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# 1 Combined approach of FT-Raman, SERS and IR micro-ATR 2 spectroscopies to enlighten ancient technologies of painted and varnished 3 works of art

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## 16 17 18 **Abstract**

19  
20 The characterization of materials involved in painted works of art provides a better knowledge  
21 of artworks through the understanding of artistic and technological processes. In this study, some  
22 pieces selected from a large corpus of French Decorative Arts objects from 18<sup>th</sup> century museum  
23 collections were analyzed. These materials are complex system made of a multilayered colored  
24 background, covered with varnish layers. Colored or gilded ornaments are applied, representing  
25 different characters, flowers, or landscapes, then varnished again. The aim of this study was to  
26 improve the painting and varnishing techniques knowledge in the Decorative Arts field during the 18<sup>th</sup>  
27 century.

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

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

39

## 40 **Keywords**

41

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

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## 45 **Introduction**

46

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

65 The main existing studies are based on historical and stylistic approaches<sup>[6, 7]</sup>, thus, the  
66 characterization of materials involved in this kind of painted works of art can provide a better  
67 knowledge of artworks through the understanding of these technological processes, and their evolution  
68 through time. However, the main constraints when working on cultural heritage artifacts are the  
69 availability and representativity of the probed matter. When sampling is possible, it is limited to very  
70 small amounts (sample can be as small as 200  $\mu\text{m}$  in size and 20 micrometers thick).

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

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

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

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

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

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

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

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

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

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

121

122

## 123 **Experimental**

124

### 125 **Reference samples**

#### 126 *Dyes and lake pigments*

127 Natural organic dyes can be extracted from plants or insects, and the resulting molecules are  
128 mainly, for red dyes, a mix of anthraquinone type skeleton. These molecules may be complexed by  
129 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  
130 calcium carbonate ( $\text{CaCO}_3$ ) leading thus to what is called lake pigments<sup>[20]</sup>.

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

135

#### 136 *Organic materials: model varnishes and binders*

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

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

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

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

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

159

160

## 161 **Samples collected from painted and varnished works of art**

162 In order to get information on the whole multi-layered system, it was necessary to sample the  
163 different museum objects and to work on selected levels. Therefore, samples were collected from 35  
164 18<sup>th</sup> century painted and varnished objects issued from French Decorative Arts museum collections.  
165 Among all these samples, and according to the samples size and shape, 16 could be analyzed using  
166 vibrational spectroscopies and only a few were successfully characterized, the others leading to poor  
167 quality spectra. They belong to the following objects: a weaving shuttle (*inv13377, musée des Arts*  
168 *Décoratifs, Paris; fig. 2 a)*), a commode “Adelaide” (*invVI965, musée national du château de*  
169 *Versailles, Versailles; fig. 2 b)*) with a beige background and decorated with pink floral motifs, a blue  
170 silver case « Carnet de bal » (*invI1854, musée des Arts Décoratifs, Paris; fig.2 c)*), and a golden glass  
171 holder (*invPR.2013.2.515, musée des Arts Décoratifs, Paris, fig. 2 d)*).

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

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

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187

## 188 **Raman instrumentation**

### 189 *Visible excitation wavelength: Raman and SERS analyses*

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

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

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201

### 202 *Near Infrared excitation wavelength: FT-Raman analyses*

203 FT-Raman analyses were performed using a near infrared excitation at 1064 nm provided by  
204 an Nd-YAG laser diode available on a Bruker RFS 100/S spectrometer based on a Michelson-type  
205 interferometer, and equipped with a liquid nitrogen-cooled germanium detector. The commercial  
206 references were analyzed using a microscopic interface equipped with a 40x objective, allowing a spot  
207 size of 30  $\mu\text{m}$  approximately. The sampled objects were analyzed using a 100x objective leading to an  
208 about 15 $\mu\text{m}$  spot size. The laser power was adjusted depending on the analyzed sample. Reference  
209 materials and the objects' samples were placed on a gold mirror to improve the collected Raman signal  
210 intensity. Spectra were recorded between 3500 and 50  $\text{cm}^{-1}$  with a 4  $\text{cm}^{-1}$  resolution, and with 1000 to  
211 1500 scans to optimize the signal-to-noise ratio.

