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The shining brightness of daylight fluorescent pigments: Raman and SERS study of a modern class of painting materials

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(Article begins on next page)

1 **The shining brightness of daylight fluorescent pigments: Raman and**
2 **SERS study of a modern class of painting materials**

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38 **Keywords**

39 Daylight fluorescent pigments; Raman; SERS; Thin-layer-chromatography

40 **Abstract**

41 Raman and surface enhanced Raman spectroscopy (SERS) are established techniques allowing for
42 fast and sensitive identification of dyes and pigments. To date, Raman has only limitedly been
43 applied to the identification of daylight fluorescent pigments, despite this modern class of materials
44 has been adopted by several significant artists (e.g. Frank Stella, Peter Halley, Andy Warhol, and
45 Keith Haring).

46 In this study, seven commercial daylight fluorescent pigments from Radiant were investigated by
47 Raman and SERS spectroscopy. A new type of silver colloid, constitute mainly by rod-like silver
48 nanostructures, has been employed for this purpose.

49 As the number of fluorescent dyes suitable for the manufacturing of daylight fluorescent pigments
50 is limited, these materials are often constituted by a mixture of dyes. Since SERS is not able to
51 physically separate multiple dyes in mixtures, to reveal the complex composition of these materials
52 the coupling of SERS with a separation technique proved to be mandatory. Thin-layer
53 chromatography, being a cost-effective and fast procedure, was chosen for this purpose. The
54 identification of each component was made possible by the comparison of SERS spectra from
55 standard fluorescent dyes, thus increasing the available SERS database for modern materials.

56 Lastly, the analytical protocol was applied to a modern artwork called "*Rosso verde nero*", made in
57 1968 by the Italian artist Carla Accardi, who used to paint on plastic surfaces with fluorescent
58 colours.

59 **1. Introduction**

60 Nowadays, while the analysis of traditional paint materials may be considered a consolidated
61 practice in cultural heritage studies, the characterization of compounds used in modern and
62 contemporary art deserves a major attention because very little is known on the composition and
63 ageing processes of these new industrial materials. Talking about conservation issues of
64 contemporary art may sound a contradiction, because recent artworks should not need any
65 restoration yet. On the other hand, contemporary artworks show degradation pathways that are
66 sometimes even quicker and more severe when compared to those occurring in ancient works of art,
67 and the main reason of this fragility lies in the physical-chemical properties of the materials they are
68 made of. Indeed, in contemporary art, traditional paint materials are frequently substituted or mixed
69 with modern products, not chosen in order to last for centuries and designed for industrial or
70 domestic use. Moreover, the wide variety of materials used by contemporary artists, due to the fast
71 development of synthetic pigments, dyes and binders, makes the identification of such mediums
72 much harder.

73 In the 1930s Robert and Joe Switzer developed a new class of pigments, called Day-Glo by their
74 daylight fluorescent behaviour. During the Second World War, Day-Glo products were extensively
75 used by the U.S. military in applications where visibility was required [1]. Since then, after an
76 initial slow growth, daylight fluorescent paints (DFPs) production made a considerable progress and
77 these pigments have been used in several technical fields, e.g. printing inks, moulded plastics
78 colouration, dyeing of synthetic fabrics, industrial safety applications and advertising. Starting from
79 1944, also several artists adopted these pigments for their artworks, including Frank Stella, Lucio
80 Fontana, Ryan McGinness and Peter Halley, exhibiting their works either under visible light or in a
81 darkroom under UV-light [2,3].

82 Generally, in DFP, a dye (e.g. acidic and basic representatives of the xanthene and
83 aminonaphthylimide dye class) is dispersed in low amount (0.1-5%) into a transparent resin carrier.
84 Most fluorescent pigments are of the toluenesulfonamide–melamine–formaldehyde resin matrix
85 type, to which anti-foam agents, UV-stabilizers and optical brighteners are commonly added. Only
86 a small number of fluorescent dyes is suitable for this application, thus the different hues are
87 generally obtained by mixing multiple fluorescent dyes, eventually with the addition of non-
88 fluorescent ones [4].

89 Despite even a real artistic current has been developed under the name “Black Light Art”, daylight
90 fluorescent pigments have received minimal attention in the field of cultural heritage research, if we
91 consider that the manufactures of these pigments provide only few information on their
92 composition.

93 Only a limited number of work in the literature addresses with the study of DFP, namely by
94 fluorescence [5,6] and Raman spectroscopy [7,8], and in none of them Surface Enhanced Raman
95 Spectroscopy (SERS), having a recognized role in the analysis of dyes and pigments [9], has been
96 employed.

97 Thus, the aim of this study is the investigation of commercial DFPs composition by Raman and
98 SERS, with the view of providing a better understanding of the fluorescent material and their
99 ageing behaviour, and helping conservators and museum professionals in their exhibition and
100 conservation decisions.

