



Micro infrared spectroscopy discrimination capability of compounds in complex matrices of thin layers in real sample coatings from artworks



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ABSTRACT

The presence of coating on manufactures either to protect them from the environment, or to give them specific properties—as well as simply to change their aspect—has been shown to be a constant practise throughout history. Their characterization is complex not only because of the inherent variability and diversity of the composition, but also due to the small amount of sample material available. A methodology to study those coatings using microFTIR is proposed. In some cases, the use of microSR-FTIR, which heavily increases spatial resolution particularly appropriate for the analysis of these heterogeneous samples, is also proposed. Data processing tools such as distribution maps of specific infrared bands and curve fitting facilitate the interpretation of the spectra and help identify heavily overlapped spectra. Through the identification of individual bands, it has been possible to discriminate materials and comprehend the interaction processes during aging. Infrared spectra from reference aged materials of known production dates and which are essential in understanding those processes are given. A set of selected case studies including materials of different chemical natures and various historical periods are presented: identification of guanine on the inner coating of a hope chest; determination of a protein glue coating from a gilded Baroque altarpiece; assessment of a beeswax superficial application during the historical restoration of a late 19th century canvas painting; identification of impurities of shellac wax in a shellac coating on a wood moulding from a medieval altarpiece; aging and reaction compounds in *Pinus* resin, drying oil and green copper pigment mixtures used as colour coatings on Baroque and modern desks.

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1. Introduction

The application of organic coatings on historic manufactures either to protect them from the environment or to give them specific properties—as well as simply to change their aspect—has been a constant practise throughout history [1].

The materials used for the purpose are very diverse in nature, depending on what the covering was intended for, the availability of the materials, the ease of application, or simply the fashion in the historic period [2].

Being at the surface, such covering layers are often totally/partially lost depending on the material properties, and frequently appear substituted by modern materials. Their characterization is, in general, complex not only because of the inherent variability and diversity of the substances present, but also due to the small amount of sample material available, generally a micrometric layer (between 5 and 10 μm), often modified by subsequent restorations [3].

As in other studies related to cultural heritage materials, the aging and alteration of the original materials, that is, the chemical reactions

occurring with atmospheric pollutants and among the substances—contemporaneous or not to the piece under study—must be taken into account. This implies that the reference materials we have access to can hardly correspond to the historic materials as they reached us.

Knowledge of the nature of these materials is, however, of great interest for a number of reasons; first, the historical insight obtained about the techniques used in the manufacture of the objects: the making of, including processing from the centre of production to the finished artwork, their relationship to contemporary artists or workshops, and the identification of the natural sources. Secondly, elucidating the conservation conditions in order to plan, if necessary, the optimal restoration strategy.

The availability of standardized and increasingly faster infrared (IR) equipment together with the intrinsic high sensitivity of the absorption set-up in the mid-infrared spectral range have made IR one of the most widely used techniques for the characterization of cultural heritage materials [4]. The principal advantages are related to the small quantity of sample needed, the ease of identification of very diverse materials, the speed at which results can be obtained via IR fingerprinting, the low cost of analysis and the non-destructive character of the technique.

The coupling of IR spectroscopy to a microscope extends its capabilities into the microanalytical range, providing the spatial resolution

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necessary for the identification of submillimetric structures/particles. It is more and more common to find infrared microscopes in laboratories dedicated to the microanalysis of cultural heritage materials. Adequate selection of the samples for analysis is especially challenging given the small quantity of material available from the historic objects [5,6].

Fourier transform infrared (FTIR) spectrometry is the standard lab method that provides easy spectral information and identification of the coating materials when a reference database is available [7–9]. The main objective of this article is to demonstrate the advantage of this technique for the identification of those coatings over more precise or costly and lengthy techniques such as GC-MS [10]. Nevertheless, when those techniques are needed, the information that is available from FTIR microanalysis (μ FTIR) has always been shown to be key in the characterization process and its optimization [11].

Another objective of this research is to investigate the spectral and spatial features across the submillimetric historic surface layer, identifying the spatial distribution of the chemical substances. For this reason synchrotron radiation FTIR microspectroscopy (μ SR-FTIR) was used to obtain the necessary spectral quality—high signal-to-noise ratio—at the maximum IR magnification available ($36\times$) for an improved minimum detection limit and reliable interpretation of the spectra within the spatial resolution of a few microns [5,12]. This goes beyond the limits of spectral interpretation by conventional IR techniques and is vital for the study of historical samples.

Many types of coating materials have been used over time. They can be essentially classified into five main groups: waxes, oils, gums, resins and protein materials [13]. The resins used are secretions of animal or vegetal origin, which can be chemically differentiated into several large families; sesquiterpenoids (shellac), triterpenoids (mastic, elemi and dammar), diterpenoids based in the communic acid (sandarc, amber and copal) and diterpenoids based in the abietic acid (colophony and turpentine) [13]. However, we sometimes find unexpected substances whose presence must be accounted for.