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## 214 **Infrared instrumentation**

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

222

223

## 224 **Results and discussion**

225

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

231

### 232 **Pink objects: characterization of the pictorial layers**

#### 233 *Red lake dyes*

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

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

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

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



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

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

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

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

270

271

## 272 *Binder and charges*

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

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

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

291 Most of these results are confirmed by the analysis performed on this sample using FT-Raman  
292 spectroscopy with a  $1064\text{ nm}$  excitation wavelength. The resulting Raman spectrum presented in fig. 5  
293 has a high similarity to the spectrum of a linseed oil reference film, particularly concerning the C-H  
294 bending vibrations at  $1305\text{ cm}^{-1}$ ,  $1445\text{ cm}^{-1}$  and stretching vibrations around  $2900\text{ cm}^{-1}$ , and the  
295 stretching of the C=C bonds at  $1602\text{ cm}^{-1}$ . It is also clearly different from the two other binders spectra  
296 presented in fig. 5 c) and d). However, since Raman and IR spectroscopies can not differentiate  
297 between siccative oils <sup>[28]</sup> and since linseed oil is the most commonly used, an assumption can be made  
298 that linseed oil was employed for this painting.<sup>[11]</sup> The sample Raman spectrum also reveals a strong  
299 and sharp signal related to lead white at  $1051\text{ cm}^{-1}$ , characteristic of the  $\text{CO}_3^{2-}$  group vibration.

300 Two infrared spectra were obtained from samples taken from the commode (see fig. 4 spectra  
301 b) and c)). One of the spectra (fig. 4 b)) shows the characteristics bands of siccative oil: the CH  
302 stretching band at  $2900\text{ cm}^{-1}$  which profile is characteristic of an oil as well as the  $1700\text{ cm}^{-1}$  C=C  
303 stretching band. More intense bands located at  $1449\text{ cm}^{-1}$  and  $875\text{ cm}^{-1}$  are assigned to the vibration of  
304 the  $\text{CO}_3^{2-}$  group in calcium carbonate ( $\text{CaCO}_3$ ). The presence of lead white is also demonstrated in this  
305 case by the presence of its typical bands at  $1414\text{ cm}^{-1}$ ,  $1045\text{ cm}^{-1}$  and  $683\text{ cm}^{-1}$  on spectrum c) in fig. 4.

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

310

311

## 312 **Pure organic layers: underlayers and superficial varnishes**

### 313 *General remarks*

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

325 The spectra were baseline corrected to improve the observation of vibrational features and are  
326 presented in fig. 6 a') to c'). These spectra were compared to the spectra of two reference media that  
327 were highly employed during the 18<sup>th</sup> century in Europe for varnishes production: a linseed oil film  
328 (fig. 6 e)) a colophony resin film (fig. 6 f)) and a copal resin film (fig. 6 g)). The observed vibrational  
329 features are very similar to the reference media ones, in terms of bands position and profile. These  
330 bands are underlined in fig. 6: the CH stretching vibrations band around 2900 cm<sup>-1</sup>, the C=C stretching  
331 vibration band at 1640 cm<sup>-1</sup>, the CH bending vibration at 1440 cm<sup>-1</sup>, the OH bending vibration band at  
332 1300 cm<sup>-1</sup> and finally the C-O stretching band at 1090 cm<sup>-1</sup>.<sup>[27]</sup>

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

343

#### 344 *Data treatment: spectral decomposition*

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

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

363

## 364 **Conclusions**

365

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

371 We were thus able to characterize – for two objects – the whole composition of some painting  
372 layers: very small (10 µm in size) particles of red dyes as madder and cochineal lakes using SERS  
373 (458 nm excitation wavelength and silver colloids) without any extraction or pretreatment; lead white  
374 or calcium carbonate as major mineral pigments, and Prussian blue added to slightly modify the pink  
375 color to a more lilac or purple color using IR-ATR mode; and finally the binder as a siccativ oil using  
376 IR-ATR and FT-Raman.

