DOI : 10.1002/(ISSN)1097-4555
ISSN (print) : 0377-0486
ISSN (electronic) : 1097-4555
ID (product) : JRS
Title (main) : Journal of Raman Spectroscopy
Title (short) : J Raman Spectrosc
DOI : 10.1002/jrs.v9999.9999
Copyright (publisher) : © 2020 John Wiley & Sons, Ltd.
Numbering (journalVolume) : 9999
Numbering (journalIssue) : 9999
CoverDate : 2020
DOI : 10.1002/jrs.5868
ID (unit) : JRS5868
ID (society) : JRS-19-0293.R3
Count (pageTotal) : 1
Title (articleCategory) : RESEARCH ARTICLE
Title (tocHeading1) : RESEARCH ARTICLES
Copyright (publisher) : © 2020 John Wiley & Sons, Ltd.
Event (manuscriptReceived) : 2019-08-17
Event (manuscriptRevised) : 2020-02-22
Event (manuscriptAccepted) : 2020-02-26
Event (xmlCreated) : 2020-03-03 (SPi Global)
Numbering (pageFirst) : n/a
Numbering (pageLast) : n/a

SelfCitationGroup : Boscacci M, Francone S, Galli K, Bruni S. The brightest colors: A Fourier-transform Raman, surface-enhanced Raman spectroscopy, and thin-layer chromatography-surface-enhanced Raman spectroscopy study of fluorescent artists' paints. *J Raman Spectrosc*. 2020. https://doi.org/10.1002/jrs.5868

Link (toTypesetVersion) : file:jrs5868.pdf
Link (toAuthorManuscriptVersion) : file:jrs5868_am.pdf

Short Authors: Boscacci et al.

The brightest colors: A Fourier-transform Raman, surface-enhanced Raman ~~spectroscopy~~, and thin-layer chromatography-surface-enhanced Raman spectroscopy study of fluorescent artists' paints

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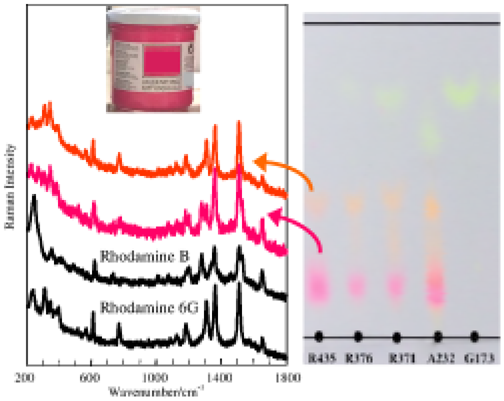
Abstract

Among the so-called "special effect" pigments, fluorescent ones play an important role, thanks to their application to a wide range of objects in everyday life. Also in the artistic field, they have been exploited since 1950s by several painters (among others Andy Warhol and Frank Stella), thus representing a particular class of materials with which conservators must confront themselves.

Not much information is available about the complete composition of commercial fluorescent paints that are based on fluorescent dyes dispersed in a transparent and brittle resin. Herein, Fourier-transform Raman spectroscopy and surface-enhanced Raman spectroscopy (SERS) were used to recognize the main dye components of the paints, whereas thin-layer chromatography was coupled with SERS to better distinguish further chromophore mixes responsible for the color and/or the fluorescence emission due to the presence of optical brighteners. This<<Query: AUTHOR: 'This methodology results suitable to more fully define the composition of such fluorescent paints originally used by artists in their works by now providing valuable information to conservators for restoration and retouching efforts.' The meaning of this sentence is not clear; please rewrite or confirm that the sentence is correct. Ans: The sentence has been corrected and should now be clearer.>> methodology results suitable to more fully define the composition of such fluorescent paints originally used by artists in their works, thus ~~by now~~ providing valuable information to conservators for restoration and retouching efforts.

Graphical Abstract

Fluorescent pigments have nowadays a wide range of applications, but they have been used also in the artistic field since 1950s. Nevertheless, scarce information is usually available about their composition. Raman spectroscopy, both as normal FT-Raman and SERS, resulted to be a valuable technique for identifying the components of fluorescent paints, responsible for their color and emission properties. Complex compositions, based on mixture of dyes, could be elucidated by the combined TLC-SERS technique.



Keywords: fluorescent paints; fluorescent pigments; FT-Raman,SERS, TLC-SERS

Table S1 – List and molecular structures of the fluorescent dyes and optical brighteners used as reference materials in the present work and not included in Table 2.

Figure S1 - FT-Raman spectra of the Flashe Fluo colors (a) Blue 029 and (b) Green 590. Legend: * bands due to melamine resin.

Figure S2 - (a) FT-Raman spectrum of the current Flashe Fluo color Blue 029 (the wavenumbers of the bands characteristic of phthalocyanine blue PB15 are reported); (b) FT-Raman spectrum of the old Flashe Fluo color Blue 029 found in the atelier of the painter Mario Agrifoglio; (c) FT-Raman spectrum of the current Flashe Fluo color White 001 (the wavenumbers of the band characteristic of the optical brightener Tinopal® OB are reported); (d) FT-Raman spectrum of the old Flashe Fluo color White 001 from the artist's atelier; (e) FT-SERS spectrum of the current Flashe Fluo color Red 376 (the wavenumbers of the bands characteristic of rhodamine 6G are reported); (f) FT-SERS spectrum of the old Flashe Fluo color Red 376 from the artist's atelier. Legend: * bands due to melamine resin (wavenumbers reported in the main paper); ♦ bands due to vinyl binder (wavenumbers reported in the main paper).

Figure S3 - FT-Raman spectra of the Flashe Fluo colors (a) Yellow 173, (b) Orange 232, (c) Red 371, (d) Red 376 and (e) Red 435. In spectrum (a) the wavenumbers of bands due to Solvent Yellow 160:1 are reported; in spectra (b), (c), (d) and (e) the wavenumbers of bands due to rhodamine 6G are reported, with the exception of the band at 1283 cm^{-1} marked in spectrum (e) and assigned to rhodamine B. Legend: * bands due to melamine resin (wavenumbers reported in the main paper); ♦ bands due to vinyl binder (wavenumbers reported in the main paper); ♦ bands due to Ssolvent Y~~y~~ellow 160:1 observed in the spectra of Orange 232 and Red 371.