101

102

103 **2. Experimental**

104 **2.1. Materials and Artwork**

105 Ultrapure deionized (DI) water prepared with an Elga Purelab-UV system (Veolia Environment,
106 France) was used throughout. Acetone (for HPLC, $\geq 99.8\%$), isopropyl alcohol (for HPLC,
107 $\geq 99.8\%$), ammonium hydroxide solution (ACS reagent, 28.0-30.0% NH_3 basis),
108 trimethyltetradecylammonium bromide (TTDB, $\geq 99.0\%$), sodium hydroxide (reagent grade, $\geq 98\%$),
109 sodium citrate tribasic dehydrate (ACS reagent, $\geq 99.0\%$), sodium borohydride (NaBH_4 , purum p.a.,
110 $\geq 96\%$) and ascorbic acid (reagent grade) were purchased from Sigma Aldrich (Milan, Italy). Silver
111 nitrate (AgNO_3 , $\geq 99.8\%$) was purchased from Merck. TLC Silica gel 60 plates (aluminium sheets)
112 were purchased from Supelco. Pure acrylic binding media (Plextol® D498) was purchased from
113 Kremer Pigmente GmbH & Co. KG (Germany).

114 7 DFP, illustrated in Table S.1, were supplied by Radiant Color NV as a selection from their
115 Radglo®PS series, based on a dyed/pigmented thermoset sulphonamide-melamine-
116 paraformaldehyde resin. Reference mock-ups were made by mixing with a paintbrush the acrylic
117 binder and the pigments in a mixing ratio of about 6:1. Once a proper paste consistency was
118 obtained, the paint was cast on glass slides.

119 The painting “Rosso verde nero” was realized in 1968 on “Sicofoil” by the Italian artist Carla
120 Accardi. “Sicofoil” is a plastic transparent sheet, produced during these years by the Italian
121 company Mazzucchelli 1849 S.p.a. The artwork is composed by two transparent cellulose acetate
122 sheets mounted on a wooden frame and painted directly on plastic with fluorescent colours.

123 The most relevant conservation issues were the degradation of the plastic material and the fragility
124 of the paint surface. In this study case, the conservation intervention focused on the treatment of
125 several big cracks on the plastic surface and the subsequent strip lining with non-visible options, in
126 accordance with the nature of the paint.

127

128 **2.2. Preparation of Ag nanoparticles**

129 The synthesis of the silver nanorods (AgNRs) was adapted from Ref. [10]. Briefly, silver seeds
130 were prepared by mixing deionized H₂O (95 mL), aqueous trisodium citrate (1 mL, 30 mM, freshly
131 prepared), and aqueous AgNO₃ (2 mL, 5 mM, freshly prepared) were mixed in a flask immersed in
132 an ice bath. Aqueous NaBH₄ (1.5 mL, 50 mM, freshly made prior to injection by adding ice-cold
133 water to NaBH₄) was quickly injected into the vigorously stirred, ice-cold solution. The reaction
134 was allowed to proceed for ~20 min, and during this time, 3-5 drops of NaBH₄ solution were added
135 every two minutes to the solution. The resulting Ag colloid was aged overnight under stirring in the
136 dark. For AgNRs, 4.65 mL of H₂O, 0.125 mL of 10 mM AgNO₃, 0.25 mL of 100 mM ascorbic
137 acid, 125 mg of TTDB and 0.125 mL of seed solution were mixed. Finally, 0.025 μ L of 1M NaOH
138 was added. Rods were concentrated and partially separated from spheres and surfactant by
139 centrifugation at 6000 rpm for 30 min. The supernatant was removed and the solid was redispersed
140 in deionized water to obtain a 10-fold preconcentration.

141

142 **2.3. TLC-SERS procedure**

143 The components of DFP and real samples were separated by TLC utilizing a silica gel plate as
144 stationary phase and a 11:1:2 isopropyl alcohol:acetone:ammonia solution as eluent. A portion of
145 sample was scratched directly from mock-ups and suspended in acetone. A small amount (~2 μ l) of
146 the extract was deposited onto the TLC plate by means of a glass capillary and eluted in a glass-
147 developing chamber. The separated spots were visualized under a UV lamp at 254 and 365 nm. The
148 separated components were analyzed directly on the TLC plate by placing 1 μ l of AgNRs on top of
149 each spot.

150

151 **2.4. Instrumentation**

152 Raman and SERS measurements were made on a Renishaw RM 2000 instrument coupled with an
153 optical Leica DLML microscope, equipped with a NPLAN objective 20 \times . The spectrometer
154 consists of a single grating monochromator (1200 lines mm⁻¹), coupled with a CCD detector, a
155 RenCam 578 \times 400 pixels (22 μ m \times 22 μ m) cooled by a Peltier-element. The excitation wavelength
156 was obtained respectively by a Nd:YAG laser at 532 nm and a He-Ne laser at 633 nm. Typical
157 measurements conditions were 30 s integration time and 1 accumulation with a laser power at the
158 sample lower than 0.1 mW for both lasers. The spectral calibration of the instrument was performed
159 on the 520.5 cm⁻¹ band of a pure silicon crystal. Raman measurements were made on the dye

160 powder directly. SERS measurements were made by drying at room temperature 1 μ L of AgNRs on
161 sample mock-ups or by drying on a glass slide 1 μ L of AgNRs and 1 μ L of sample extract in
162 acetone.

