Combined approach of FT-Raman, SERS and IR micro-ATR spectroscopies to enlighten ancient technologies of painted and varnished works of art

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Abstract

The characterization of materials involved in painted works of art provides a better knowledge of artworks through the understanding of artistic and technological processes. In this study, some pieces selected from a large corpus of French Decorative Arts objects from 18th century museum collections were analyzed. These materials are complex system made of a multilayered colored background, covered with varnish layers. Colored or gilded ornaments are applied, representing different characters, flowers, or landscapes, then varnished again. The aim of this study was to improve the painting and varnishing techniques knowledge in the Decorative Arts field during the 18th century.

Vibrational spectroscopies, Raman, SERS (Surface Enhanced Raman Spectroscopy) and infrared, were used to analyze some specific parts of these objects, especially organic materials such as lake pigments, binders and varnishes, and some of them were identified. For this purpose, a set of experimental setups and parameters were used according to the samples. The performed analyses were thus done using conventional FT-Raman at 1064 nm, SERS with a 458 nm excitation wavelength, infrared using a micro-ATR mode, and by defining for each technique and each analysed sample the best set of analytical parameters. The results obtained are all complementary, and allowed us to completely identify and characterize multilayered paint systems as well as varnish compositions using specific data treatment methodology. This study is a description of the various possibilities that

vibrational spectroscopies can provide when the right settings are employed, with a deeper look into the vibrational features using new data treatments.

Keywords

FT-Raman, SERS, IR-microATR, lake pigments, varnish

Introduction

Cultural heritage paintings and painted objects are usually heterogeneous and complex. They consist of a support, on which preparatory grounds, paint layers, decorative settings and varnishes have been applied. So even if layers vary in their number, properties and function, these objects are built up by the successive applications, which thickness can be in the micrometer order. The complexity increases with the wide variety of used constituent materials: pigments, dyes, lakes, additives, adhesives, binders, medium, varnishes... Furthermore these materials have been transformed, mixed, subject to interactions, altered through time, either under manufacturing processes, ageing or restoring treatments. Concerning the 18th century Decorative Arts objects, only few studies were done to document the emergence and development of painting and varnishing techniques in Paris or Europe^[1, 2]. At this time, Paris was a bustling center for technological innovations to produce varnished objects, mainly thanks to four brothers “the Martins” and their descendants^[3]. Their productions were initiated to satisfy an increasing taste for Asian lacquers and their decors^[4] that were highly imitated using black, red and golden oriental models. The Martin family gave its name to an enigmatic varnish that Watin, in his treatise (1772) “*L’art de faire et d’employer les vernis (The art of making and using varnishes)*”^[3] considers as a white luxurious and glossy varnish made of copal. Then, among the 18th century, the painters and varnishers developed a totally new French style with a large palette of colors and ornaments using European raw materials and techniques.^[5]

The main existing studies are based on historical and stylistic approaches^[6, 7], thus, the characterization of materials involved in this kind of painted works of art can provide a better knowledge of artworks through the understanding of these technological processes, and their evolution through time. However, the main constraints when working on cultural heritage artifacts are the availability and representativity of the probed matter. When sampling is possible, it is limited to very small amounts (sample can be as small as 200 μm in size and 20 micrometers thick).

Vibrational spectroscopies are widely used to characterize mineral pigments or organic dyes in the cultural heritage field. Indeed, they present the advantage of being fast without any sample

preparation steps, non-destructive - the collected sample can be re-used for further analyses - and finally, the possibility of *in-situ* analyses with miniaturized portable devices^[8, 9].

Raman and infrared (IR) spectroscopies can also be coupled to a microscope allowing the reduction of the probed volume to a micrometric resolution in order to perceive heterogeneities, layering, and thus provide chemical information of a large class of amorphous or crystallized materials present in a same sample such as a pictorial layer.

In this study, some pieces of a large corpus of painted and varnished objects from 18th century French Decorative Arts collections have been selected to be characterized using a combined approach of Raman, SERS and IR techniques to evaluate the ability of vibrational spectroscopies to identify the components of these complex mixture samples. Among the studied materials, we mainly focused on the most challenging analytical characterization, i.e.: layers containing organic materials, pictorial layers with red dye particles and binders, and pure organic layers as varnishes.

