



# Multivariate analysis of combined reflectance FT-NIR and micro-Raman spectra on oil-paint models<sup>☆</sup>



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## ABSTRACT

The potential of principal component analysis (PCA), on combined first derivative near-infrared and Raman spectra, was explored and tested in order to exhaustively characterize different oil-paint models, prepared with linseed and poppy-seed oil, and to verify the behavior of these binders in the presence of a pigment.

A series of oil-paint models, selecting pigments employed in artworks both in antiquity (like lead white, azurite, Afghanistan ultramarine) and contemporary art (such as phthalocyanine blue, zinc oxide and synthetic ultramarine blue), were prepared and analyzed by means of reflectance near-infrared and micro-Raman spectroscopic techniques.

At first, PCA was applied by taking into account all oil-paint models, pigments and drying oils. Subsequently, new statistical models were built focusing only on single pigment subsets, hence offering a more realistic application of this method once the pigment had been identified. The proposed procedure allowed us to recognize the pigments and binding media used to prepare each model. In addition, it proved to be even sensitive to the drying oil employed in the oil-paint mixture, enabling its identification. The application of PCA to a combination of different spectral regions ( $6000\text{--}3900\text{ cm}^{-1}$  along with  $1900\text{--}260\text{ cm}^{-1}$ ) allowed an enhanced level of spectral information to be extracted, with respect to its application on separated data sets. It represents also a powerful tool to differentiate oil-paint models on the basis of their composition, including oils and pigments.

Moreover, we verified that after a natural ageing of 9 months, and in presence of a pigment, it is still possible to obtain information regarding the functional groups directly involved in the drying process (e.g., the 1st overtones of methylenic stretching,  $5800\text{ cm}^{-1}$  and  $5698\text{ cm}^{-1}$ , the C–H combination bands of methylenic stretching and bending modes,  $4340$  and  $4261\text{ cm}^{-1}$ , and the  $\nu(\text{C}=\text{C})$  stretching,  $1654\text{ cm}^{-1}$ ).

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## 1. Introduction

The knowledge of the materials present in artworks is crucial to ensure appropriate conservation procedures and to gain insight into their historical evolution. This knowledge is especially important when dealing with paintings because they are complex systems, composed of various supports, preparation layers and painting materials, such as pigments and binders.

While the identification of pigments in paintings is today a relatively straightforward process in most cases, the identification of binding media remains a challenge [1]. The fact that organic materials are often added in scant quantity, in contrast with the presence of the high amounts of inorganic materials, as pigments and dryers, may

hinder their reliable identification [2]. Furthermore, organic materials are less stable and deteriorate faster than the inorganic components so that they often only remain at trace levels in centuries-old paintings, thus making their identification even more difficult. Consequently, the analytical techniques employed need to provide high sensitivity and specific information to avoid ambiguities or misinterpretations. To achieve this requirement, the most prudent approach is to apply more than one analytical procedure in order to gather complementary information. The most commonly employed techniques used in this type of study are chromatography [3,4] and spectroscopy [5].

The main advantages of spectroscopic techniques, such as reflectance and Raman, are that in many cases they can be applied without sampling or in a non-destructive way. In addition, they do not need any sample pre-treatment, the time of analysis is short, and they allow very small areas of the surface of the artwork to be studied [6,7]. Nevertheless, data analysis performing one-by-one or peak-by-peak comparison of sample spectra with those of the standard materials, especially in the case of natural binding media, is a tedious time-consuming

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methodology that is not always effective. The management of all the information obtained from the data collected by the different spectroscopy techniques is improved considerably by using chemometric analysis assistance. Indeed, it is highly worthwhile to characterize artworks by non-destructive analytical techniques combined with statistical methods, such as multivariate chemometric tools, in order to extract the maximum information concerning composition and to detect slight disparities between the spectroscopic data [8,9]. One of the most employed exploratory tools in chemometrics is the principal component analysis (PCA). The main benefit of PCA is its capability to reduce dimensionality of the original data set by representing them in terms of new coordinates, the principal components (PCs), which contain more interpretable and representative information of the system under investigation [10].

This work is aimed at exploring the possibility of fully characterizing complex systems, such as oil-paint models, using multivariate analysis on combined Fourier transform near-infrared (FT-NIR) and Raman spectroscopic techniques, and to differentiate between the oil-paint models according to the spectral differences attributable to the binder.

A set of model samples were prepared by mixing linseed oil, which was used in the Middle Ages, and poppy-seed oil, which has been utilized especially for artistic purposes since the 17th century [11], with a series of pigments employed in artworks, both in antiquity (like lead white, azurite, Afghanistan ultramarine) and contemporary art (such as phthalocyanine blue, zinc oxide and synthetic ultramarine blue). These models were analyzed by means of reflectance NIR and micro-Raman spectroscopic techniques.

The combination of FT-NIR and micro-Raman spectroscopy techniques, which furnish complementary information due to the different physical processes involved, has already demonstrated the ability to provide a much deeper insight into the characteristic structure and binding properties of different and partially aged (3 months of natural ageing) drying oils [12]. Indeed, the application of PCA to a combination of different spectral regions allowed an enhanced level of spectral information to be extracted. This non-invasive approach revealed to be a valuable, rapid and meaningful tool able to distinguish these organic compounds, up to the tracing of the manufacturer (in the case of drying oils)[12].