163 The multiband and fluorescence images were acquired using Multispectral IMAGING system
164 equipped with a high resolution MOROVIAN G2-8300 (CCD KAF 8300 18.1 \times 13.7 mm pixels 5,4
165 \times 5,4 μ m), high dynamic range (16 bits). Multi-band images were acquired using three interferential
166 filters (centred at 450, 550 and 650 nm, with band-pass \pm 25 nm) in front of the CCD sensor. All the
167 images were white-balanced using a reference barium sulphate white and then combined to form
168 single high-resolution images of the whole sample. The UV–Visible fluorescence image was
169 obtained illuminating the painting with UV LEDs emitting at 365 nm.

170 UV–vis measurements were performed using a Perkin Elmer Lambda 25 double beam
171 spectrophotometer. Scans were performed from 300 nm to 600 nm (scan rate 240 nm/min, 1 nm
172 slits).

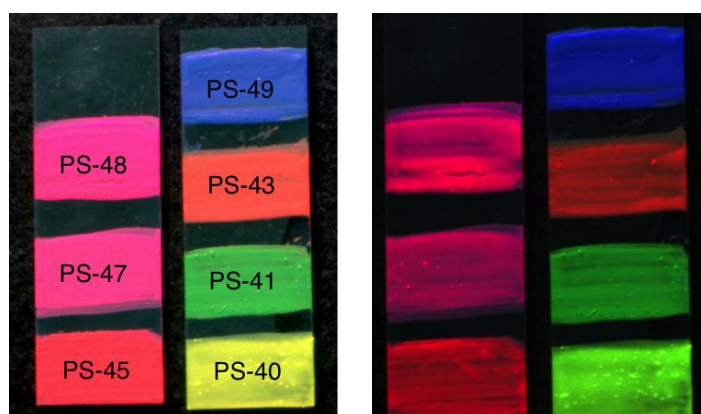
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175 3. Results and discussion

176 3.1. Investigations on DFP mock-ups

177 The composition of DFP is usually not provided by the manufactures, but it is of utmost importance
178 for the restoration process of fluorescent artworks. Fluorescent dyes having the same appearance
179 under visible light may indeed respond differently when exposed to UV light, thus the correct
180 determination of these pigments is necessary to maintain the original message intended by the artist.
181 The appearance of the prepared mock-ups under visible and UV black light is shown in Figure 1.



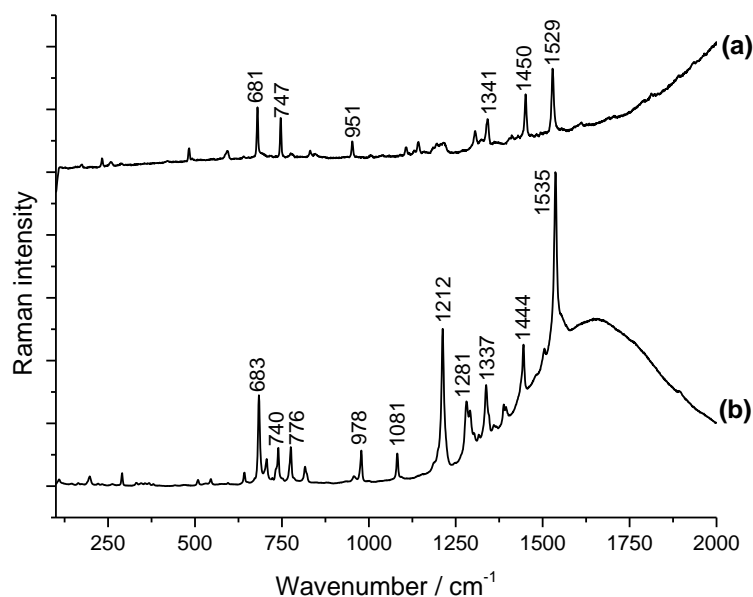
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183 **FIGURE 1** | Fresh mock-ups. Left RGB (visible light), right UV (Wood's lamp, \sim 365nm) acquisition.