Red organic dyes have already been successfully identified using Raman and infrared spectroscopies in many contexts: dyed fibers,^[10-12] manuscripts inks,^[13, 14] ancient cosmetics,^[15] frescoes,^[16, 17] paintings,^[18-21] violin varnishes^[22] or polychrome sculptures.^[23]

These techniques have also highly been employed to characterize natural organic media that can be used in painting layers or varnishes,^[24, 25] to differentiate between these materials,^[26-28] or to study the ageing and degradation of such materials.^[29-32]

However, one major issue to Raman spectroscopy when organic products are analyzed is the important fluorescence emission that may hide the Raman features.^[33] Sometimes, fluorescence can be hindered when using a near IR excitation wavelength at 1064 nm for dyes,^[16, 34] or other organic media^[35-37]. Some studies show new mathematical developments in order to remove the fluorescence background and get the vibrational features;^[11, 38] or new instrumental developments allowing to improve the signal by Resonance Raman Spectroscopy (RRS)^[39]. But the mostly used technique to get rid of this luminescence phenomenon is Surface Enhanced Raman Spectroscopy (SERS)^[40] with sometimes extraction of the dye,^[10, 41] the application of colloids on small samplings^[42, 43], after HF hydrolysis^[44] or even directly on the work of art^[12, 45]. Several preparation protocols for SERS surfaces are being developed,^[46-49] and new improvements allow now non-invasive *in situ* study of the works of art using specific gels in which metallic colloids are embedded^[50, 51] or using tip-enhanced SERS (TERS) and advanced functionalized SERS-active optical fibers.^[52-54]

IR spectroscopy can be used to get complementary information about the studied materials since it does not generate fluorescence emission. It can be used to characterize binders and minerals in multilayered samples such as painting layers or glazes^[55, 56], or varnish layers using synchrotron radiation^[57-59]. Mathematical developments can also be considered to determine mixtures' components such as first and second derivatives of the spectra^[60], spectral decomposition^[61], or Principal Component Analyses.^[62-64]

The aim of the present study was to develop a convenient analytical strategy, as non-destructive as possible, that allows the identification of a wide range of materials involved in painted works of art from organic substances to mineral materials. A multi-step analytical methodology, based on the use of complementary Raman, SERS and infrared microATR-spectroscopy and the optimization of the experimental settings used was elaborated; and mathematical treatments such as spectral decomposition were applied.

In this work, reference materials - alizarin red, cochineal lake, and home-made varnishes consisting of drying oil and colophony - and samples collected from four painted and varnished objects from French 18th century collections were investigated: a commode, a weaving shuttle, a blue silver case and finally a glass holder. The obtained results report the performance of the complementary approach involving vibrational spectroscopies, and enlighten the painting and varnishing techniques during the 18th century in France.

Experimental

Reference samples

Dyes and lake pigments

Natural organic dyes can be extracted from plants or insects, and the resulting molecules are mainly, for red dyes, a mix of anthraquinone type skeleton. These molecules may be complexed by mineral substrates or inorganic salts called “mordents” as for example alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) or calcium carbonate (CaCO_3) leading thus to what is called lake pigments^[20].

For this study, we mainly focused on two different commercial references of lake pigments taken from the C2RMF materials library. First, red carmine lake (Mermeri, Milan), extracted from cochineal insects with major component carminic acid (fig. 1a), and second, madder lake (Lefranc) mainly composed of alizarin dye (fig. 1b).

Organic materials: model varnishes and binders

Model varnishes prepared on glass slides during the 1970's from commercial materials were used as reference materials. Since these organic substances are known to evolve during the curing and ageing of the varnish, it is preferable to compare the spectra obtained on the studied varnished museum objects with already dried and slightly oxidized varnishes. Three experimental films were thus considered, according to the most famous varnishes employed during the 18th century for furniture or luxury objects in France: linseed oil, colophony and copal, referring to the “verniss Martin”.

Linseed oil is made of triglycerides with 68% of polyunsaturated fatty acids that play a major role in the varnish drying process. Linoleic acid (C18:2) and linolenic acid (C18:3) are the main compounds of linseed oil (fig. 1d) ^[65].

Colophony is a diterpenic resin that exudates from *Pinus sp.* trees. Its major component is abietic acid (fig. 1c) and is known to easily undergo oxidation reactions, leading to degradation products built on the same chemical skeleton ^[66].

