



# Microanalytical method for studying paintings by use of fluorescence spectroscopy combined with principal component analysis



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## ARTICLE INFO

### Article history:

Received 22 May 2013

Accepted 25 May 2013

Available online 3 June 2013

### Keywords:

Microanalytical method

Binding media

Paintings

Fluorescence

PCA

## ABSTRACT

The study of several different naturally aged films of organic painting materials, is described. Materials studied include drying oils (walnut, poppy seed and linseed oil) resin-based paint varnishes (the triterpenoid dammar and the diterpenoids sandarac and turpentine) and protein-based binding media (egg yolk and casein).

A not expensive methodology for a rapid identification of binding media and varnishes, that applies principal component analysis (PCA) to Excitation Emission (EE) fluorescence spectra, is proposed. PCA was performed on a data matrix where the rows represent studied materials and columns the variables; the variables include the fluorescence intensities associated to different points (coordinates are  $\lambda_{ex}/\lambda_{em}$ ) in EE spectra. Results suggest that the new method can be used to classify micro samples on the basis of their fluorescence spectra, because the placement of the different materials in the score plot reflects their origin and chemical composition. The method described has been used for the analysis of materials of an oil painting on canvas, representing a mother with her child and on three mural paints. A small area of painting has been sampled with a cotton swab soaked in acetone, and subsequently the same area was sampled with a cotton swab and diethyl ether. The results of the application of the proposed microanalytical method to oil painting show that the author has used the linseed oil as binding medium and subsequently the surface of painting has been treated with a varnish containing the sandarac as resin.

Given the great diversity and complexity of the products used for the realization of a painting, Fourier Transform Infrared (FTIR) spectra of acetone and diethyl ether solutions have been performed, confirming the results of PCA applied to EE spectra.

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## 1. Introduction

Among the most important contributions that chemistry can offer to cultural heritage conservation are the understanding of the execution techniques and the identification of the materials that are contained in microscopic fragments from works of art.

The cultural heritage objects include ceramics, textiles, statues, glass, furniture, books, plastics, metals artifacts and paintings. A painting generally consists of several layers. The support, the main structural layer of a painting, has been principally canvas, wood or wall. Generally a painted surface consists of two paint layers on top of a ground layer on the support. The ground layer, also known as primer or preparation layer, is the stratum on which a drawing is made before the paint is applied and acts as a barrier between the paint and the support. The primer is often gypsum, chalk or a paint (generally white) containing animal glue [1,2].

The paint consists of one or more pigments and a binding medium. Most paint pigments are inorganic compounds. A range of materials has been used as paint binders over the years: egg white, egg yolk,

casein, animal glue, vegetable gums and several siccativ oils. Oils are pressed out of a variety of plant seed and they were used as binders from the 15th century until the 20th century. The principal oil used by artists for traditional paintings are walnut, poppy and, particularly, linseed oil. These oils, known as drying oils, form a solid film when exposed to air due to oxidation and cross-linking reactions, thus they assume good working properties as binding media [2]. A transparent varnish layer is used to protect the paint layers from dust, moisture and abrasions, and also provides gloss and color improvement. Historically, paint varnishes have undergone changes in composition and application. Oil varnishes, prepared by mixing natural resins like sandarac, mastic or colophony with drying oils, have been commonly applied by artists from the 11th century. Starting from the 16th century they were gradually replaced by solvent or "spirit" varnishes, that are solutions of terpenic resins in volatile solvents. The terpenic resins commonly used as artists' materials were diterpenic as sandarac and Manila copal that are exuded from two species of trees, *Tetraclinis articulata* and *Agathis dammara*, respectively, belonging to the *Coniferae* family, colophony and Venice turpentine that exude from trees belonging to the conifer subfamily *Pinaceae*, and triterpenic resins as dammar and mastic, exudate of various species of the *Diptocarpaceae* family [2]. Because of their

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light stability and transparency, solvent varnishes containing dammar (introduced only in the 19th century) are considered the best ones [3].

Binding media and varnishes are subjected to aging processes that are typically represented by physical, chemical and biological phenomena. Photo-oxidation is one of the degradation mechanisms most involved in the aging of painting media [4]. During aging, the chemical composition of varnishes changes qualitatively and quantitatively because of oxidation, polymerization causing the yellowing and brittle cracking that degrades both the optical properties of the varnishes and its protective function [5].

The aging phenomena, the restriction of sample amounts (in the micro or submicro range) and the presence of different analytes in the samples make studies dealing with the analysis of work of art pieces very difficult. This is the reason for which many analytical studies in the field of conservation of art require the use of different analytical techniques to obtain a characterization of samples extracted from the paintings.

The use of scientific techniques in materials conservation has notably expanded in recent decades [6]. There is much interest in identifying the materials used in paintings. In order to know the chemical characteristics of organic and inorganic materials used in culturally important objects, various techniques can be adopted: Raman spectroscopy [7–9], Infrared spectroscopy [10–12], UV-vis spectroscopy [13], Photoluminescence spectroscopy [14], Scanning Electron Microscopy (SEM) [15,16], Inductively Coupled Plasma emission spectrometry (ICP-OES) [17,18], Gas Chromatography/Mass Spectrometry (GC/MS) [19–24], Thermally assisted Hydrolysis and Methylation–GC/MS (THM–GC/MS) [25,26], Pyrolysis–Gas Chromatography/Mass Spectrometry (Py–GC/MS) [27–29]. GC/MS techniques, the most widely used in routine analysis for organic materials, have been successfully used to analyze oils used as binders in paintings. Unfortunately, the process often requires a complicated sample preparation process [30], and although the technique is reliable, it presents many complications.