Figure S4 – FT-SERS spectra of the Flashe Fluo colors (a) Orange 232, (b) Red 371, (c) Red 376 and (d) Red 435. The observed bands are due to rhodamine 6G, with the possible exception of the band at 1275 cm^{-1} that could be assigned to rhodamine B.

Figure S5 - FT-SERS spectra obtained on the TLC plate for: (a) orange spot of Orange 232 (bands assigned to rhodamine 6G); (b) pink spot of Red 371 (bands assigned to rhodamine B); (c) yellow spot of Green 590; (d) spot with light blue fluorescence of White 001; (e) spot with light blue fluorescence of Blue 029. The band around 940 cm^{-1}, marked with an asterisk, is due to the ClO_4^- anion of the aggregating agent.

Figure S6 - Normal Raman spectra (λ_{exc} = 532 nm) of: (a) Tinopal® OB in the solid state; (b) Tinopal® SWN in the solid state.

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1 INTRODUCTION

Ultraviolet (UV)- and daylight-fluorescent pigments belong to the wide group of the so-called “special effect” colorants and pigments.[1]

Fluorescent pigments are complex coloring materials, containing one or more organic fluorescent dyes dissolved in transparent solid carriers such as synthetic resins (e.g., formaldehyde-based ones).[2]

The first fluorescent dyes were synthesized in 1920s and were red (rhodamine B) and yellow-green (auramine O and thioflavine).[2] By combining them, also orange hues could be obtained.

In 1930s, the American brothers Joseph and Robert Switzer were able to develop fluorescent paints based on shellac mixed with fluorescent dyes that required UV excitation to display their optical properties.[3] They were at first employed for advertising boards and theatre sets. In the following decade, the Switzer brothers succeeded in formulating the so-called “daylight” fluorescent pigments, that could shine also if irradiated with visible light.[3] Paints based on such pigments were particularly exploited during the Second World War for visual signaling. Afterwards dyes began to be mixed with melamine resins, and in 1960s, a new thermoplastic resin, based on modified sulfonamide, proved to be particularly useful to this aim. Indeed, it is friable and can be ground to obtain small-sized pigment particles. Moreover, it increases the lightfastness of the pigments and also the resulting fluorescence.[4]

Presently, fluorescent pigments are composed of a 5% dye diluted by a transparent resin, typically a p-toluensulfonamide-melamine-formaldehyde copolymer. Typical dyes are Basic Violet 11, Basic Violet 10 (rhodamine B), Basic Red 1 (rhodamine 6G), Acid Red 52, Solvent Yellow 44, Basic Yellow 40, Solvent Yellow 135 e Solvent Yellow 160:1.[2] This rather limited set is used to obtain a wide range of hues; therefore, a pigment can contain more than one dye. Moreover, the final formulation of the paint can include, besides the binder, also additives such as anti-foaming agents and UV stabilizers as well as optical brightener agents. The latter are fluorescent organic compounds with absorption maxima in the near UV, from 340 to 400 nm, and emission maxima between 430 and 460 nm. They are used industrially to hide the yellowish shade of paper, textiles, and plastics, yielding a bright bluish-white color.[1]

The exceptional brightness of daylight fluorescent pigments is due to the fact that, upon visual observation, light reflected by them results to be combined with emitted light, giving an apparent reflectance above 100%. Thanks to this property they are commonly used nowadays in a variety of applications, from safety and road signs to stationery items, toys, fashion, sportswear, sports equipment, advertising boards, and covering of vehicles.

In the artistic field, such pigments began to be employed sporadically in 1940s. The Italian-Argentine painter Lucio Fontana exploited their properties in his “black light” (UV light) installation “Spatial environment in black light” exhibited in Milano as early as 1949. Fluorescent colors were widely employed in their works by American painters such as Andy Warhol and Frank Stella in 1960s and 1970s and also Peter Halley and Ryan McGinness in more recent years. Their works of art had to be displayed as appropriate in daylight or UV light.

From the conservation point of view, the retouching of paintings where such pigments are present poses a problem even more challenging than those usually encountered in the restoration of contemporary works of art. Indeed, the aesthetic message must be preserved together with the peculiar optical properties of the coloring materials. This task is however hindered by the fact that the components of fluorescent paints, even pigments or dyes, are usually not declared by the manufacturers. Thus, the identification of the pigments is of particular interest for the conservator. Indeed, such knowledge would allow him also to make retouchings that could be distinguished from the original paint film, for example~~,~~ by mixing pigments themselves with a different binder: in this way, as recommended by the modern theoretical approach to conservation, the aesthetic message of fluorescent paintings will be preserved, and the authenticity respected.

A methodology based on fluorimetry combined with thin-layer chromatography (TLC) separation was already reported in the literature to investigate the formulation of fluorescent pigments.[5]

In the present work, an analytical approach based on Raman spectroscopy is proposed for the identification of pigments directly in fluorescent artists' colors, that is, commercial paints, as these are the materials actually used by painters. This approach was previously summarized by ~~the~~ Bruni and Guglielmi[6] and Francone et al.,[7] and its experimental specifics~~details~~ and results are now described in detail. It is worth remembering that, by using Raman-based techniques, the authors could also examine some colors still preserved in the atelier of the Italian artist Mario Agrifoglio (1935–2014), who began experimenting with fluorescent paint in the 1970s, and compare them with products of the same brand and tints available nowadays.[7]

Raman spectroscopy is particularly suitable to the purpose of identifying fluorescent pigments. Indeed, its specificity makes it preferable in comparison with electronic spectroscopy. Moreover, its sensitivity towards molecular structures based on carbon–carbon double bonds with extensive conjugation makes it possible to detect the signals due to dyes notwithstanding their high dilution in the resin and the presence of the binder in the paint formulation. On the other hand, infrared spectra of the same paints are dominated by bands due to the resin and the binder (unpublished results). Indeed, the use of Raman technique was previously suggested to obtain a fingerprint of fluorescent pigments as such.[8, 9] The aim of the present work was instead of providing as far as possible a precise identification of the dyes composing the pigments in the final product formulation. Therefore, a series of fluorescent commercial paints, including red, orange, yellow, green, blue, and white colors, was examined.