Copal is a diterpenic resin as well, that have various geographical and so botanical origins. Some are from *Araucariaceae sp.* trees (Manila copal) with sandaracopimaric and agathic acids as main components; and others from *Fabaceae sp.* trees (Madagascar or African copals) with copalic and osic acids as main compounds.

Concerning the different binders - or different chemical families of binders - that could have been used in these 18th century paintings, different films were analyzed. They were made of linseed oil as oil binder, gum Arabic as polysaccharidic binder and rabbit skin glue as proteinaceous binder. The sample were prepared during the early 2000 from commercial materials (from Laverdure, Paris and Sennelier, Paris) dissolved in ethanol and then applied on glass blades and left for drying.

Samples collected from painted and varnished works of art

In order to get information on the whole multi-layered system, it was necessary to sample the different museum objects and to work on selected levels. Therefore, samples were collected from 35 18th century painted and varnished objects issued from French Decorative Arts museum collections. Among all these samples, and according to the samples size and shape, 16 could be analyzed using vibrational spectroscopies and only a few were successfully characterized, the others leading to poor quality spectra. They belong to the following objects: a weaving shuttle (*inv13377, musée des Arts Décoratifs, Paris*; fig. 2 a)), a commode “Adelaide” (*invVI965, musée national du château de Versailles, Versailles*; fig. 2 b)) with a beige background and decorated with pink floral motifs, a blue silver case « Carnet de bal » (*invI1854, musée des Arts Décoratifs, Paris*; fig.2 c)), and a golden glass holder (*invPR.2013.2.515, musée des Arts Décoratifs, Paris*, fig. 2 d)).

For the two former objects, the pink pictorial layers were investigated. Fig. 2 a') and b') present the stratigraphy of these two objects, where the pink layers appear to be a mixture of a white pigment with red particles of variable size. Some inclusions of blue grains can also be noticed in these layers. On the weaving shuttle's stratigraphy (fig. 2 a')), a strong discoloration is observed on the surface: the pink particles seem absent from the upper part of the stratigraphy. Indeed, these particles are organic pigments which were probably discolored due to a strong lighting. On the commode's sampling (fig. 2 b')), we can observe two different pink layers: the lowest one seems to be the original ornament, and the second was probably applied during a later intervention.

For the blue case and the glass holder, merely organic layers were sampled. Flakes of about 300 μm in size were taken from the upper layer - the final varnish - of these two objects (fig. 2 c') and d')), but also from the lowest layer - the underlayer - that is directly in contact with the support (fig. 2 c'') and d'')). This thick underlayer was probably applied on their metallic support as a waterproofing treatment (to protect the support from any corrosion) or as an adhesion level for the following painting layers.

Raman instrumentation

Visible excitation wavelength: Raman and SERS analyses

Raman spectroscopy measurements were performed using a LabRam HR800 (Horiba-Jobin Yvon) instrument characterized by a focal length of 800 mm and edge filters. The analyses were done using the 458 nm excitation wavelength of a water-cooled Ar⁺ laser and a 600 lines/mm grating. The detector is a CCD camera with a Peltier effect cooling system. Spectral resolution was around 2 cm^{-1} , and calibration was checked with respect to the 520.5 cm^{-1} silicon band. The spectrometer is coupled to an Olympus microscope equipped with a 100x Olympus objective which allows a $\sim 1\mu\text{m}$ diameter spot size. The laser power was adjusted depending on the analyzed sample (nearly 50 μW at the sample for most of them) and the counting time was between 30 sec to 1 min.

Silver colloids were prepared following the procedure of Lee and Meisel ^[67] by reduction of silver nitrate with sodium citrate adapted from Van Elslande et al ^[15].

Near Infrared excitation wavelength: FT-Raman analyses

FT-Raman analyses were performed using a near infrared excitation at 1064 nm provided by an Nd-YAG laser diode available on a Bruker RFS 100/S spectrometer based on a Michelson-type interferometer, and equipped with a liquid nitrogen-cooled germanium detector. The commercial references were analyzed using a microscopic interface equipped with a 40x objective, allowing a spot size of 30 μm approximately. The sampled objects were analyzed using a 100x objective leading to an about 15 μm spot size. The laser power was adjusted depending on the analyzed sample. Reference materials and the objects' samples were placed on a gold mirror to improve the collected Raman signal intensity. Spectra were recorded between 3500 and 50 cm^{-1} with a 4 cm^{-1} resolution, and with 1000 to 1500 scans to optimize the signal-to-noise ratio.