184

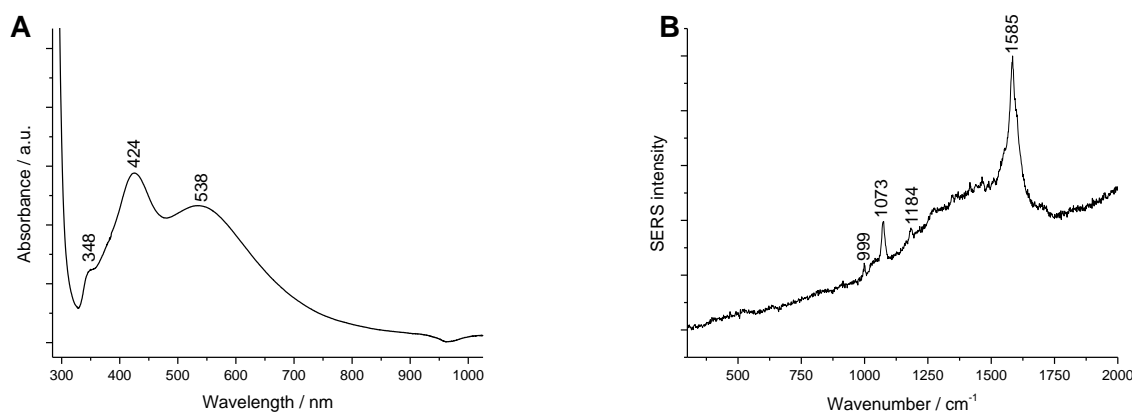
185 At first, Raman analysis conducted on the mock-ups resulted in readable spectra only for the blue
186 (PS-49) and the green (PS-41) DFP, corresponding to PB:15 and PG7, respectively (Figure 2) [11].

187 However, as phthalocyanines are not fluorescent pigments, other compounds that confer to the DFP
188 their special appearance must be present in the original DFP formulation.



189
190 **FIGURE 2** | Raman spectra of (a) PS-49 and (b) PS-41, acquired at 532 nm.

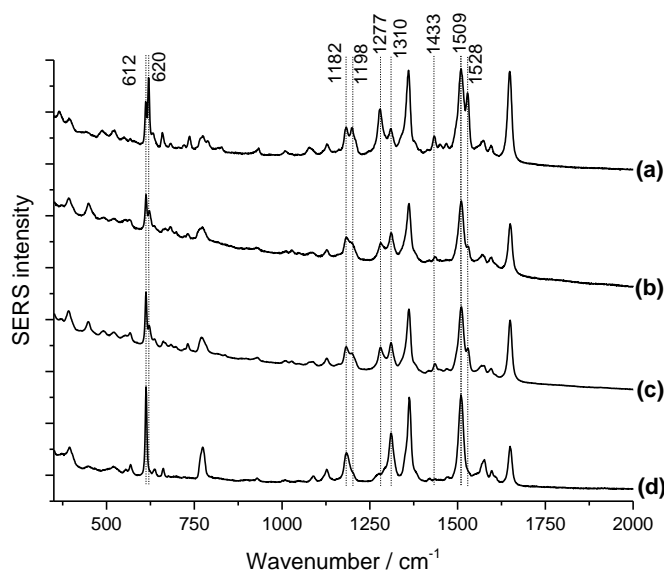
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192 For the analysis of the remaining pigments, SERS proved to be necessary as their Raman signals
193 were suppressed by fluorescence. For this purpose, AgNRs have been synthesized and characterized
194 by the analysis of their UV–Vis absorption spectrum, which is related to their surface plasmon
195 resonance. In Figure 3A the transverse plasmon band at 424 nm and the longitudinal plasmon bands
196 at 538 nm are clearly recognizable, together with the out-of-plane quadrupole resonance at 348 nm.
197 The SERS spectrum of AgNRs after centrifugation appears quite clean (Figure 3B), showing four
198 main signals which could be ascribed to CH₂ rocking in tail and N⁺(CH₃)₃ group (1585 cm⁻¹), CH₂
199 rocking (1184 cm⁻¹), CH₂ twisting (1073 cm⁻¹), C-C symmetrical stretching and CH₂ wagging (999
200 cm⁻¹) [12].



201
202 **FIGURE 3** | Characterization of AgNRs. (A) UV-vis spectrum; (B) SERS spectrum.

203

204 SERS analysis was done by drop-casting 1 μ L of AgNRs directly on DFP mock-ups. In Figure 4 are
205 shown the SERS spectra from PS-43 (orange), PS-45 (red), PS-47 (pink) and PS-48 (magenta),
206 which appears as a mixture at different proportions of rhodamine 6G and rhodamine B, clearly
207 distinguishable by their characteristic peaks at 620 and 612 cm^{-1} , respectively. The assignment of
208 the peaks for rhodamine 6G and B is reported in the literature [13].