In the approach here discussed, the problem of fluorescence emission, possibly hiding Raman scattering, was faced by the choice of near-infrared (NIR) exciting radiation (1,064 nm) using a Fourier-transform (FT) Raman spectrometer or, even better, of surface-enhanced Raman spectroscopy (SERS). Indeed, the latter technique gives rise to an intensified Raman response of the analyzed dyes and at the same time quenches their fluorescence emission, as demonstrated in the literature both for natural[10] and synthetic[11] dyes. Finally, in order to identify dyes in mixture, as commonly encountered in commercial fluorescent paints, SERS was combined with TLC as separation technique, as already suggested in the literature for the natural dye Syrian rue[12] and the first synthetic dye mauve.[13] Pure fluorescent dyes and optical brighteners were examined for comparison by the same techniques.

2 EXPERIMENTAL SECTION

2.1 Materials

The fluorescent vinyl colors Flashe Fluo Lefranc & Bourgeois (Figure 1) were purchased from an artists' paint shop.

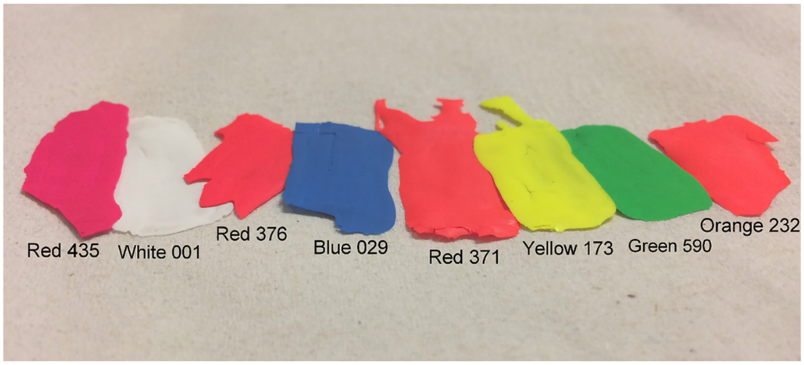
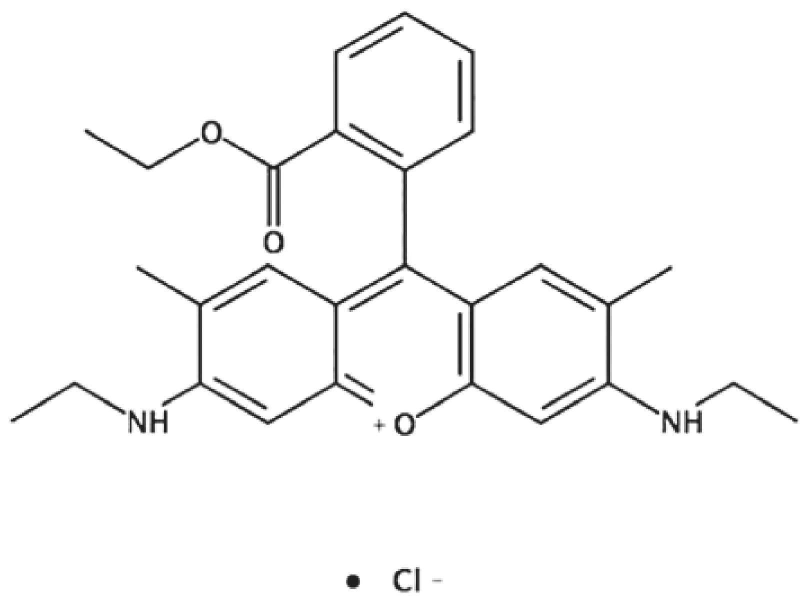
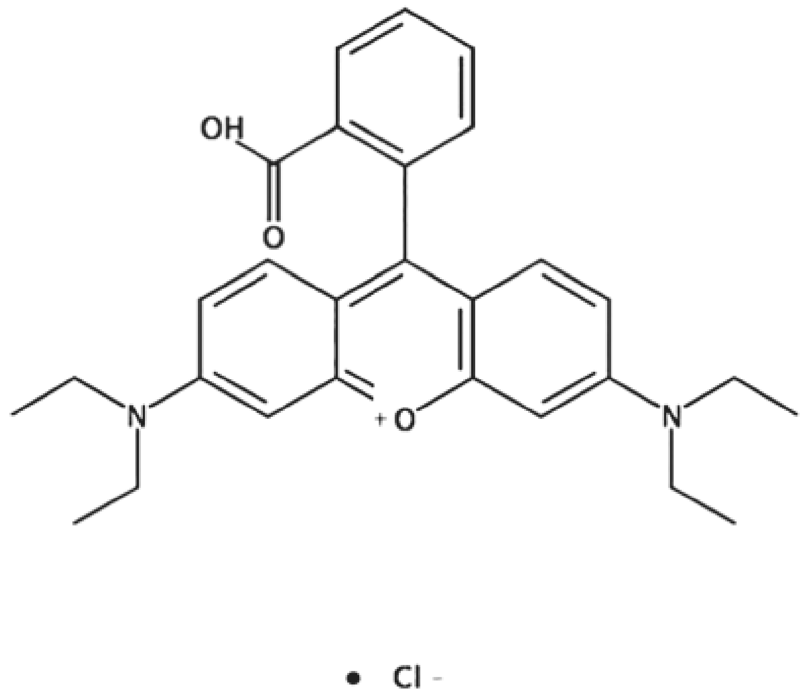
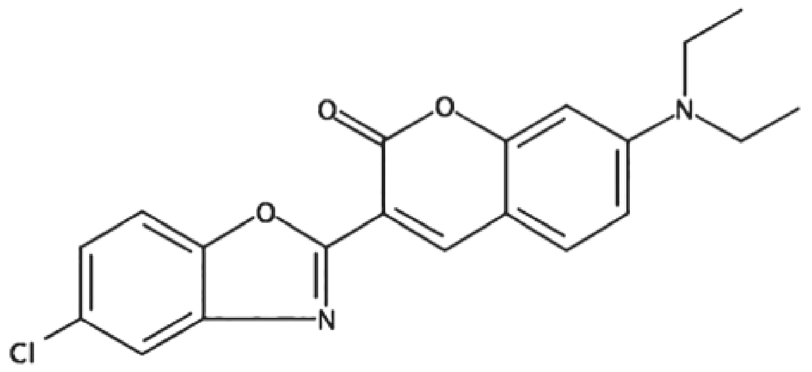
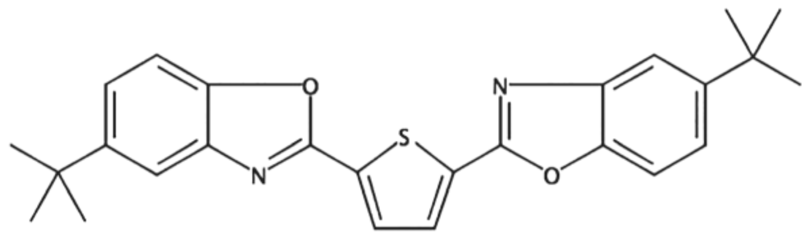
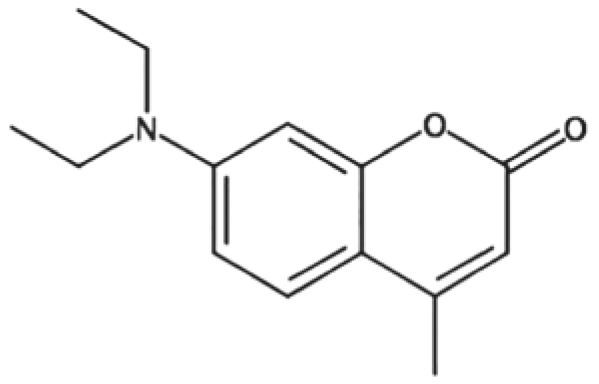