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

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

389

390

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393

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401 for the SEM-EDS study of the samples' mineral parts and for the colloids preparation respectively.

402

403

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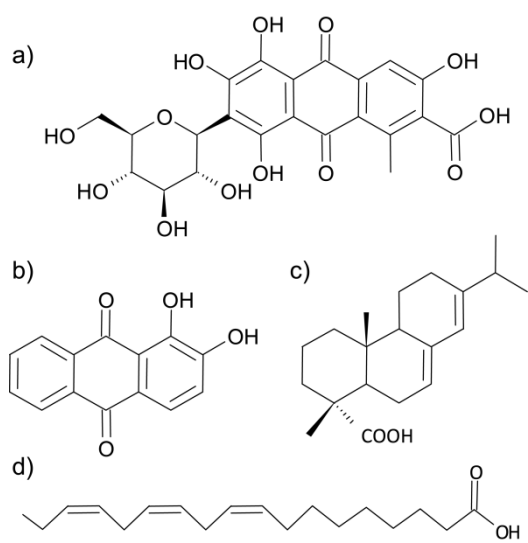
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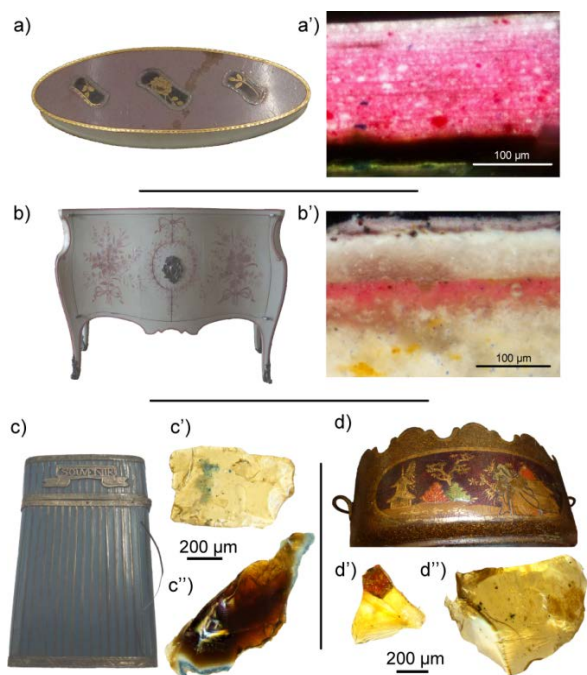


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**Fig. 1 : Main compounds of the reference materials. a) carminic acid (carmine lake), b) alizarin (madder lake), c) abietic acid (colophony), and d) linolenic acid (linseed oil).**

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512 **Fig. 2 : Photography of the 4 studied objects and of some stratigraphic view of the samples. a) Weaving shuttle**

513 **(inv13377, musée des Arts Décoratifs, Paris), a') statigraphy of a weaving shuttle sample, b) Commode "Adélaïde"**

514 **(inv1965, musée national du château de Versailles), b') stratigraphy of a commode sample. c) Silver case "Carnet de**

515 **bal" (inv11854, musée des Arts Décoratifs, Paris), c') Silver case - upper varnish flake, c'') Silver case - underlayer**