The results obtained by the present work are very beneficial for research concerning the characterization and the identification of the materials present in a pictorial layer because they mark an important step forward with respect to similar former studies, due to the choice of the laser source (785 nm wavelength) to acquire Raman spectra, which is important both to prevent fluorescence issues, and to work in a non-destructive way, contrary to FT-Raman analysis [13].

## 2. Materials and methods

### 2.1. Oil-paint model samples

For this work, four blue pigments (azurite (A), Afghanistan ultramarine (AU), synthetic ultramarine (SU) and phthalocyanine blue (PB)) and two white pigments (lead white (LW) and zinc white (ZW)) were selected on the basis of their chemical and mineralogical properties, according to their widespread use in easel paintings throughout history. The A, AU, SU and PB pigments were purchased from Zecchi (Florence, Italy), while the rest of pigments were supplied by Sigma-Aldrich (Milano, Italy). Linseed oil (L) and poppy-seed oil (P) from Zecchi (Florence, Italy) were selected as binding media and were used as supplied.

Twelve oil-paint models were prepared according to the recipes reported in original treaties and artists' accounts [14] by mixing these pigments with linseed or poppy-seed oils on the smooth surface of a panel glass. The list of samples together with their denomination is reported in Table 1. The powdered pigments were initially crushed in an agate mortar in order to obtain a homogeneously fine particle grain

**Table 1**

The oil mixtures analyzed and their corresponding identification symbols.

Pigment	Drying oil	Symbol
Lead white (LW), $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$	+ Linseed oil (L)	LWL
	+ Poppy-seed oil (P)	LWP
Zinc white (ZW), ZnO	+ Linseed oil (L)	ZWL
	+ Poppy-seed oil (P)	ZWP
Phthalocyanine blue (PB), $\text{C}_{32}\text{H}_{16}\text{N}_8\text{Cu}$ /copper phthalocyanine	+ Linseed oil (L)	PBL
	+ Poppy-seed oil (P)	PBP
Azurite (A), $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$	+ Linseed oil (L)	AL
	+ Poppy-seed oil (P)	AP
Synthetic ultramarine blue (SU), $\text{Na}_{810}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_2\text{-4}$	+ Linseed oil (L)	SUL
	+ Poppy-seed oil (P)	SUP
Afghanistan ultramarine blue (AU), $(\text{Na,Ca})_8[(\text{S,Cl,SO}_4,\text{OH})_2/(\text{Al}_6\text{Si}_6\text{O}_{24})]$	+ Linseed oil (L)	AUL
	+ Poppy-seed oil (P)	AUP

size without lumps. The exact concentration of the pigment with respect to drying oil was not determined *a priori*; instead for each case, a mixture of similar consistency was used to prepare the paint models so that they could be applied with a fine brush as a single thick layer onto microscope glass slides and allowed to dry on a bench top. Four sets of oil-paint models were prepared, obtaining a total of forty-eight samples. The paint films had rough non-homogeneous surfaces as would be expected in real samples. Neat samples of the binding materials were also applied as films on four microscope glass slides and left to dry for a total of eight samples. All oil-paint models and neat binders were analyzed after a natural ageing of 9 months. It has been shown that it represents a time-lapse during which the polymerization process is not yet completed and the hydrolysis or (photo-)oxidation reactions, characteristic for the degradation of these materials, have not started yet [15,16]. We are then evaluating a sort of intermediate step in the natural ageing process of both the drying oils and the oil-paint models.

The neat powdered pigments were directly analyzed without any preparation.

### 2.2. FT-NIR spectroscopy

FT-NIR reflectance spectra were recorded using a portable ALPHA FTIR spectrometer (Bruker Optics), equipped with the external reflection module. Total reflection spectra (including both the specular and diffuse reflection contributes) were collected *in situ*, in the 7500–3900  $\text{cm}^{-1}$  spectral range with a resolution of 4  $\text{cm}^{-1}$  over 128 scans. The spectral sampling distance used for each scan was 2  $\text{cm}^{-1}$ . An area of approximately 3 mm diameter was analyzed. The background was acquired using a gold mirror as reference sample.

A total of 320 spectra were recorded at four different positions for each sample.

### 2.3. Micro-Raman spectroscopy

The Raman spectra were collected using a Renishaw 2000 micro-Raman spectrometer equipped with a 785 nm diode laser. To analyze neat drying oils and powdered pigments, the laser was focused using a 50 $\times$  objective lens, so that an area of approximately 2  $\mu\text{m}$  diameter was considered. For the study of oil-paint models, a 20 $\times$  objective lens was used so an area of about 5  $\mu\text{m}$  diameter was investigated. In order to have an adequate sampling, we marked on the samples the spots characterized by FT-NIR and we made 16 different Raman measurements within the FT-NIR areas. We noticed that for each Raman single measurement we always obtained signals from both the pigment and the binder; furthermore, the repeatability within the 16 measurements was quite good. Spectra were recorded in the 2000–200  $\text{cm}^{-1}$  spectral range with a spectral resolution of 4  $\text{cm}^{-1}$ . To improve signal/noise ratios, we acquired spectra of 25 s and 100 s exposure time (averaged 3 times) for neat binders/pigments and for oil-paint models, respectively. The spectral sampling distance used for each scan was 1  $\text{cm}^{-1}$ .

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