Figure 1 Sample layers of the eight <<Query: AUTHOR: Figures 1 and 5 are recommended for color online and in print. Please note that there will be additional charge for images printed in color (UK £300 per color figure). Ans: The authors prefer to retain the color images just in the online version of the paper.

In Figure 1 the different colors can be recognized from their names. For Figure 5, the colors of the spots are reported in Table 1 and the different components can also be distinguished thanks to their position (Rf value) on the plate.>>Flashe Fluo vinyl fluorescent paints [Colour figure can be viewed at wileyonlinelibrary.com]

The fluorescent dyes Solvent Yellow 160:1, Basic Yellow 40, Solvent Yellow 44, and Acid Red 52 were generously gifted by Softer Color (Forlì, Italy). The fluorescent brighteners of the series Tinopal®, OB (benzoxazole derivative), SWN (coumarin derivative), CBS-X (distyryl biphenyl derivative), and DMA-X (diamino stilbene derivative), were kindly supplied by BASF Italia (Cesano Maderno, Italy); Novatex® OB (benzoxazole derivative) was offered by Novachem (Milano, Italy). Rhodamine 6G and Rhodamine B were donated by Dr Stefania Righetto (Università degli Studi di Milano). The molecular structures of all fluorescent dyes and optical brighteners listed above are reported in Tables 1 and S1.

Table 1 Dyes or optical brighteners identified ~~in the present work~~ as components of the commercial fluorescent colors by the different Raman-based techniques used in the present work

Fluorescent dye or optical brightener	**Molecular structure**	**FT-Raman**	**FT-SERS**	**SERS 785 nm**	**SERS 532 nm**	**TLC-SERS 785 nm**	**TLC-SERS 532 nm**
Rhodamine 6G (Basic Red 1)			Red 435 Red 371 Red 376 Orange 232	Red 435 Red 371 Red 376 Orange 232		*orange spot (Rf 0.42)* Red 435 Red 371 Red 376 Orange 232	
Rhodamine B (Basic Violet 10)				Red 435		*pink spot (Rf 0.16)* Red 435 Red 371 Red 376 Orange 232	
Solvent Yellow 160:1					Yellow 173		*yellow spot (Rf 0.77)* Yellow 173 Red 371 Red 376 Orange 232 Green 590[a]
Tinopal® OB, Novatex® OB		White 001					*colorless*[2] *spot (Rf 0.9)* White 001
Tinopal® SWN							*colorless*[2] *spot (Rf 0.86)* Blue 029[3]

Abbreviations: FT, Fourier transform; SERS, surface-enhanced Raman spectroscopy; TLC, thin-layer chromatography.

[1] For Green 590, the nonfluorescent pigment phthalocyanine green PG7 was also recognized by FT-Raman spectroscopy.

[2] These colorless spots exhibit a light blue fluorescence if observed under a ultraviolet lamp at 365 nm.

[3] For Blue 029, the nonfluorescent pigment phthalocyanine blue PB15 was also recognized by FT-Raman spectroscopy.

Samples of three old ~~“~~Flashe Fluo~~”~~ paints (Red 376, Blue 029, and White 001) were taken from small containers dating back to the 1990s, found in the studio of the artist Mario Agrifoglio.

Trisodium citrate, 2-propanol, methanol, and ~~potassium nitrate~~sodium perchlorate were purchased from Sigma-Aldrich, acetone from Carlo Erba, while silver nitrate and ammonia from VWR Chemicals.

The aqueous solutions used for the silver colloid synthesis were prepared using 18-MΩ ultrapure water (Millipore Simplicity 185 water purification system).

2.2 Analytical methods

For the acquisition of normal Raman spectra, the commercial paint samples were spread on microscope glass slides, and the reference dyes or brighteners were used as powders.

For SERS and TLC-SERS analyses, the Flashe Fluo colors were diluted in methanol. Solutions of the reference fluorescent dyes and brighteners were also prepared in methanol with concentration 10^{-4} M.

The nanostructured substrate used for SERS was an aqueous Ag colloid prepared by reduction of $AgNO_3$ with trisodium citrate, according to the Lee–Meisel procedure.[14] The SERS activity of the colloid remained substantially unaltered for about a month, as it was checked by acquiring SERS spectra of alizarin as probe dye.

For SERS analyses with excitation at 532 or 785 nm, first, 41.5-µl $NaClO_4$ 1.8-M was added to 1-ml Ag colloid under magnetic stirring to promote the aggregation of silver nanoparticles. A 100-µl analyte was then added to the colloid in the same conditions. For FT-SERS analyses, the same protocol was used, but a greater volume of aggregating agent, that is, 60-µl $NaClO_4$ 1.8-M, was added to 1-ml colloidal solution.