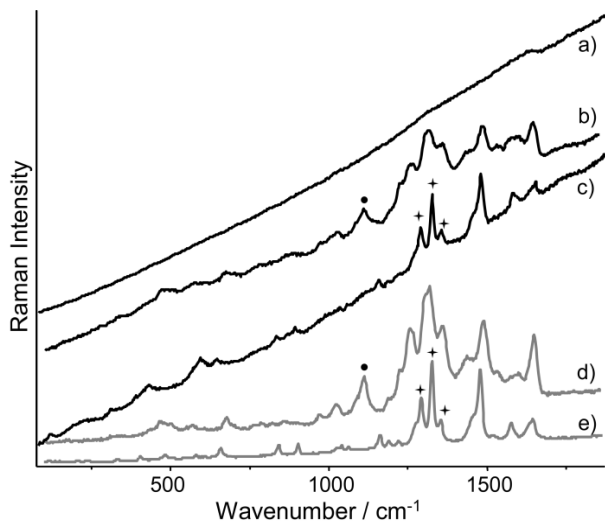
516 **flake, d) Glass holder (invPR.2013.2.515, musée des Arts Décoratifs, Paris), d') Glass holder - upper varnish flake, and**

517 **d'') Glass holder - underlayer flake.**

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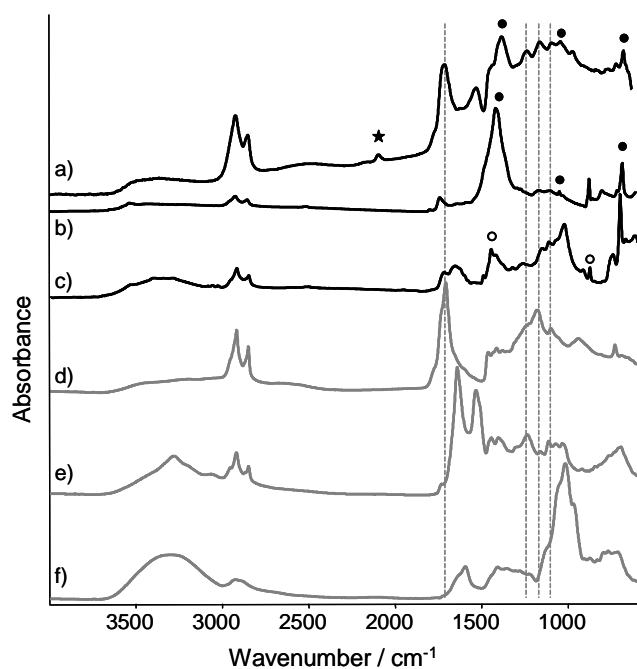


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526 **Fig. 3 : Raman and SERS spectra (458nm) on the red particles: a) Raman spectrum of the weaving shuttle red**  
527 **particle, b) SERS spectrum of the weaving shuttle red particle, c) SERS spectrum of the commode red particles, d)**  
528 **reference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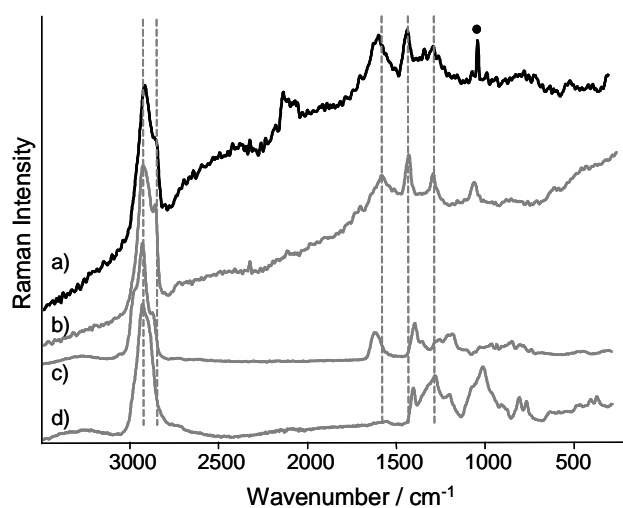