A methodology for the analysis of the coatings using μ FTIR is herewith proposed that permits to obtain definitive results, or at least to delimit the analysis features in an easier and more focused way. With the advantage of being non-destructive, the same sample preparation may be reused. Various examples corresponding to materials of different chemical natures applied with different purposes and at different historical periods are shown.

2. Materials and methods

2.1. Reference samples

A set of reference materials has been collected, selected and naturally aged from different restoration workshops, dry goods shops and commercial products and of natural origin from the author's own collection. In addition, naturally aged *Pinaceae* resin materials (about two centuries) were supplied by "Economic Botany Collection of the Royal Botanic Gardens, Kew", in Richmond (Greater London, UK). Moreover, a resin from the 14th century was obtained from a knot of a dated coffered ceiling made of *Pinus* wood. Finally, copper abietate was synthesized following the method from L. Steele [14] using abietic acid (Fluka Analytical ref. 101392305) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Panreac ref. 131270.1211).

2.2. Historic coatings

Historic coating samples, a few hundred micrometres in size, extracted from several artworks, have been analysed. The samples were obtained from a 16th century hope chest (MADB9909 reference number), an early 20th century writing desk (MADB71747 reference number) and a writing desk from the last quarter of the 17th century (MADB64160 reference number); all belonging to the Museu del Disseny de Barcelona [15]. Some other samples were obtained from a

Baroque altarpiece dedicated to Santa Càndia from the Cathedral of Santa Maria de Tortosa (Catalonia); a canvas entitled *View of the Barcelona Port* ($2.18 \text{ m} \times 7.30 \text{ m}$ in size) by Francesc Soler i Rovirosa, painted in 1889 from the Museu Marítim de Barcelona [16]; a gothic altarpiece dedicated to Our Lady, by Pasqual Ortoneda, on display at the Museum Vinseum (Vilafranca del Penedès, Catalonia); and a polychrome wood coffered ceiling in the 14th century from Santa Maria de Paretdelgada Chapel (La Selva del Camp, Catalonia).

2.3. Analytical instrumentation and methods

2.3.1. Microscopic observations (OM)

The microsamples were observed, handled and fragments selected for analysis with a Stereomicroscope, SMZ800 Nikon. Flat sites from selected fragments were observed with an Optical microscope Eclipse LV100 Nikon under visible and UV light.

2.3.2. Scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectrometry (EDS)

Scanning electron microscopy (SEM), JEOL-5600, with elemental analysis using the PCXA LINK EDS microanalyzer were used in order to obtain information of the composition and thickness of the layers of the samples. Small fragments were carbon-coated to ensure electrical conductivity.

2.3.3. Infrared spectroscopy

Selected fragments were analysed using mid-infrared microspectroscopy, μ FTIR. The measurements were taken in transmission mode using an AIM-8800 microscope with an MCT detector coupled to the Shimadzu IRAffinity-1 FTIR spectrometer. A transmission spectrum requires a flat sample with an adequate thickness. For this, selected fragments were squeezed between two diamonds into an anvil cell. The spectra were taken from one of the diamonds and a spot of 100×100 and 40×40 square micrometres surface area was analysed. This procedure helps the separation of the different compounds present. The measurement interval was $4000\text{--}700 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} and 256 scans.

Synchrotron-based infrared microspectroscopy (μ SR-FTIR) measurements were taken at beamline MIRIAM B22 of the Diamond Light Source [17]. Two Bruker 80 V Fourier Transform IR Interferometers are equipped with Hyperion 3000 microscope, and broadband and high-sensitivity MCT detectors. The spectra were obtained in transmission mode from a sample dispersed on a diamond window following the same compression cell preparation method described above, using a small beamspot of 12×12 square microns, 4 cm^{-1} resolution, co-adding 256 scan at scanner velocity 80 kHz (35 sec), in the 4000 to 650 cm^{-1} or 500 cm^{-1} wave number range. IR maps of the molecular composition were obtained by scanning the sample via a micrometric resolution motorized X–Y stage.

An accurate analysis of the spectrum is able to resolve overlapped bands [18]; when needed, overlapped bands have been processed using the curve-fitting software from OPUS 7.2. First, the spectra were baseline-corrected and then the band positions were found from the second derivative of the curve, and finally, the spectrum was fitted by a set of Lorentzian curves. The method is applied to fit all the bands appearing; although only the significant ones are shown.

3. Results and discussion

3.1. Guanine, unexpected coating

The first example corresponds to the coating material from the interior of a hope chest dated from the 16th century by historians, and was obtained during the process of restoration.

The very thin coating layer was directly applied onto the wood; the sample was mechanically extracted under a stereomicroscope to help

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