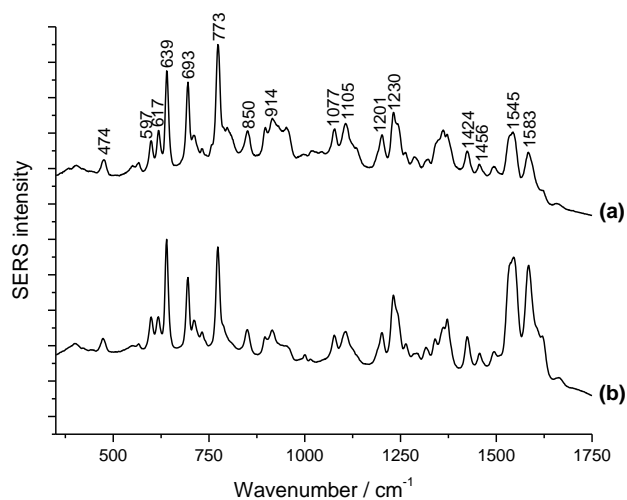


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210 **FIGURE 4** | SERS spectra of (a) PS-48, (b) PS-47, (c) PS-45 and (d) PS-43, acquired at 633 nm.

211

212 The SERS analysis of PS-40 (yellow) revealed the same spectrum obtained for the extract of PS-41
213 (green) in acetone, as shown in Figure 5. Thus, PS-41 is obtained by mixing the phthalocyanine PG-
214 7 with a fluorescent yellow dye.



215

216 **FIGURE 5** | SERS spectra of (a) PS-40 mock-up and (b) PS-41 extracted in acetone, acquired at 532 nm.

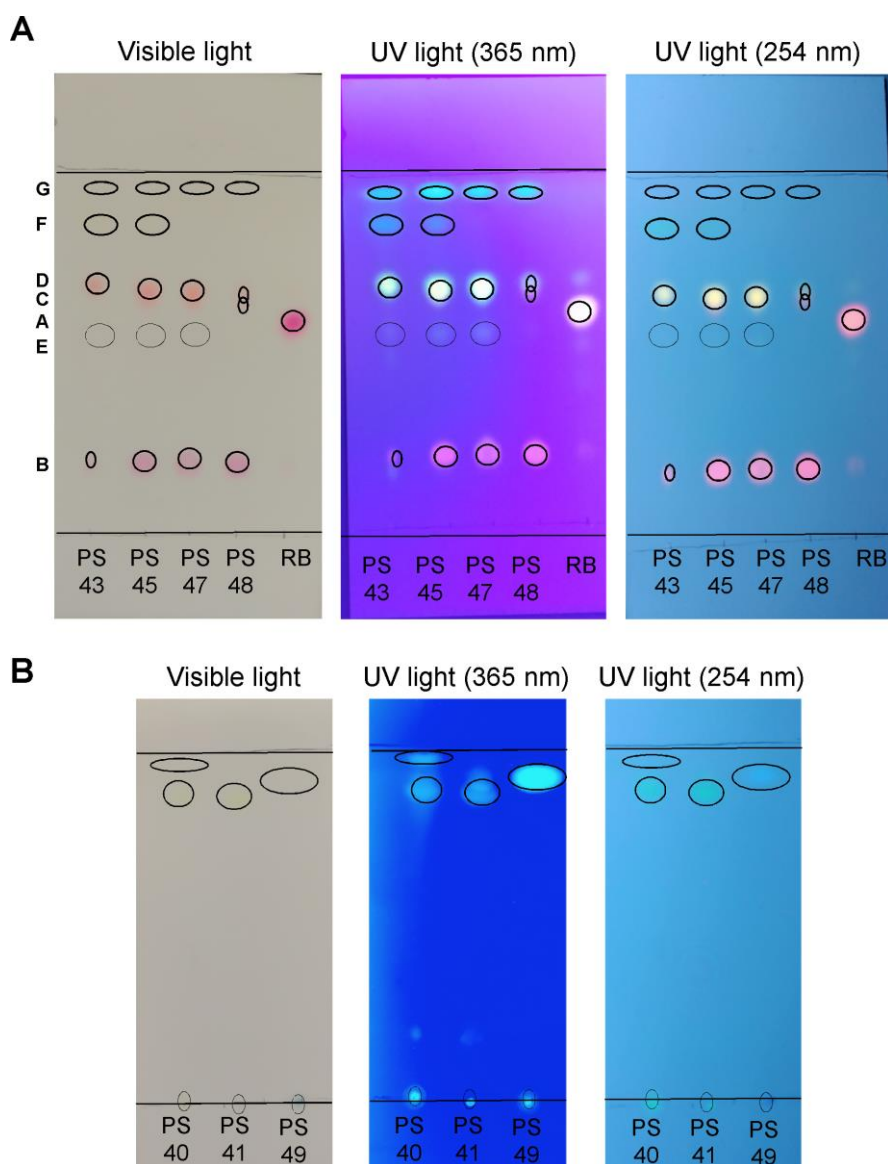
217

218 The identification of the yellow dye was made possible by the creation of an in-house database of
219 common fluorescent dyes and the comparison with the analyzed samples. We found that the yellow
220 component of PS-40 and PS-41 corresponds to Solvent Yellow 160:1, a dye belonging to the class
221 of coumarins (reference wavenumbers and corresponding Raman assignments for Solvent Yellow
222 160:1 are reported in Table 1S).