For TLC analyses performed on fluorescent colors, ALUGRAM® Xtra SIL G/UV silica plates were used. The selected mobile phase was 2-propanol: acetone: ammonia (22:1:2).[5] TLC separations were performed for each Flashe Fluo commercial color and for the reference dyes and optical brighteners. At the end of the run, each plate was observed in visible light and under a Wood's lamp at 365 and 254 nm, so the retention factor Rf could be calculated for each separated spot. SERS analyses were performed directly on the TLC plate depositing on top of each spot 5 µl of Ag colloidal solution preaggregated by addition of $NaClO_4$ as described above.

2.3 Instrumentation

SERS spectra were acquired by a Jasco RMP-100 probe equipped with a notch filter for the rejection of Rayleigh scattering and a 50× objective for microanalysis; the probe is interfaced by optical fibers to the laser source and to a Lot-Oriel MS125 spectrometer equipped with an Andor charge-coupled device detector (1,024 × 128 pixels) cooled by a Peltier device. Two different laser sources were used: a frequency doubled Nd:YAG laser emitting at 532 nm and a diode laser emitting at 785 nm. For the first excitation wavelength, a 1,800 lines per millimeter grating was employed with a resulting resolution of 8 cm^{-1}, while a 1,200 lines per millimeter was used for the second one with a resolution of 3 cm^{-1}. In both cases, the incident power was limited to few milliwatts. Each spectrum was recorded as sum of 30 scans with an exposure time of 2 s.

FT-Raman analyses were performed by a Jasco RFT-600 spectrophotometer with 180° backscattering geometry. The source was a Nd-YAG laser emitting at 1,064 nm, with a power on the sample comprised between 180 and 200 mW. Each spectrum was acquired averaging about 128 scans, with the exception of the spectra of the Flashe Fluo colors White 001 and Green 590 for which 1,000 scans were averaged to obtain a better signal-to-noise ratio.

3 RESULTS AND DISCUSSION

All the color samples of the Flashe Fluo series were first subjected to ordinary spectroscopic investigations such as FT-Raman and Raman with excitation at 785 and 532 nm. Fluorescence emission dominated Raman spectra recorded by using the green excitation wavelength, whereas better quality spectra were acquired upon NIR excitation at 785 nm. However, especially for the red colors, the fluorescence background could be satisfyingly removed only by means of the FT-Raman technique, and the results obtained by such technique will be reported below.

In those cases, where recognition of the dyes was not possible by normal Raman analysis, the color samples were examined by SERS spectroscopy. Finally, the multicomponent paints were separated by TLC, and each spot was analyzed directly on the plate by SERS. The components detected for each commercial fluorescent paint by the overall experimental approach based on FT-Raman, SERS, and TLC-SERS techniques will be detailed below and are summarized in Table 1.

Raman bands due to the resin and the polyvinylacetate binder appear with variable intensity in many of the acquired spectra, particularly normal Raman ones. In detail, if present, the most intense bands of the melamine formaldehyde resin are located at 1,600, 1,153, 1,093, 1,048, 978, 797, 635, and 543 cm^{-1},[8] whereas signals due to polyvinylacetate can be detected at 1,445 and 1,380 cm^{-1}.[15]

3.1 FT-Raman analyses

By means of conventional FT-Raman analysis, it was possible to identify with a high level of confidence the component responsible both for the fluorescence emission and the color of White 001. Figure 2 shows the FT-Raman spectra of the commercial color and of the optical brighteners that were available as reference materials. Indeed, in the spectrum of the white color (Figure 2a), apart from the above-listed peaks attributable to the resin and the binder, it is possible to recognize the most intense signals of the benzoxazole optical brightener Tinopal® OB (Table 1), at 1,615, 1,568, 1,421, and 1,224 cm^{-1} (Figure 2b). The observed bands can be mostly referred to vibrational modes of the benzoxazole moieties of the molecule, in particular to stretching modes of the benzene rings and of the C—N bond of the oxazole ring (1,615, 1,568, and 1,421 cm^{-1}) and in-plane bending modes of C—H bonds of the benzene rings and of the oxazole ring (1,224 cm^{-1}).[16] A contribution due to vibrations of the thiophene ring is possibly present in the 1,421-cm^{-1} band.[17]

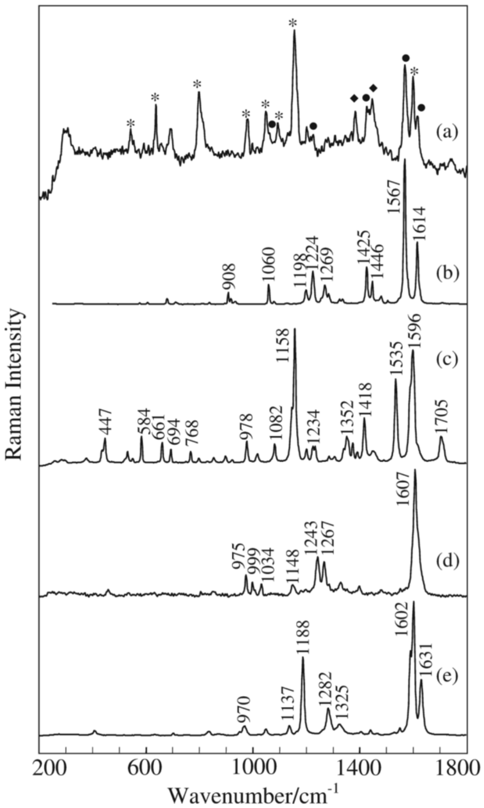


Figure 2 Fourier-transform Raman spectra of (a) Flashe Fluo color White 001, (b) optical brightener Tinopal® OB, (c) optical brightener Tinopal® SWN, (d) optical brightener Tinopal® DMA-X, and (e) optical brightener Tinopal® CBS-X. Legend: ● bands of the commercial color (spectrum a) corresponding to those of Tinopal® OB; * bands due to melamine resin; ♦ bands due to vinyl binder

With this technique, it was also possible to detect the components responsible for the colors of Blue 029 and Green 590. As shown in Figure S1, the peaks due to phthalocyanine blue PB15 and, respectively, phthalocyanine green PG7 are present in the FT-Raman spectra of the two commercial paints. Bands characteristic of the former pigment are observed at 1,528, 1,451, 1,342, and 748 cm^{-1} (Figure S1a), whereas the signals of the latter lie at 1,538, 1,337, 1,29~~2~~0, 1,204, 777, 740, and 686 cm^{-1} (Figure S1b).[18, 19] However, it is evident that these copper (II)-containing pigments cannot be responsible for the fluorescence emission of the two colors, which will be due to other components of the commercial paints, as demonstrated by the further analyses described below.