Infrared instrumentation

Micro-infrared spectroscopy analyses were performed in an Attenuated Total Reflectance mode (mono reflection-ATR) using a Bruker Equinox 55 spectrometer coupled to an IRscope II microscope equipped with a 20x ATR objective with a Germanium crystal. This crystal needs a contact with the analyzed object, and depending on the material hardness it can lead to some damage, but the sample can still be collected for further analyses. A liquid nitrogen-cooled MCT detector was used, and a background was collected before each sample's spectra. 200 scans were accumulated between 4000 and 600 cm^{-1} with a 4 cm^{-1} resolution.

Results and discussion

This part presents the obtained results on several objects and samples. Pictorial layers of the two pink objects were investigated using SERS for the red dyes particles, FT-IR and FT-Raman for binders and charges. Pure organic layers (protective underlayers and upper varnishes) found on metallic objects were analyzed using FT-Raman, and mathematical treatments of the signals obtained were performed in order to identify the precise composition of such organic layers.

Pink objects: characterization of the pictorial layers

Red lake dyes

On samples taken from the two pink objects (weaving shuttle and commode), we observed heterogeneous pictorial layers composed of a mixture of white and deep red spots (see fig. 2 a') and b')). Each analysis on these samples using Raman or infrared spectroscopy was performed pointing at these red particles.

Generally, the complexation of the dye molecule on the inorganic substrate, implied by the making of the lake pigment, involves spectral modifications compared to the pure organic dye spectrum. Since only lake pigments are used in pictorial layers, and to ensure a proper comparison with the museum samples spectra we choose to analyze commercial lake pigments as references, instead of pure dyes.

The samples taken from the colored layers of the two pink objects have been first analyzed by Raman spectroscopy using a 458 nm excitation laser. However, the high fluorescence background observed prevents the observation of the Raman features of the lake pigment on each sample. This fluorescence background may be due to the organic dye itself or the organic binder used in the pictorial layer. One of these spectra is shown in fig. 3 a), in the case of the weaving shuttle red particles.

In order to access the most colored areas and avoid the binder contribution to the Raman spectra, the samples were cut using a scalpel. A silver colloids aliquot was deposited directly on the

sample to produce a SERS effect. This procedure is easily implemented as it does not require any additional preparation treatments. Fig. 3 shows the SERS spectra obtained from samples of the two objects (fig. 3 b) and c)) and from the two suspected lake pigment commercial references (carmine and madder, fig. 3 d) and e)) analyzed in the same conditions.

The spectrum of the weaving shuttle sample has a close similarity to the spectrum of the carmine lake reference, displaying particularly a band at 1109 cm^{-1} attributed to bond vibrations (C-C and C-OH) of the glucose group of carminic acid (fig. 3 b) and d) plain dots, see also fig. 1 a))^[10, 34].

The spectrum obtained from a sample of the commode shows a profile similar to the madder lake reference, and in particular three bands characteristic of the C=C stretching in madder lake skeleton at 1291 cm^{-1} , 1326 cm^{-1} and 1355 cm^{-1} (fig. 3 c) and e), stars)^[10, 34]. Moreover, on this sample, both of the two pink layers (see fig. 2 b')) were analyzed, and exactly same spectra were obtained (not shown here).

By using silver colloids and a 458 nm Raman excitation wavelength, we were able to properly characterize by SERS the lake pigments (cochineal and madder) used in the two pink objects. On the commode sample, both original and restoration pink layers were done using same pigment, madder lake. However, SERS enhances the Raman signal of molecules adsorbed on the silver colloids, hiding thereby the other compounds signals. If we want to go beyond pigment identification and try to determine the other constituents, further techniques must be used: infrared and FT-Raman spectroscopies.