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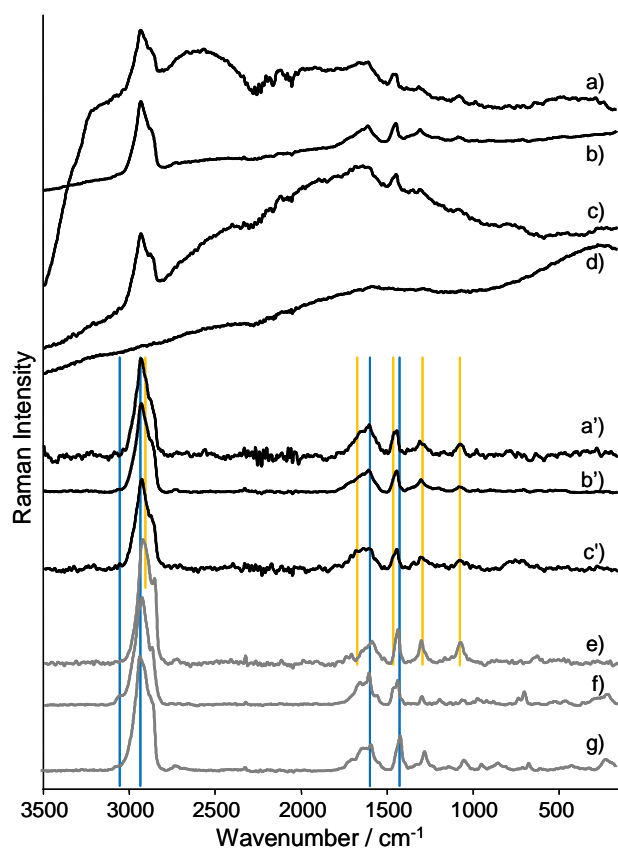
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535 **Fig. 4 : IR-ATR spectra of: a) a sample taken from the weaving shuttle pictorial layer, b) and c) samples of the**  
536 **commode pictorial layers, and d) to f) linseed oil, rabbit skin glue and gum Arabic reference films respectively. Dotted**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