Interestingly by the FT-Raman technique, it was possible to compare the old White 001 and Blue 029 Flashe Fluo colors from the atelier of Mario Agrifoglio with the corresponding paints commercially available nowadays. As reported in Francone et al.[7] and shown in Figure S2, the same composition seems to have been retained for the two colors at least in the last two decades.

For the remaining colors, especially the red ones, FT-Raman spectra resulted to be dominated by the bands due to the melamine resin, as shown in Figure S3. Thus, to obtain a better selectivity towards the dye molecules, the SERS technique was applied both with NIR and visible excitation.

3.2 SERS analyses

By the SERS technique with NIR excitation at 785 nm, it was possible to recognize, as shown in Figure 3, the presence of rhodamine 6G (Table 1) in the Flashe Fluo colors Orange 232, Red 371, Red 376, and Red 435. Similar results were obtained by FT-SERS (Figure S4), that gave an identical response for the old fluorescent color Red 376 taken from the studio of Mario Agrifoglio (Figure S2 and Francone et al.[7]). The characteristic bands of the dye are located at 1,648, 1,511, 1,362, 1,310, 1,184, 769, 610, 568, 398, 348, and 310 cm^{-1}. According to the literature,[20, 21] the four bands at higher wavenumbers can be assigned mainly to stretching modes of the xanthene ring. The band at 1,184 cm^{-1} is attributed to the xanthene ring deformation and to C—H and N—H bending modes, whereas the signals at 769 and 610 cm^{-1} are related respectively to out-of-plane C—H bending of the xanthene ring and to in-plane bending of the xanthene and phenyl rings. Finally, the bands at lower wavenumbers are assigned to torsional and bending vibrations of the phenyl ring and the methyl and ethylamine groups. As the four colors have different hues, from orange to a sort of magenta, it is evident that other dyes besides rhodamine 6G should be contained in their formulation. Indeed, at least in the SERS spectrum of Red 435, bands attributable to rhodamine B (Table 1) can also be observed, in particular at 1,528 (shoulder), 1,280, and 1,202 cm^{-1} (Figure 3d). To identify all the components of the four colors, it proved then necessary to combine SERS analysis with the separative TLC technique, as detailed in the next section.

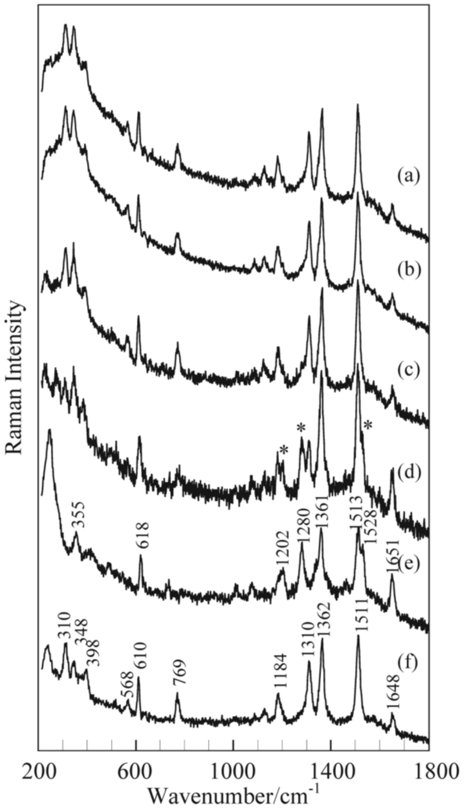


Figure 3 Surface-enhanced Raman ~~spectroscopy~~ spectra (λ_{exc} = 785 nm) of the Flashe Fluo colors (a) Orange 232, (b) Red 371, (c) Red 376, and (d) Red 435 and of the dyes (e) rhodamine B and (f) rhodamine 6G. The bands observed for the commercial colors lie at wavenumbers corresponding to those of Rhodamine 6G. For Red 435 (spectrum d), bands attributable to rhodamine B are marked with an asterisk

However by means of the SERS technique alone, but with excitation at 532 nm, it was also possible to identify as Solvent Yellow 160:1 (Table 1) the fluorescent dye of the Flashe Fluo color Yellow 173 (Figure 4b,c). Characteristic bands of this dye lie at 1,687, 1,58~~0~~1, 1,536, 1,362, 1,325, 1,238, 966, 920, 855, 772, 696, 642, and 615 cm^{-1}. The bands at the highest wavenumbers, from 1,700 to 1,200 cm^{-1}, can be reasonably assigned to stretching modes of the coumarin ring,[22] also thanks to their correspondence with those observed in the SERS spectrum of the optical brightener Tinopal® SWN (see below, Figure 7b), which is indeed a coumarin derivative; at lower wavenumbers, in the interval from 1,000 to 600 cm^{-1}, bands with remarkable intensity can be assigned to the benzoxazole moiety,[16] whose oxygen atom is most probably involved in the interaction with Ag nanoparticles together with the C–O group of the coumarin part of the molecule.

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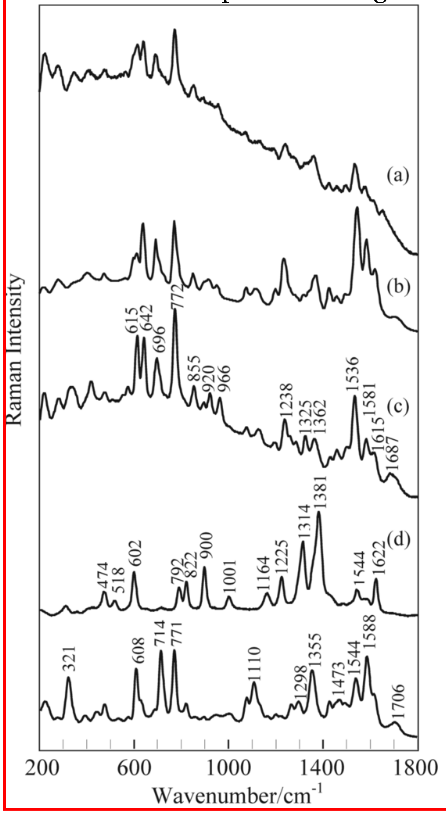

