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Towards a non-invasive quantitative analysis of the organic components in museum objects varnishes by vibrational spectroscopies: Methodological approach

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ABSTRACT

The compositions of ancient varnishes are mainly determined destructively by separation methods coupled to mass spectrometry. In this study, a methodology for non-invasive quantitative analyses of varnishes by vibrational spectroscopies is proposed. For that, experimental simplified varnishes of colophony and linseed oil were prepared according to 18th century traditional recipes with an increasing mass concentration ratio of colophony/linseed oil. FT-Raman and IR analyses using ATR and non-invasive reflectance modes were done on the "pure" materials and on the different mixtures. Then, a new approach involving spectral decomposition calculation was developed considering the mixture spectra as a linear combination of the pure materials ones, and giving a relative amount of each component. Specific spectral regions were treated and the obtained results show a good accuracy between the prepared and calculated amounts of the two compounds. We were thus able to detect and quantify from 10% to 50% of colophony in linseed oil using non-invasive techniques that can also be conducted in situ with portable instruments when it comes to museum varnished objects and artifacts.

1. Introduction

The works of art varnishes have miscellaneous roles. It protects the work of art (painting, music instrument, or furniture) against the aggression of various environmental factors such as dust, air pollutants or light and to resist over time; but it also has an important esthetic role to enhance or create visual effects. Indeed, this thin transparent layer has some optical properties that enhance contrast, saturate the colors, and give depth and a glossy effect to the painting or the wooden artifact.

Varnishes are made of resins dissolved in a solvent, mostly siccative oil, and for some historical periods or specific uses, alcohol or spirit. Sometimes, mineral siccative agents or pigments can be added to the varnish (especially for music instruments, or furniture) to give a slight and attenuated color to the object, while keeping the transparency and glossy effects. Depending on the desired finish of the surface, but also on the proper preparation viscosity for an optimal application, the craftsman or the artist adapts the proportions of each constituent. Defining a methodology to detect and quantify different materials in a varnish is a way to enlighten ancient varnishing techniques, thus enhancing our knowledge in History of art and techniques.

Varnishes have been widely studied in order to get information about their compositions [1–5], the possible technologies used (heating, mixing), but also to identify their degradation and yellowing mechanisms by comparison with artificial ageing in order to characterize their original state [6–11], and even the quantification of their oxidation states [12–14]. Moreover, beside the alterations related to the chemical nature of the materials used, some studies are done on the possible biodegradation of varnishes due to some bacteria or fungi [15,16]. All these studies were mostly developed using separation methods coupled to mass spectrometry. Indeed, when working on varnishes, the presence, simultaneously, of different markers will give the varnish composition. However, these techniques are destructive and require an appropriate choice of analytical conditions and pre-treatments which are mostly time consuming.

Vibrational spectroscopies – Raman and infrared – are now being more and more developed following the performance enhancement of instrumentation. New horizons are now open, especially for the study of Cultural Heritage artifacts, thanks to the miniaturization of the devices and the development of portable instruments to get rid of the inflexible geometry of bench top spectrometers. These non-destructive and even non-invasive

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techniques do not require any sample preparation and allow on-site analysis directly on the artifacts whether for IR spectroscopy with different analytical modes such as diffuse and specular reflectance, or in the near-IR (NIR) range [17–19] or for Raman spectroscopy in the NIR [20–22]. Mathematical approaches are also being developed to get an improved exploitation of the obtained signatures and to establish new data treatment protocols easy to be applied to different issues. The spectra are no more studied in their raw form but are subjects to spectral derivatives [23], Principal Component Analyses [24–30] or spectral decomposition [31,32].

However, none of these techniques has yet been developed for quantitative purposes. One paper by Derrick [33], deals with some computer addition of pure material spectra in order to be compared to a varnish (mixture) spectrum. However, this work presents just one example, and the spectra comparison is mainly qualitative. The aim of this study is to develop a methodology to detect and quantify different components in a varnish by using FT-Raman spectroscopy and IR analyses in two analytical modes: ATR and specular reflectance, promoting non-destructive or even non-invasive analytical approaches. The very first idea to determine the presence of a compound in a mixture using its IR and Raman spectra would be to look for the presence of specific bands. However, varnishes are made of natural media that present the same chemical groups, and thus similar vibrational signatures. It becomes difficult to attest the presence of a compound in a mixture since its bands can be mixed up or hidden by another constituent of the varnish. It is therefore necessary to go deeper in the spectral interpretation and consider the profiles of the different constituents' spectra [26].