Binder and charges

Analyses on samples taken from the weaving shuttle were performed using ATR infrared spectroscopy. The corresponding spectrum presented in fig. 4 a) reveals a band at 1707 cm^{-1} assigned to the stretching vibration of the C=O bonds, and bands appearing at 1241 cm^{-1} , 1159 cm^{-1} and 1097 cm^{-1} assigned for the first one to the bending vibration of COH bonds^[27], and for the two other bands to the stretching vibrations of CO bonds. These bands suggest the presence of siccative oil used as a binder in this pictorial layer, confirmed by the comparison with the spectrum of a linseed oil reference film (fig. 4 d)). Indeed, the comparison with other kinds of binders, such as rabbit skin glue (proteins, fig. 4 e)) or gum Arabic (polysaccharides, fig. 4 f)) shows that the bands specific of these two materials such as the two amides bands between 1500 and 1600 cm^{-1} , and the NH stretching vibration at 3250 cm^{-1} for the glue, and the C-O stretching band at 1050 cm^{-1} for Arabic gum are totally absent from the sample spectrum.

On the same spectrum (fig. 4 a)), a band of small intensity appearing around 2087 cm^{-1} is attributed to the C≡N vibration of Prussian blue ($\text{M}^+\text{Fe}^{3+}\text{Fe}^{2+}(\text{CN})_6.n\text{H}_2\text{O}$, $\text{M}=\text{Na}, \text{K}, \text{NH}_4$) which might have been added to the pictorial layer to slightly modify the reddish color to a more purple color (see also fig. 2 a')). The shuttle IR spectrum reveals also a broad band at 1414 cm^{-1} , a band of weak

intensity at 1045 cm^{-1} and a sharp band at 683 cm^{-1} . These bands are attributed to the CO_3^{2-} vibration of lead white $(\text{PbCO}_3)_2\text{Pb}(\text{OH})_2$ (white pigment) which is employed in mixture with carmine lake, as shown in the stratigraphic view of the sample (see fig. 2 a')).

Most of these results are confirmed by the analysis performed on this sample using FT-Raman spectroscopy with a 1064 nm excitation wavelength. The resulting Raman spectrum presented in fig. 5 has a high similarity to the spectrum of a linseed oil reference film, particularly concerning the C-H bending vibrations at 1305 cm^{-1} , 1445 cm^{-1} and stretching vibrations around 2900 cm^{-1} , and the stretching of the C=C bonds at 1602 cm^{-1} . It is also clearly different from the two other binders spectra presented in fig. 5 c) and d). However, since Raman and IR spectroscopies can not differentiate between siccative oils^[28] and since linseed oil is the most commonly used, an assumption can be made that linseed oil was employed for this painting.^[1] The sample Raman spectrum also reveals a strong and sharp signal related to lead white at 1051 cm^{-1} , characteristic of the CO_3^{2-} group vibration.

Two infrared spectra were obtained from samples taken from the commode (see fig. 4 spectra b) and c)). One of the spectra (fig. 4 b)) shows the characteristics bands of siccative oil: the CH stretching band at 2900 cm^{-1} which profile is characteristic of an oil as well as the 1700 cm^{-1} C=C stretching band. More intense bands located at 1449 cm^{-1} and 875 cm^{-1} are assigned to the vibration of the CO_3^{2-} group in calcium carbonate (CaCO_3). The presence of lead white is also demonstrated in this case by the presence of its typical bands at 1414 cm^{-1} , 1045 cm^{-1} and 683 cm^{-1} on spectrum c) in fig. 4.

We were able to characterize, using IR and FT-Raman spectroscopies, the different pictorial layers of the pink objects. Siccative oil was used as binder, and lead white, Prussian blue and calcium carbonate have been employed to alter the red color, giving pink and lilac shades to the objects' pictorial layers.

Pure organic layers: underlayers and superficial varnishes

General remarks

Pure organic layers were found at different stratigraphic levels of the multilayered systems: a first thick protective or waterproofing layer for some objects, and a thinner upper varnish for all the studied objects. These two different layers were sampled from the blue silver case (see also fig. 2 c') and c'')) and the glass holder (see also fig. 2 d') and d'')) and analyzed using FT-Raman spectroscopy. Fig. 6 presents the obtained raw spectra for these two objects: a) and b) are respectively the upper varnish and the underlayer of the glass holder, and c) and d) are respectively the upper varnish and the underlayer of the silver blue case. First, we can notice that spectrum d) in fig. 6 does not show any Raman bands, all being hidden by a very intense fluorescence background. The a), b) and c) spectra show vibrational features, characteristics of natural organic materials^[27]. On spectrum a) a heating bump between 3000 and 2500 cm^{-1} is observed; but the sample does not show any visible damage after the analysis.

