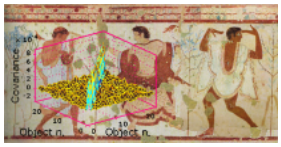

Principal Component Analysis of Reflectance Medium Infrared Spectra for the Non-Invasive Identification of Organic Materials in Wall Paintings

A. Daveri[1], G. Verri[2], F. Rosi[1], C. Miliani[3], P. Benedetti[1], F. Piqué[4]

[1]Dip. di Chimica, Univ. degli Studi di Perugia, via Elce di Sotto 8, 06123 Italy
[2]The British Museum, Great Russell Street, WC1B 3DG London, U.K.
[3]CNR-ISTM, Dip. di Chimica, Univ. degli Studi di Perugia, via Elce di Sotto 8, 06123, Italy
[4]The Getty Conservation Institute, 1200 Getty Center Drive, Los Angeles, 90049 CA, U.S.A.

Abstract

The aim of this study is to show how chemometrics, in particular PCA, applied to reflectance mid-FTIR spectra can be a useful approach to better understand and manage the enormous amount of data acquirable by a non invasive scientific measurement campaign.

Fiber optic midFTIR technique is a very promising method for the non invasive and *in situ* characterization of binders in wall paintings. Wall painting replicas of known composition from the collection of the Tintori Center in Prato have been employed to test the multivariate approach for the treatment of reflectance mid-FTIR spectra.

Introduction

The study, here presented, is part of a wide project (Organic Materials in Wall Paintings, OMWP) coordinated by the Getty Conservation Institute. The final objective of OMWP is to develop a protocol for the identification and mapping of organic binders in wall paintings, first testing the response of non-invasive techniques (UV-Vis fluorescence, reflectance midFTIR) and micro-destructive methods (micro-FTIR, GC-MS, etc.) on model samples from the collection of the Tintori Center in Prato[1].

Recent advances in mid infrared fiber optic technology have made vibrational spectroscopy in reflectance mode very promising for the *in situ* non invasive detection and identification of organic and inorganic compounds [2, 3]. The optical layout in use by the portable equipment does not allow to separate any of the contribution to the reflectance, it means that a combination of specular and diffuse spectra are collected. Thus spectral features depend not only from the infrared properties of the material but also on its surface roughness, making difficult their interpretation and any comparison with available transmittance infrared database.

An appropriate chemometric procedure has been here tested in order to extract the relevant chemical information contained in the reflectance spectra, eventually covered by optical and matrix effects.

Materials & Methods

Reflectance midFTIR spectra were recorded using the portable JASCO VIR 9500 spectrophotometer equipped with Remspec mid-infrared fiber optic probe. The instrument is made of a Midac Illuminator IR radiation source, a Michelson interferometer, and a liquid nitrogen cooled MCT (Mercury Cadmium Telluride) detector. The fiber optic probe contains 19 chalcogenide glass fibers that allow for the collection of spectra from 900 to 6000 cm^{-1}.

About 174 wall painting replicas of known composition (carbonate or silicate pigments mixed with casein, egg, siccative oil) and painting technique (*fresco*, *stanco* and *secco*), have been employed.

PCA, calculated by Golpe (Multivariate Infometric Analysis, Perugia, Italy), has been applied to dataset constituted by midFTIR spectra as objects and frequencies in the range 900-4000cm^{-1} as variables. All the FTIR spectra have been pre-treated in order to remove any experimental non-

systematic variations. For this proposal each data has been baseline corrected in the last 100 variables, and divided by the average value calculated on all the spectrum.

Results

PCA has been carried out on resulting dataset containing the same pigment and two different binders (egg and casein). The PC1-PC2 scores plot (~70% of the total variance) is reported in figure 1a. It shows how the first two components are able to separate objects in to the diverse painting techniques (*fresco*, *stanco, secco*). The fresco cluster is remarkably separated by the *secco* and *stanco* groups. This behaviour suggests that the vibrational FTIR spectroscopy in reflectance mode technique is largely sensible to the painting technique due to the strong influence of the carbonate matrix which stoutly distorts the spectral features, overall in the case of fresco where the binder is strictly bound with the carbonate plaster. The effect of the binder is evidenced by the third component PC3. In fact, egg and casein are well separated along the third component as showed in

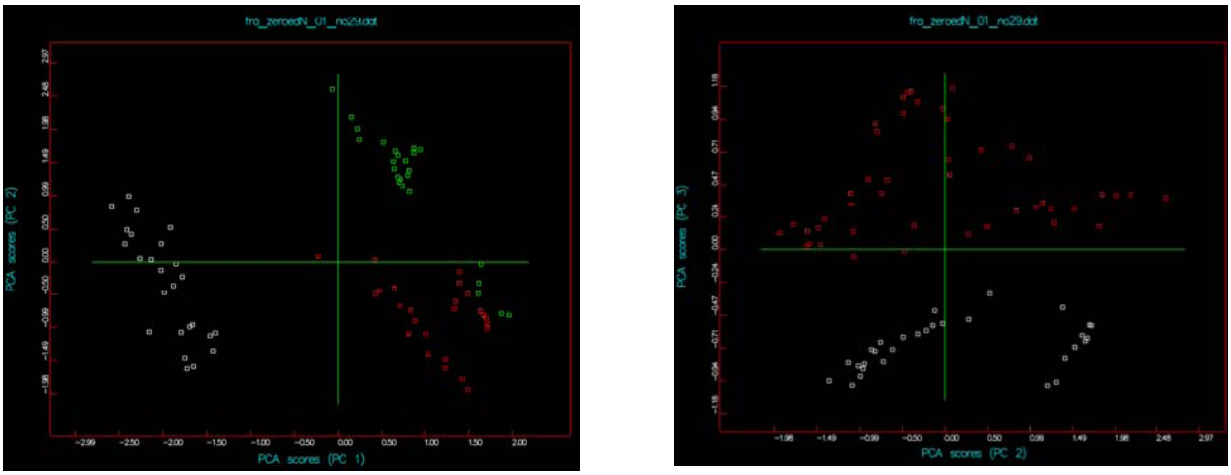

Fig.1: a) PC1-PC2 score plot (white=fresco, red=secco, green=stanco); b) PC2-PC3 scores plot (white=casein, red=egg)

figure 1b.

The PC3 loading plot showed that the meaningful variables for the binder discrimination are those related the C-H stretchings that lie in a spectral region less affected by the carbonate matrix.

Conclusions

Wall painting replicas of known composition from the collection of the Tintori Center in Prato have been employed to test the multivariate approach for the treatment of reflectance mid-FTIR spectra. PCA, calculated by Golpe on pre-treated spectra, resulted to be very useful in managing spurious reflectance effects related to optical properties and matrix, highlighting the spectral features that are effective for discriminating different organic binders. These results represent the first step toward the development of an appropriate PCA modelling to be applied on spectra collected from real wall paintings.

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