223

224 The tendency to mix different dyes is a common practice in DFP manufacturing, to make available
225 more colour hues from a limited number of molecules having this “special effect”. As SERS is not
226 able to physically separate mixtures, most of the times differences in SERS cross-section, solubility,
227 or affinity towards the colloidal substrate allow the detection of only the signals from the main
228 component in the mixture. To evaluate the ability of the synthesized AgNRs to differentiate
229 xanthene dyes mixtures, standard solutions of rhodamine 6G and B were mixed in different
230 proportions. Specifically, 1 μ L of AgNRs was mixed with 1 μ L of rhodamine 6G and B solution
231 having the appropriate concentration of the two dyes, then 1 μ L of the mixture was drop casted onto
232 a glass slide and dried at room temperature before SERS analysis. We found that the minimum
233 relative proportion of rhodamine B allowing for the dye to be consistently detected in the mixture
234 was rhodamine B/rhodamine 6G 5:1 (see Figure 1S). As we can assume a comparable solubility of
235 the two compounds, it is possible to presume that the rapid evaporation of the drop prevents the
236 colloid–dye system from reaching an equilibrium, resulting in the rhodamine 6G preferential
237 binding to silver through its carboxylic functional group.

238 Thus, to solve the complex composition of the studied DFP, the coupling of thin-layer
239 chromatography (TLC) with SERS was preferred as a first, immediate solution allowing one to
240 combine an equipment- and cost-effective separation method with the fingerprinting ability of
241 SERS. The DFPs were extracted in acetone and 1 μ L of each extract was separated on a silica plate.
242 The results in Figure 5 show the presence of at least two components for each sample, except for
243 PS-41 (green) and PS-49 (blue), for which just one component is observed.

