysis with a Labview-based software and chemometric treatments (SIMCA and PLS-DA) under SIMCA-P software (Umetrics AB, Umeå, Sweden) were tested in order to identify both pigment and technique of the reference samples. In addition some experiments were carried out on site on real unknown pigments and the 2 treatments were applied to test on site performances of each method.

Results

First, we worked on the reference database of spectra (25 for each pigment/technique group) in order to define the most efficient method to use for identifications on site. For classical spectral analysis, the identification of both pigment and technique was considered as the only correct answer. It provided 66% of right attribution of pigment/technique for validation spectra.

Secondly multivariate treatments were used to build identification models with the 25 reference spectra. Models are designed either to give the pigment or the technique. The SIMCA method was chosen in the first case. Each class corresponded to a pigment (25 spectra per class, 29 classes in total). This method gave 81% of correct identification for the test set (5 spectra for each pigment/technique group). In a second time, on the same set of data a PLS-DA has been carried out for technique identification assigning a class to each technique (5 in total). 99% of right technique identification has been obtained with this method. In Fig.1 we report the schema of the methodology used for the identification of pigments and techniques of wall painting on reference models and on site spectra.

As far as the on site identification is concerned, an adapted signal processing is still in progress. Actually the main problem that we have to resolve is the gap of intensity level between experimental spectra and the reference database.
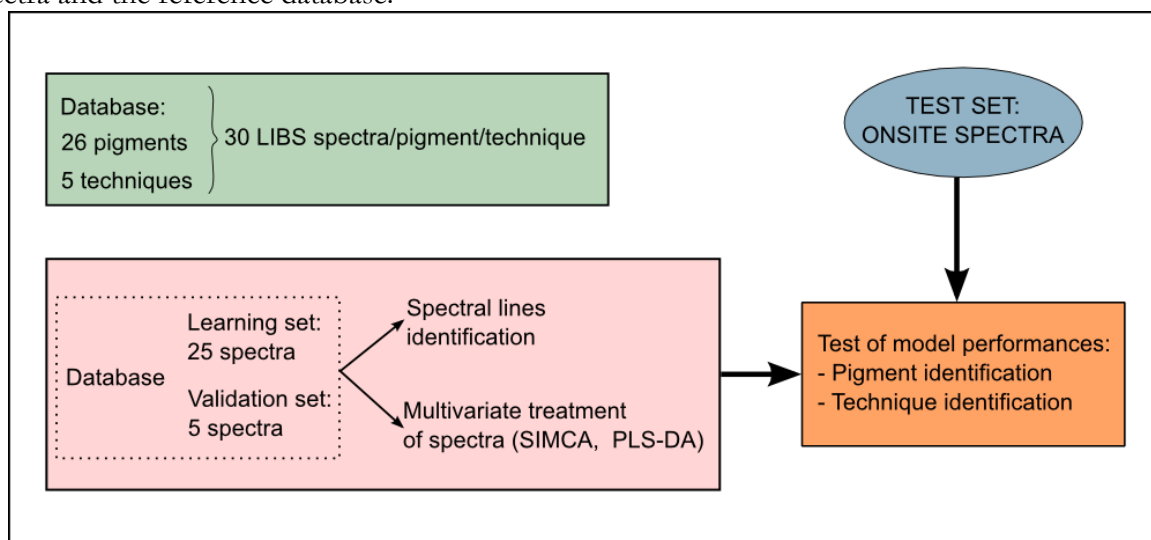

Fig. 1 Schematic methodology for pigments and techniques identification.

Conclusions

The different treatments performed on the reference database give good rates of correct identification for both pigment and technique and allow a significant improvement of the recognition of unknown spectra acquired in laboratory. The on site identification is more difficult because signal intensities from the database and from the experimental spectra are quite different. A method of signal processing is still in elaboration to achieve the correct identification of pigments directly on site.

References

1) C. Cennini, Il libro dell'arte, Neri Pozza, 2003, ISBN: 8873059104
2) D. L. Massart, B. G. M. Vandeginste, S. N. Deming, Y. Michotte, L. Kaufman, Chemometrics: a textbook, Elsevier Science Publishers B.V., 1988, ISBN-10: 0-444-42660-4
3) J. B. Sirven, B. Sallé, P. Mauchien, J. L. Lacour, S. Maurice, G. Manhès, Feasibility study of rock identification at the surface of Mars by remote laser-induced breakdown spectroscopy and three chemometric methods, J. Anal. At. Spectrom., 22, (2007) 1471-1480