The materials used for this study were chosen depending on the most used materials for varnishing, especially for wooden objects such as music instruments or furniture since the 14th century and commonly employed during the 18th century. For example, previous studies about stringed instruments [3] using IR spectroscopy and separation methods (GC/MS) show the presence of a curing oil and a diterpenic resin (probably a pine resin). Moreover, this kind of objects is quite easy to analyze when working with non-invasive spectroscopies especially Raman and IR in reflectance mode. We chose thus to prepare mixtures of linseed oil and colophony. The multivariate approach here developed is based on the spectra of the materials present in the mixture whom linear combination must fit the mixture spectrum. For this purpose, experimental varnishes were prepared with increasing amounts of colophony in linseed oil, and the obtained results in terms of spectral adjustment and quantification, with each analytical approach, are discussed in this study. The novelty of this non-destructive and quantitative approach using portable IR in reflectance mode, and the analytical limits we faced mostly due to the materials natural alteration, are also taken in consideration. Finally, in order to monitor results from our vibrational methodology, some GC analyses, already approved for quantitative studies, were performed on the experimental varnishes.

2. Materials and samples

2.1. Chemical composition

The two employed materials have different chemistry. Indeed, colophony is a residue of the distillation of pine trees exudates and has as major diterpenic components abietic acid and its degradation products based on the abietane skeleton (Supplementary data S1): dehydroabietic acid (DHA), dehydro-dehydroabietic acid (dehydro-DHA), and 7-oxodehydroabietic acid (7-oxo-DHA) [34]. Linseed oil is made of triglycerides including 68% of polyunsaturated fatty acids allowing an important polymerization of the oil films. The majors fatty acids (Supplementary data S1) contained in linseed oil are linoleic acid (C18:2), linolenic acid (C18:3), and oleic acid (C18:1) [35].

2.2. Varnishes preparation

It is known that varnishes can be prepared in different and very complex manners, with different heating times, and mainly the addition of various inorganic compounds as dryers for a better and faster curing of the varnish. For our study we aimed to quantify only the main components of varnishes to establish the general framework of a varnish recipe. We therefore focused on organics which will provide the main vibrational features of the varnish, avoiding minor inorganic compounds and their possible vibrational signatures.

In order to develop a quantification methodology using vibrational spectroscopy, a test set of varnishes with different mass concentrations of colophony/linseed oil was prepared and then applied to obtain different samples of varnish films.

Several preparations were so formulated: two are made only of the “pure” materials: colophony and linseed oil; then varnishes with an increasing mass concentration ratio of colophony/linseed oil were prepared, and the samples named with their respective content of colophony/linseed oil as the following: 05/95, 10/90, 20/80, 30/70, 40/60 and 50/50 wt%. The proportions were chosen in order to have relatively fluid varnishes easily applicable with a paintbrush (most common application form) on glass slides. One weak concentration (5%) of colophony was chosen in order to have an evaluation of the limit of detection of this organic compound by Raman and Infrared spectroscopies. The preparation protocol was the following:

Crushing the resin.
Weighing the powder.
Dissolving the resin powder in ethanol.
Weighing the oil.
Homogenizing the mixture (stirring/warming at 90 °C, above ethanol boiling point).
Storing the varnish in a glass bottle.
And finally applying it on a glass support and leaving it for drying. The varnish films are with three layers thick (~100 μm), each layer being applied after the previous one got dry. All the varnishes were prepared at the same time, and let for drying with the same atmospheric conditions (air and daylight), and analyzed after 8 weeks of drying.

In the text, two representative conditions will be discussed in details the 05/95 (5% of colophony and 95% of linseed oil) and 40/60 (40% of colophony and 60% of linseed oil) mixtures.

3. Instrumentation

3.1. Raman spectroscopy

To overcome fluorescence of the studied substances we performed FT-Raman analyses using a near infrared excitation at 1064 nm (Nd-YAG laser diode) associated with a Bruker RFS 100/S spectrometer built from a Michelson-type interferometer, and equipped with a liquid nitrogen-cooled Ge detector. The studied varnishes were analyzed using a macroscopic interface with a 90° collection objective, allowing a spot size of 100 μm approximately, and a power at the sample of 400 mW (maximum nominal power of 500 mW).