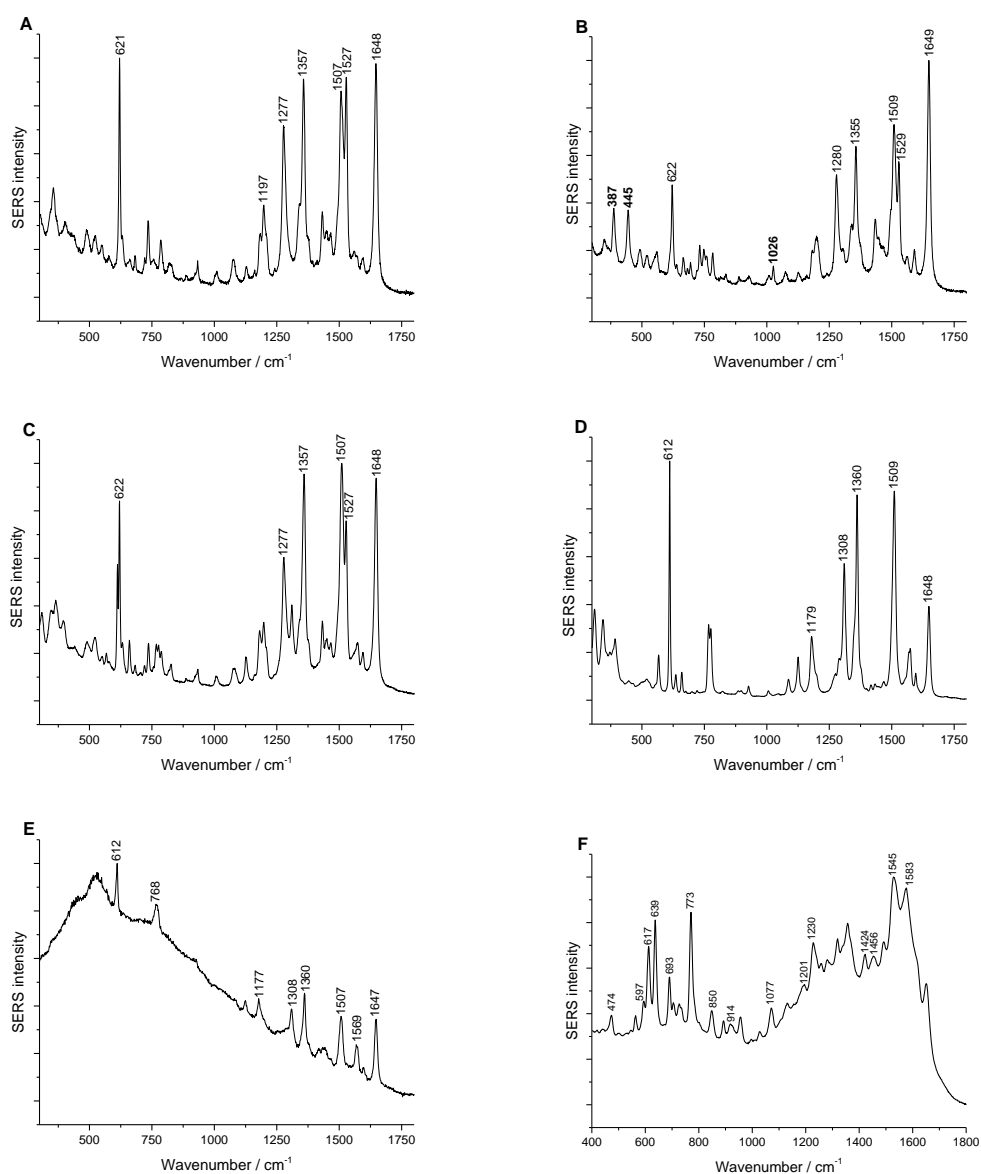


244
 245 **FIGURE 5** | TLC of the studied DFPs under visible and UV (365nm and 254nm) light. **(A)** TLC of PS-43,
 246 PS-45, PS-47, PS-48 and a standard solution of rhodamine B (RB); the lower cases indicate the sampling
 247 point for SERS analysis **(B)** TLC of PS-40, PS-41 and PS-49.
 248

249 The deposition of 1 μ L of AgNRs allowed for the acquisition of SERS spectra from the selected
 250 sampling points indicated in Figure 5A. The advantage of AgNRs over traditional spherical
 251 nanoparticles is the formation of aggregated silver clusters on the top of the silica layer, on which it
 252 is possible to focus directly the laser to acquire intense SERS spectra.

253 The presence of rhodamine 6G in samples PS-43, PS-45, PS-47 and PS-48 was confirmed (Figure
 254 6D), together with the occurrence of a compound in samples PS-43, PS-45 and PS-47 (sampling
 255 point e in Figure 5A) having a SERS spectrum closely related to that of rhodamine 6G (Figure 6E).
 256 The molecule could be a degradation product of rhodamine 6G such as its de-ethylated form,
 257 considering that lower retention factors (R_f) can be correlated with molecules having medium-high
 258 polarity.

259 The analysis of a standard of rhodamine B revealed that, despite our starting hypothesis, this
 260 compound is not present in DFPs except as a minor component in PS-48 (see Figure 5A). The
 261 SERS spectra from rhodamine B and from the sampling point c are shown in Figure 6A and 6C.
 262 The “pink” component having a low R_f factor (therefore a more polar molecule than rhodamine B)
 263 displays a SERS spectrum having the same features as that of rhodamine B, except for three
 264 characteristic peaks at $387 - 445 - 1026 \text{ cm}^{-1}$. To confirm the identity of this compound, the
 265 analysis of reference dyes by TLC-SERS proved to be necessary and allowed us to identify the pink
 266 component of DFPs as Acid Red 52 (reference spectrum in Figure 3S).



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FIGURE 6 | TLC-SERS spectra from separated DFPs components acquired at 633 nm; see Figure 5A for the corresponding sampling points.

273 From the TLC of PS-43 and PS-45 the presence of the Solvent Yellow 160:1, previously detected in
274 PS-40 and PS-41, can be assumed. The nature of this component was further confirmed by SERS
275 analysis (Figure 6F).

276 The component with the highest R_f factor, common to all the DFPs except for PS-41, presumably
277 corresponds to the optical brightener, a compound that by absorbing the UV light and transmitting it
278 in the blue range counters the tendency of many organic materials to yellow under UV or visible
279 light. The absence of the optical brightener in PS-41 is not surprising as also from the multispectral
280 acquisition this pigment appears as the less bright. Thus for this pigment, the fluorescent behaviour
281 has to be ascribed to the yellow component only.

282

283 3.2. Application to a real case-study

284 Since their introduction in late 900', DFPs have been adopted by several artists, such as Carla
285 Accardi (1924 –2014), an Italian abstract painter associated with the Arte Informel and Arte Povera
286 movements which in 1965 abandoned the traditional tempera paint in favour of fluorescent
287 pigments applied directly on transparent plastic supports. Here, a work of the artist named “Rosso
288 verde nero” (Figure 7), recently restored at the Fondazione Centro Conservazione e Restauro La
289 Venaria Reale (Turin), has been analyzed to identify the used pigments.