Figure 4 Surface-enhanced Raman ~~spectroscopy~~ spectra (λ_{exc} = 532 nm) of (a) yellow spot separated on TLC plate (see Figure 5) for Flashe Fluo colors Yellow 173, Orange 232, Red 371, Red 376, and Green 590; (b) Flashe Fluo color Yellow 173; (c) Solvent Yellow 160:1; (d) Solvent Yellow 44; and (e) Basic Yellow 40. The bands observed for the commercial color (spectra a and b) lie at wavenumbers corresponding to those of Solvent Yellow 160:1

3.3 TLC-SERS analyses

By applying the TLC separation technique to all examined Flashe Fluo colors, the results shown in Figure 5 and summarized in Table 1 were obtained. Pure reference dyes and optical brighteners were also analyzed for comparison in the same experimental conditions (Figure 5). As reported in Francone et al.[7], TLC was also applied to the three colors from the studio of Mario Agrifoglio, and their separation resulted to be similar to that of the currently available paints.

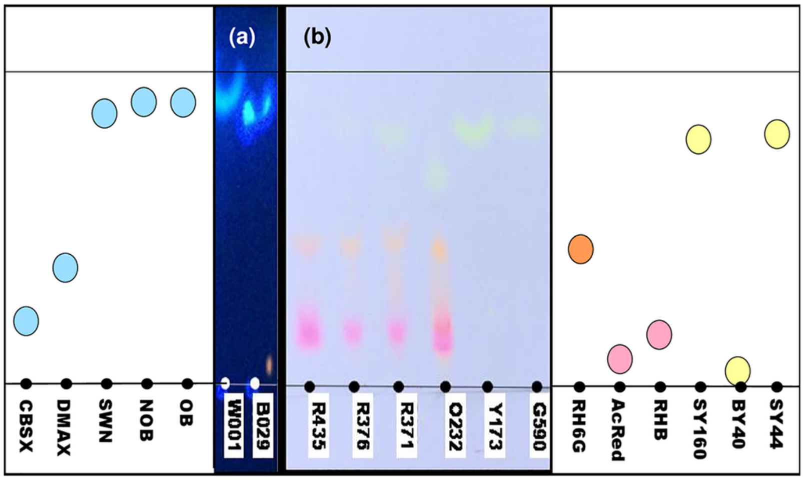

Figure 5 Photographs of thin-layer chromatogra~~phy~~ms of (a) the Flashe Fluo colors White 001 and Blue 029, observed in ultraviolet light at 365 nm; (b) the Flashe Fluo colors Red 435, Red 376, Red 371, Orange 232, Yellow 173, and Green 590, observed in visible light. For comparison, a schematic representation of the spots resulting from pure reference dyes and optical brighteners is also shown [Colour figure can be viewed at wileyonlinelibrary.com]

SERS spectra with visible or NIR excitation were then acquired from the different spots, thus allowing us to identify each component dye of the commercial colors. As detailed below, the best results were obtained, depending on the dye, using the 785- or 532-nm wavelength, whereas spectra acquired on TLC plates by FT-SERS are reported in Figure S5.

In particular, on the basis of SERS analyses at 785 nm, it was possible to recognize the dyes responsible for the pink and orange spots observed for Orange 232, Red 371, Red 376, and Red 435. The pink spot was due to rhodamine B and the orange one to rhodamine 6G, respectively, as demonstrated by the SERS spectra shown in Figure 6.

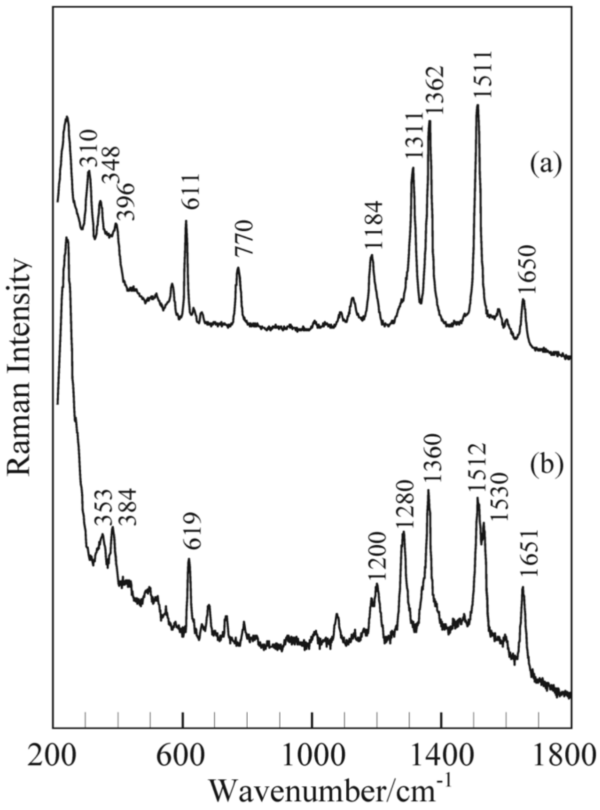

Figure 6 Surface-enhanced Raman ~~spectroscopy~~ spectra (λ_{exc} = 785 nm) obtained on the ~~thin layer chromatography~~TLC plate in correspondence of (a) orange spot observed for Flashe Fluo colors Orange 232, Red 371, Red 376, and Red 435; (b) pink spot observed for Flashe Fluo colors Orange 232, Red 371, Red 376, and Red 435. The bands observed in spectrum (a) presents a very good correspondence with those of rhodamine 6G (see Figure 3f), whereas the bands observed in spectrum (b) match with those of rhodamine B (see Figure 3e)

A yellow spot with identical Rf values was also obtained from the TLC separation of three of the above colors, namely Orange 232, Red 371, and Red 376, as well as of Yellow 173 (for which no other spot was observed) and Green 590 (for which a nonfluorescent component, phthalocyanine green, had already been recognized by FT-Raman analysis). The SERS spectra recorded with excitation at 532 nm on such yellow spots (Figure 4a) proved that in all cases, the corresponding dye was Solvent Yellow 160:1. This dye had been previously identified by SERS analysis alone as responsible for fluorescence emission and color of Yellow 173. It is evidently also responsible for the fluorescence emission of Green 590 because, as stated above, its green component PG7 is not fluorescent. Moreover, in mixture with the rhodamine dyes previously identified, it gives rise to the different hues of orange and red Flashe Fluo colors.