The spectra were baseline corrected to improve the observation of vibrational features and are presented in fig. 6 a') to c'). These spectra were compared to the spectra of two reference media that were highly employed during the 18th century in Europe for varnishes production: a linseed oil film (fig. 6 e)) a colophony resin film (fig. 6 f)) and a copal resin film (fig. 6 g)). The observed vibrational features are very similar to the reference media ones, in terms of bands position and profile. These bands are underlined in fig. 6: the CH stretching vibrations band around 2900 cm⁻¹, the C=C stretching vibration band at 1640 cm⁻¹, the CH bending vibration at 1440 cm⁻¹, the OH bending vibration band at 1300 cm⁻¹ and finally the C-O stretching band at 1090 cm⁻¹.^[27]

However, this data comparison is insufficient to precisely characterize the nature of these two organic compounds and especially to identify which resin was employed for the mixture preparations. It is thus necessary to go further in the data treatment and work on the bands morphology and profile. Indeed a previous study^[28] shows that using a spectral decomposition procedure of specific bands can give important and precise information. We chose to work on one specific region, the CH stretching band, for several reasons: it is the most intense band of the spectra, it is observed for all references and museum samples, it presents rather different profiles for the three organic reference compounds, and finally seems to be poorly influenced by the oxidation process that may occur in these materials. Moreover, this band is being more and more used to identify and characterize organic compounds in the cultural heritage field.^[26, 28, 31, 63]

Data treatment: spectral decomposition

The spectra were thus cut between 3180 and 2500 cm⁻¹, and spectral decomposition software (PALME, MONARIS, D. Baron) was used to process the CH band. This homemade software considers the mixture spectra as a linear combination of the pure material ones, so the sum of the pure materials spectra must fit the experimental mixture spectrum.^[68-70] Moreover, if one pure material spectrum does not contribute well to the mixture spectrum, it leads to an incorrect adjustment (see supplementary data S1), or appears negatively which means it has been rejected by the software (see supplementary data S2). This was applied to the spectra of the glass holder's upper varnish and underlayer, and the spectrum of the silver blue case's upper varnish as well. The fitting results are presented on fig. 7. It can be noticed on these three examples that the experimental varnishes spectra are well adjusted by linseed oil and colophony reference spectra, despite a noticeable noise for two of them. The shape of the CH band thus appears as quite conserved even with spectra from ancient micro samples that are not always well defined, especially in the fingerprint region. Adding this spectral decomposition step allows us to confirm the use of linseed oil and colophony in these 18th century French Decorative Art painted and varnished objects. On Supplementary Data S2, an adjustment with a copal spectrum shows a negative fit, proving the absence of copal in this varnish. Finally, further than these FT-Raman data, some destructive GC/MS analyses were performed after the vibrational

techniques on the same micro-samples. These results confirmed the identification of a mix of (linseed) oil and colophony and therefore the suitability of the proposed approach for further studies.

Conclusions

Our combined approach allows exploring, in greater depth and with details, painted and varnished works of art. Using Raman, SERS and IR spectroscopies we could get new and original information about the techniques (see supplementary data S3) used to produce several objects taken from a large corpus of the 18th century French Decorative Arts collections. Furthermore, the obtained data are highly informative on the material composition in different layers.

We were thus able to characterize – for two objects – the whole composition of some painting layers: very small (10 μm in size) particles of red dyes as madder and cochineal lakes using SERS (458 nm excitation wavelength and silver colloids) without any extraction or pretreatment; lead white or calcium carbonate as major mineral pigments, and Prussian blue added to slightly modify the pink color to a more lilac or purple color using IR-ATR mode; and finally the binder as a siccative oil using IR-ATR and FT-Raman.

Some objects presented a thick organic underlayer directly in contact with the support, that was identified, using a specific data treatment procedure on the FT-Raman spectra, as a mixture of siccative oil and pine resin, as well as the thin upper varnishes.

When several experimental settings are available such as different Raman excitation wavelengths, different sets of objectives, silver colloids for SERS analyses, it is possible to choose the right setup, according to the analyzed sample or material, in order to have the most complete characterization of the multi-layered studied objects. Moreover, these techniques can provide non-destructive analyses, a condition that is highly recommended for the study of Cultural Heritage artifacts. Finally, for some very complex samples such as mixtures, having the correct set of experimental devices is not sufficient, and further data treatments using mathematical approaches are required to get the most detailed information contained in the vibrational spectra, as here the identification of a colophony/siccative oil varnish.