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 541 Fig. 5 : FT-Raman spectra of : a) the weaving shuttle pictorial layer, b) a linseed oil reference film, c) a rabbit skin  
 543 glue reference film and d) a gum Arabic reference film. The plain dot refers to the lead white band at  $1051\text{ cm}^{-1}$   
 544 (discussed in the text), and the dotted lines to the common bands of the sample with linseed oil.  
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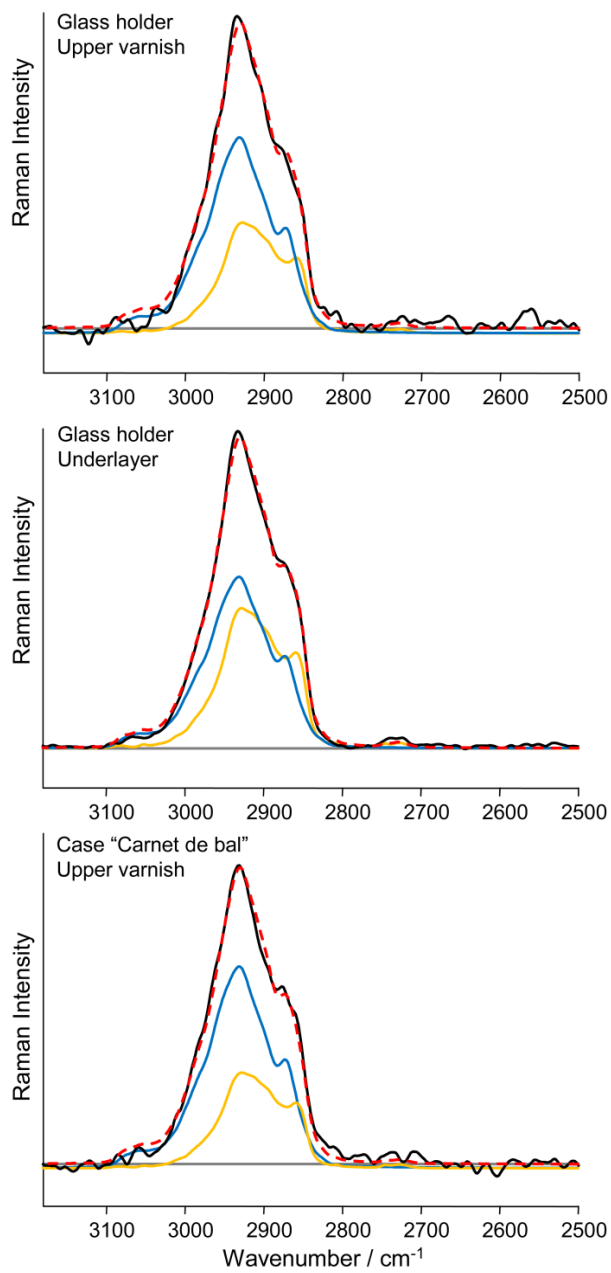
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549 **Fig. 6 : FT-Raman spectra of different organic layers taken from different objects: a) the upper varnish of the glass**  
 550 **holder, b) the underlayer of the glass holder, c) the upper varnish of the silver case, d) the underlayer of the 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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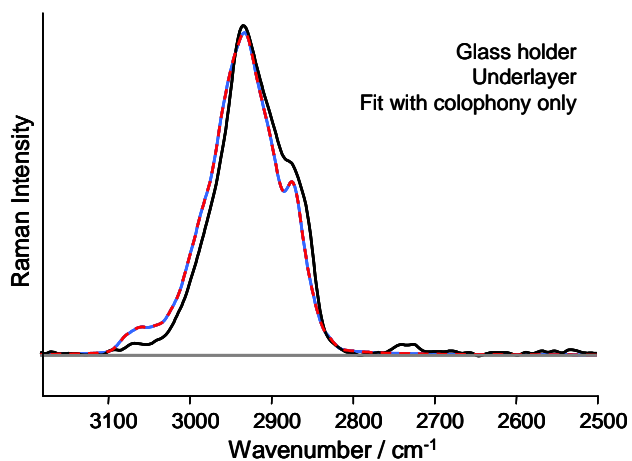
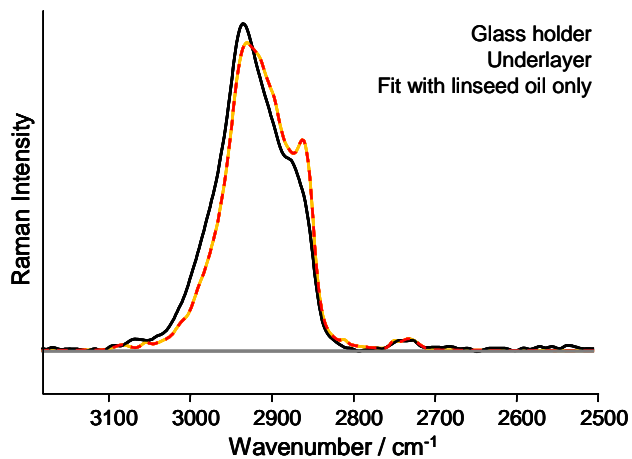
— Experimental spectrum    — Baseline    — Linseed oil  
- - - Calculated spectrum    — Colophony

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558 **Fig. 7 : Spectral decomposition of FT-Raman CH band for three organic layers (mixtures) using linseed oil and**

559 **colophony films as pure reference materials. Misfitting examples are presented as supplementary data.**