SERS analysis with excitation at 532 nm allowed us also to make a hypothesis regarding the component responsible for the fluorescence of Blue 029, whose tint is due to the nonfluorescent pigment PB15 (see above). Indeed, the colorless spot with light-blue fluorescence emission, resulting from TLC separation of the commercial color, gave a SERS spectrum (Figure 7) in which several bands correspond to those of the optical brightener Tinopal® SWN (Table 1), a coumarin derivative. In particular, these bands are located at 1,648, 1,588, 1,535, 1,352, 1,283, 1,242, 1,167, 978, and 531 cm^{-1}. Such bands have a remarkable correspondence with those reported in the literature, and assigned in detail to the molecular vibrations,[22] for the SERS spectrum with excitation at 514 nm of dye coumarin 152, that has a structure very similar to the one of the optical brightener here examined. Some bands observed for the fluorescent TLC spot of Blue 029, in particular at 1,618 and 570 cm^{-1}, could not be assigned and are possibly due to an unidentified minor component. Figure 7 reports also the SERS spectrum obtained on the TLC plate for Tinopal® OB (or the corresponding Novatex® OB), as it was the only one, among the other optical brighteners available as reference materials, for which a SERS response could be obtained in the chosen experimental conditions. It should be noted, however, that the other two products could be ruled out on the basis of their Rf values (~~Table 1~~ Figure 5), markedly different from that of the fluorescent component of Blue 029.

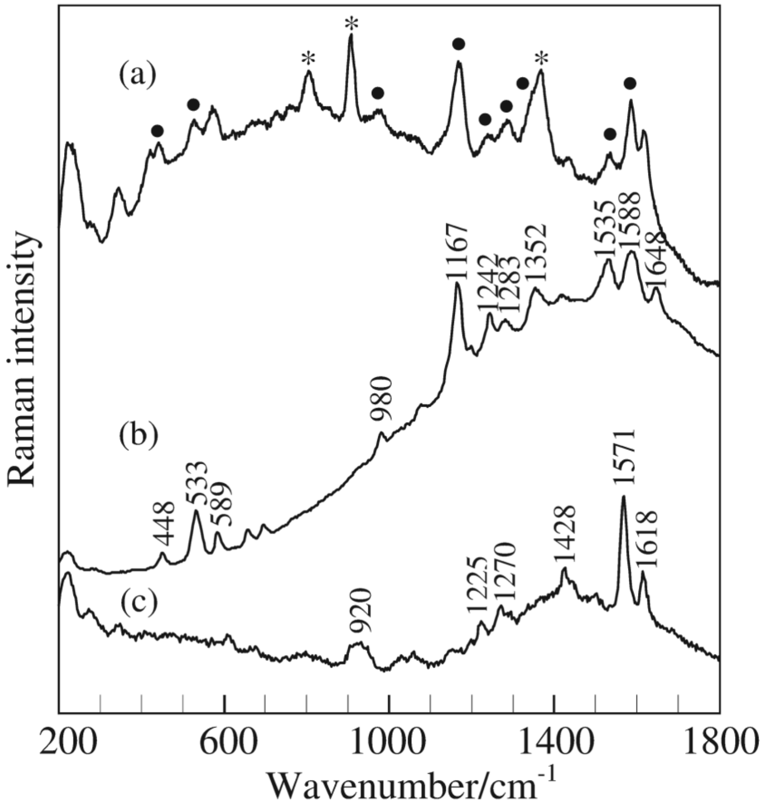

Figure 7 Surface-enhanced Raman ~~spectroscopy~~ spectra (λ_{exc} = 532 nm) obtained on the TLC plate in correspondence of (a) colorless spot with light blue fluorescence of Flashe Fluo color Blue 029, (b) optical brightener Tinopal® SWN, and (c) optical brightener Tinopal® OB. Legend: ● bands of the commercial color (spectrum a) corresponding to those of Tinopal® SWN; * spurious bands due to the silver colloid

As far as the SERS spectra of Tinopal® OB is concerned, it should be noted that no remarkable variations are observed with respect to its normal Raman spectrum, either with visible (Figure S6) or with NIR excitation (Figure 2). It can be hypothesized that the lack of carbonyl or hydroxyl functional groups in the structure of this brightener prevents significant interactions with the Ag nanoparticles.

4 CONCLUSIONS

The potentiality of Raman spectroscopy in elucidating the formulation of fluorescent paints commercialized for artistic purposes has been demonstrated for a series of vinyl colors of a renowned brand.

In particular, it was evidenced how conventional FT-Raman spectroscopy can easily supply useful information to identify fluorescent pigments in white and, to a certain extent, also yellow paint, as well as to individuate nonfluorescent pigments responsible for example of the color of green or blue paint.

SERS analysis allowed us to recognize red dyes of the rhodamine type and succeeded in distinguishing the different yellow fluorescent dyes. For paints having such tints, it was thus possible to identify the main dye component, or at least the one with the most intense SERS response. Finally, by coupling TLC separation and SERS analysis, other components of such colors could be individuated, as well as fluorescent components of those paints whose tint is due to nonfluorescent pigments.

Moreover, the best choice of the excitation wavelength was also investigated. In particular, for yellow dyes and optical brighteners, the use of visible excitation at 532 nm is preferable. In fact, this wavelength gives better resonance conditions with the plasmonic band of the aggregated Ag nanoparticles. Furthermore, in the case of yellow dyes, also~~,~~ a pre-resonance effect with their absorption band is obtained. Instead, for rhodamine dyes, the use of NIR excitation (at 1,064 or 785 nm) yields the best results, allowing to limit the strong fluorescence emission of such dyes.

A useful methodology, that could also be extended to samples from paintings, was thus made available to conservators, giving an insight about the chemical composition of fluorescent colors that were used by the artists (as was here the case of the paints from the atelier of Mario Agrifoglio) and, at the same time, that are now at the disposal of conservators' themselves for retouching purposes.

ACKNOWLEDGEMENTS

The authors wish to thank the owner of the shop Officina del Colore (Milano, Italy) and ~~Mr~~Dr Daniele Girelli (Eiconovachem, Italy) for help and advice to obtain reference materials.

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