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Fig. 1 : Main compounds of the reference materials. a) carminic acid (carmine lake), b) alizarin (madder lake), c) abietic acid (colophony), and d) linolenic acid (linseed oil).

Fig. 2 : Photography of the 4 studied objects and of some stratigraphic view of the samples. a) Weaving shuttle (inv13377, musée des Arts Décoratifs, Paris), a') stratigraphy of a weaving shuttle sample, b) Commode "Adélaïde" (inv1965, musée national du château de Versailles), b') stratigraphy of a commode sample. c) Silver case "Carnet de bal" (inv11854, musée des Arts Décoratifs, Paris), c') Silver case - upper varnish flake, c'') Silver case - underlayer flake, d) Glass holder (invPR.2013.2.515, musée des Arts Décoratifs, Paris), d') Glass holder - upper varnish flake, and d'') Glass holder - underlayer flake.

Fig. 3 : Raman and SERS spectra (458nm) on the red particles: a) Raman spectrum of the weaving shuttle red particle, b) SERS spectrum of the weaving shuttle red particle, c) SERS spectrum of the commode red particles, d) reference carmine lake SERS spectrum, and e) reference madder lake SERS spectrum. The symbols refer to the bands discussed in the text: plain dots: stretching vibration band of the glucose C-OH bond, stars: stretching vibration of the alizarin C=C bands.

Fig. 4 : IR-ATR spectra of: a) a sample taken from the weaving shuttle pictorial layer, b) and c) samples of the commode pictorial layers, and d) to f) linseed oil, rabbit skin glue and gum Arabic reference films respectively. Dotted lines: linseed oil characteristic bands, plain star: Prussian blue characteristic band, plain dots: lead white characteristic bands and empty dots: calcium carbonate characteristic bands.

Fig. 5 : FT-Raman spectra of : a) the weaving shuttle pictorial layer, b) a linseed oil reference film, c) a rabbit skin glue reference film and d) a gum Arabic reference film. The plain dot refers to the lead white band at 1051 cm^{-1} (discussed in the text), and the dotted lines to the common bands of the sample with linseed oil.

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549 **Fig. 6 : FT-Raman spectra of different organic layers taken from different objects: a) the upper varnish of the glass**
 550 **holder, b) the underlayer of the glass holder, c) the upper varnish of the silver case, d) the underlayer of the silver**
 551 **case. Spectra a') to c') are respectively the results of the baseline subtraction of spectra a) to c). e) f) and g) are the**
 552 **linseed oil reference film, the colophony reference film, and the copal reference film respectively, after the baseline**
 553 **subtraction. The blue lines refer to both resins bands, and yellow lines to linseed oil bands.**

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— Experimental spectrum — Baseline — Linseed oil
 - - - Calculated spectrum — Colophony

Fig. 7 : Spectral decomposition of FT-Raman CH band for three organic layers (mixtures) using linseed oil and colophony films as pure reference materials. Misfitting examples are presented as supplementary data.

— Experimental spectrum — Baseline — Linseed oil
 - - - Calculated spectrum — Colophony

Supl. Data S 1 : Spectral decomposition of FT-Raman CH band for the glass holder underlayer using only one pure material spectrum: linseed oil (top) and colophony (bottom). In these two examples, the adjustment is incorrect, another pure material spectrum is necessary to get a good fitting.

Supl. Data S 2 : Spectral decomposition of FT-Raman CH bands for the glass holder and the silver case upper varnishes using linseed oil and copal films as pure reference materials. In these two examples, the adjustment is incorrect, since one spectrum (linseed oil) is rejected by the software and appears negatively.

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574 **Supl. Data S 3 : Schematic representation of the multilayered system of French decorative Arts objects. All layers are**
575 **not always present.**

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Graphical TOC

Combined approach of FT-Raman, SERS and IR micro-ATR spectroscopies to enlighten ancient technologies of painted and varnished works of art

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French Decorative Arts objects from 18th century museum collections were studied. These complex materials were analyzed using FT-IR, FT-Raman and SERS, and particularly organic materials such as lake pigments, binders and varnishes were identified thanks to the right choice of analytical parameters and, for some complex mixtures specific data treatments.