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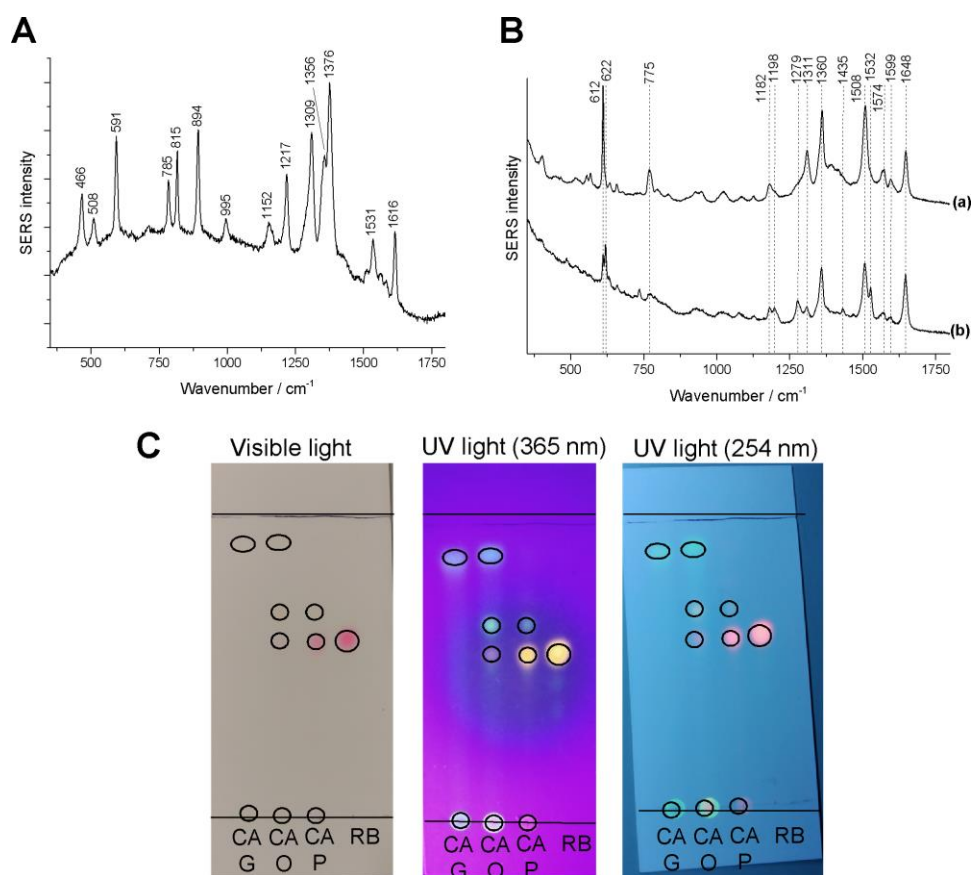
292 **FIGURE 7** | “Rosso verde nero” by Carla Accardi (private collection).

293

294 Three samples from the green (CA-G), orange (CA-O) and pink (CA-P) area of the artwork have
295 been collected and analyzed by Raman and SERS. As for Radiant colors, also in this case the

296 Raman analysis of the green component revealed the presence of Pigment Green 7. The presence of
 297 a mixture of rhodamine 6G and B in both pink and orange sample has been confirmed by SERS and
 298 TLC-SERS, while a yellow component (Figure 8A) has been detected in both orange and green
 299 sample following extraction in acetone. The comparison with yellow dyes commonly used for DFP
 300 fabrication allowed us to identify the yellow component as Solvent Yellow 44, belonging to
 301 naphthalimide class (spectrum reported in Figure 4S).
 302 The composition of these pigments appears less complex respect to Radiant colors, as shown in
 303 Table 1.

304



305

306 **FIGURE 8** | Results from “Rosso verde nero” analysis. (A) SERS spectrum of green sample extracted with
 307 acetone acquired at 532 nm; (B) comparison of SERS spectra from (a) orange and (b) pink sample acquired
 308 at 633 nm; (C) TLC of the three samples and and rhodamine B.

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320 **TABLE 1** | Summary of the results from TLC-SERS analysis of reference and real samples.
 321

<u>Sample</u>	<u>Identified colorants</u>
Radglo PS-series	PS-40 Optical brightener Solvent yellow 160:1
	PS-41 Solvent yellow 160:1 Pigment green 7
	PS-43 Optical brightener Solvent yellow 160:1 Rhodamine 6G Acid red 52
	PS-45 Optical brightener Solvent yellow 160:1 Rhodamine 6G Acid red 52
	PS-47 Optical brightener Rhodamine 6G Acid red 52
	PS-48 Optical brightener Rhodamine 6G Rhodamine B Acid red 52
	PS-49 Optical brightener Pigment blue 15:3
<i>“Rosso verde nero”, C.Accardi</i>	CA-O Solvent yellow 44 Rhodamine 6G Rhodamine B
	CA-P Rhodamine 6G Rhodamine B
	CA-G Solvent yellow 44 Pigment green 7

322
 323

324 **4. Conclusions**

325 The clarification of the composition of modern painting materials is still a hot research topic in the
 326 cultural heritage field, especially if we consider that their composition is modified continuously by
 327 the manufactures. In this work the identification of daylight fluorescent pigments was made
 328 possible by SERS spectroscopy. The coupling with TLC was mandatory considering the high
 329 complexity of the pigments, and the use of AgNRs applied here for the first time in this research
 330 field allowed a fast and reliable identification of the pigments by TLC-SERS.

331 The creation of a complete spectral database is necessary to allow the identification of more DFP,
 332 together with the comparison with older formulations that may be of interest for conservators.

333

334

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338 providing the reference samples, and Ruben Levi, the owner of “Rosso verde nero”, for let us
339 working on the artwork.

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