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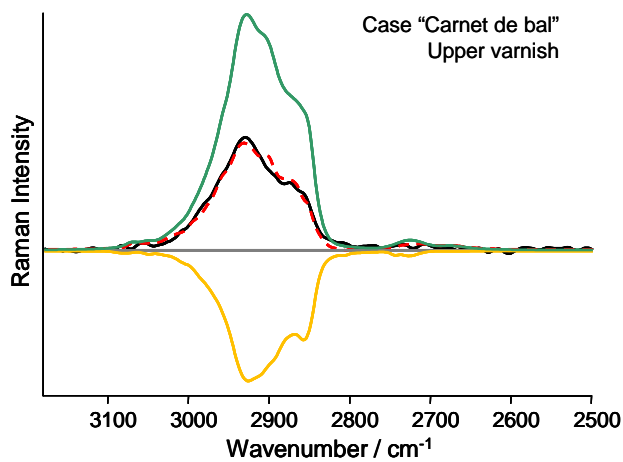
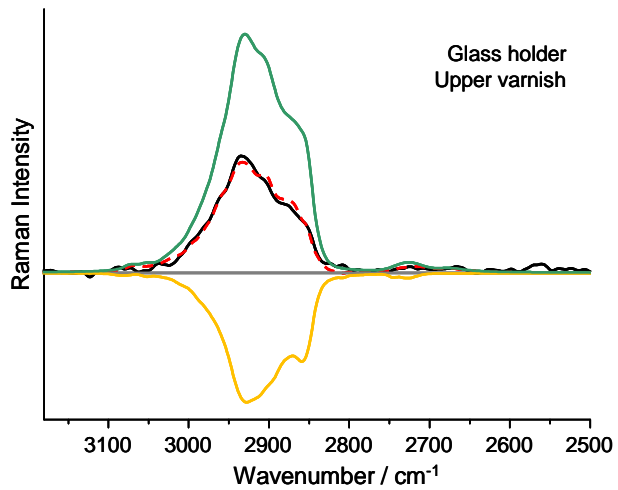


— Experimental spectrum    — Baseline    — Linseed oil  
 - - - Calculated spectrum    — Colophony

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

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

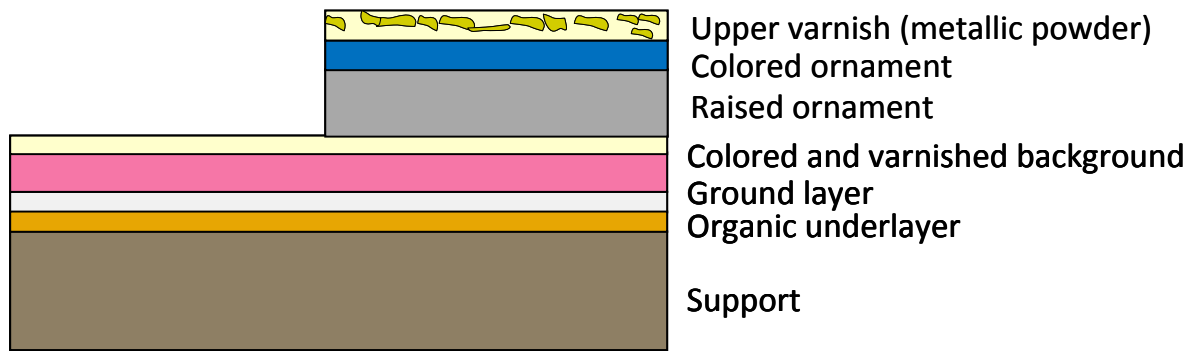
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567 **Supl. Data S 2 : Spectral decomposition of FT-Raman CH bands for the glass holder and the silver case upper**  
 568 **varnishes using linseed oil and copal films as pure reference materials. In these two examples, the adjustment is**  
 569 **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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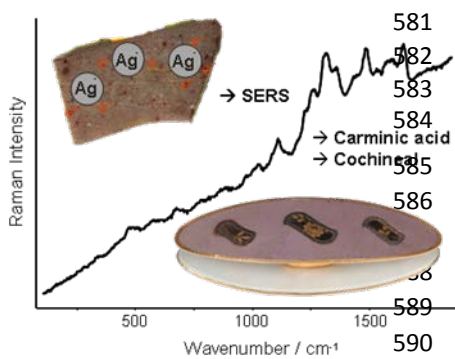


577 **Graphical TOC**

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

582 C. Daher\*, L. Drieu, L. Bellot-Gurlet, A. Percot, C. Paris, A.-S. Le Hô

583 *French Decorative Arts objects from 18<sup>th</sup> 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.*

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