In this paper a not expensive methodology for a rapid identification of binding media and varnishes, that uses synchronous fluorescence spectroscopy, is proposed.

Fluorescence spectroscopy is a well-developed and powerful technique for studying molecular properties and it has long been recognized that it may be possible to determine the composition of painting layers with this technique [31–34]. Surprisingly, detailed studies of the fluorescence properties of substances used on paintings have been limited [35,36] and, to the authors' knowledge, only few applications of the technique for the analysis of varnishes of musical instruments have been undertaken [37]. One significant disadvantage associated with fluorescence spectroscopy for the analysis of complex mixtures is that it is not generally possible to ascribe broad fluorescence emissions to specific molecules, because the observed spectrum is probably the sum of the spectra of many fluorophores present in the sample. Nevertheless, the synchronous fluorescence spectra show an improvement in the sensitivity over conventional fluorescence spectra (emission or excitation spectrum). In particular the synchronous technique can selectively increase specific peaks, whereas in conventional spectroscopy with a fixed wavelength, only the intensity of all the bands can be increased at the same time.

In order to differentiate various binding media and for the individualization of the materials used by artists for the realization of paintings, the application of chemometric analysis (principal component analysis and cluster analysis) to Excitation Emission (EE) fluorescence spectra is proposed. In recent years, chemometric techniques have been increasingly more used in the field of Cultural Heritage since they can extract information from correlated data sets, such as spectroscopic sets [38–40], or not [41].

The method described in this paper was applied to the study of materials of an oil painting on canvas made by an anonymous author and representing a mother with her child and of three fragments of a

contemporary (made in 20th century) mural painting. Given the great diversity and complexity of the products used for the realization of a painting, Fourier Transform Infrared (FTIR) spectroscopy has been used to confirm the information about the nature of materials.

## 2. Experimental

### 2.1. Description of samples

In this paper, the study of several different naturally aged films of selected organic painting materials is described. The materials studied can be used as binding media (proteins and oils) for pigments but may also be used as adhesives or surface treatments (varnishes). Materials were selected on the basis of their chemical composition, as well as their use and availability, and are not an exhaustive selection of resins, oils or proteins but rather represent general classes of materials used for realizing a painting. Materials studied include drying oils (walnut, poppy seed and linseed oil), resin-based paint varnishes (dammar, sandarac and turpentine) and protein-based binding media (egg yolk and casein). Drying oils and varnishes turpentine and dammar were purchased from Maimeri (Milano) and were used as supplied. Varnish solution of sandarac was prepared dissolving the resin in ethanol (Fluka, HPLC grade) and separating undissolved residual material after centrifugation (8000 rpm for 6 min). Protein-based binding media used in this study were prepared according to recipes from original treatises and artists' accounts [42]. Egg yolk was extracted from the egg by piercing the yolk and allowing the liquid to drip from the encasing film; the yolk was diluted in Millipore water to give a 50% w/w emulsion. Casein was purchased from Sigma-Aldrich (Milano). Casein was swollen in doubly distilled water for 12 h and the gel was then dissolved with the addition of a few drops of 0.5 M ammonium hydroxide (Fluka) to yield a transparent 5% solution.

In order to consider the fluorescence spectroscopy a technique of a general use for analytical purpose in art and art conservation, more realistic samples consisting of binding media mixed with pigments were also prepared. The test paint samples were made by mixing three pigments, Cadmium red ( $\text{CdSe}$ ,  $\text{CdS}$ ), Manganese blue ( $\text{BaSO}_4 \cdot \text{Ba}_3(\text{MnO}_4)_2$ ) and Yellow ochre ( $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ), with each drying oils. The exact concentration of the pigment to dry binder was not determined; in each case all paints were prepared to be of similar consistency so that they could be applied with a fine brush on glass disks in a single layer.

Aliquots of each material, with and without pigments, were distributed with a brush on glass disks. Films were considered immediately after drying in air and after their natural aging of 1 and 2 years.

### 2.2. Materials

Potassium bromide (Fluka, IR grade), acetone, diethyl ether and n-hexane (Fluka, HPLC grade) were used to prepare samples for analysis.

### 2.3. Fluorescence spectroscopy

#### 2.3.1. Sample preparation

Varnishes on glass disks were extracted for 30 s using a cotton swab soaked in acetone. The swab was introduced into a 5 ml glass test tube, added with 1 ml of acetone and placed for 30 min in ultrasonic bath. An aliquot of this solution was introduced in another glass test tube and placed in oven at 50 °C in order to evaporate the solvent. The solid residue was added with 1 ml of n-hexane and extracted for 30 min in ultrasound bath.

The same procedure was used for sampling of drying oils but with a different solvent. For oils, diethyl ether is shown to be the most appropriate solvent [43] both for its efficiency in extracting the sample and for its volatility. In order to verify this, a blank sample was prepared with a cotton swab extracted with diethyl ether, following

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