Research article

Journal of RAMAN SPECTROSCOPY

Received: 15 February 2012 Revised: 20 August 2012 Accepted: 22 August 2012 Published online in Wiley Online Library

(wileyonlinelibrary.com) DOI 10.1002/jrs.4186

Surface-enhanced Raman scattering (SERS) and complementary techniques applied for the investigation of an Italian cultural heritage canvas

O. M. Gui,[a,b] A. Fălămaş,[c] L. Barbu-Tudoran,[d] M. Aluaş,[c] B. Giambra[e] and S. Cîntă Pînzaru[c]*

A cultural heritage canvas from the early 19th century, painted by the Vaccaro brothers for the church of Niscemi, province of Caltanissetta, Sicily, was analyzed using Fourier transform (FT)-Raman, attenuated total reflectance-FT-infrared and surface enhanced Raman scattering (SERS) spectroscopy. The painting, still used in religious rites related to the Easter mass ('la calata da tila'), depicts the scene of the Crucifixion and is executed in a scarce palette, with white, green and blue colors. Analysing vibrational data in conjunction with scanning electron microscopy and solid -state ^{13}C-NMR signals of the linen threads, we were able to offer valuable insight into the painting technique, unknown prior to this study. SERS is usually employed in artwork diagnosis for the identification of organic lakes and dyes. Due to its sensitivity, SERS has been successfully applied for the detection of either organic painting materials (indigo) that are usually not resolved by conventional Raman spectroscopy or of inorganic pigments difficult to observe in the presence of highly fluorescent aged organic supports or binders. To the best of our knowledge, this is also the first report on the SERS investigation of flax used in linen from cultural heritage objects using Ag colloidal nanoparticles. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: canvas; linen threads; SERS; FT-Raman; NMR; ATR-FT-IR

Introduction

In the last 10 years, the investigation of cultural heritage objects has become increasingly centered on the characterization of the materials and the antique techniques[1,2] employed by artists or craftsmen, as a means of understanding the historic context, the conservation state[3] and of projecting future restoration work. Analytical methodologies that require minimum sampling or no sampling at all have been preferred, due to the unique nature of most artwork investigated. Generally, infrared spectroscopy (recently using synchrotron radiation)[4,5] and chromatographic techniques[6–8] are preferred for the characterization of organic materials, while techniques such as X-ray diffraction [9] or laser-induced breakdown plasma[10] are considered adequate for the study of inorganic art constituents. The main disadvantages of such techniques are their destructive nature and the relatively large amount of sample required, mainly in the cases where a combined analytical procedure is applied. Raman spectroscopy[11–14] proves to be a versatile tool as it can offer insight into the nature of both organic and inorganic materials, without damaging the sample and often enabling *in-situ* characterization of the artwork.[15]

However, normal Raman spectroscopy alone cannot resolve complex aged paint samples,[16] usually because of the high fluorescence caused by the degrading organic components of the paint and preparation layers. Recent advances in surface enhanced Raman scattering (SERS) for cultural heritage prompt it as a useful tool in artwork diagnosis.[17] Due to the sensitivity of this technique, SERS has been applied for the detection of trace amount of pigments that usually are not resolved by conventional Raman spectroscopy.[18] As aged organic painting materials are highly fluorescent upon visible excitation in normal dispersive Raman measurement conditions, SERS is usually employed in artwork diagnosis for the identification of organic lakes and dyes.[19–22] Recent advances in the application of SERS to the field of cultural heritage include the development of a detachable SERS substrate for *in-situ* sample-free investigations[23] or a SER spectral database of common textile dyes obtained by non-hydrolysis on the fiber analysis using Lee-Meisel Ag colloids.[24]

* *Correspondence to: S. Cîntă Pînzaru, Babes-Bolyai University, Faculty of Physics, Str. Kogalniceanu no.1, 400084, Cluj-Napoca, Romania E-mail: simona.cinta@phys.ubbcluj.ro*

a *Technical University Cluj-Napoca Faculty of Materials Science and Engineering, Str. Memorandumului no 28, 400028, Cluj-Napoca, Romania*

b *University of Art and Design Cluj-Napoca, Pta. Unirii no 31, 400098, Cluj-Napoca, Romania*

c *Babes-Bolyai University Faculty of Physics, Str. Kogalniceanu no.1, 400084, Cluj-Napoca, Romania*

d *Babes-Bolyai University Electron Microscopy Center, Str. Clinicilor no. 5-7, 400006, Cluj-Napoca, Romania*

e *Accademia di delle Belle Arti e di Restauro Abbazia di San Martino delle Scale (ABADIR), Piazza Platani no 3, 90046, San Martino delle Scale, Palermo, Italy*

The current work presents the first SERS-based study of the painting technique of a particular type of Mediterranean canvas painting, the so-called 'Easter Canvas' (tela quaresimale), which was unknown prior to this study. The SERS approach is supported by complementary Fourier transform (FT)-Raman, FT-infrared spectroscopy (IR) and 13C-NMR investigations. The subject of this research was the 19th century artwork painted by the Vaccaro brothers for the church of Niscemi (province of Caltanissetta, Sicily). The canvas, not anchored on a stretcher and measuring a massive 100 m^2, makes use of a limited palette, based on white, green and blue pigments. The painting is still used in an Easter mass ritual ('la calata da tila'), which requires the canvas to be dropped from a height of circa 10 m, revealing the altar of the church when the Resurrection is announced. Recent restoration work provided the ideal setup for an in-depth analysis of both the pigments and the canvas support, in an attempt to understand the execution technique of such artwork. In order to reduce the amount of pictorial material sampled, SERS and conventional vibrational measurements were carried out directly on microsamples of linen threads and allowed simultaneous identification of both organic and inorganic components, including the canvas support. A very recent study of an archeological Coptic textile (6^{th}–8^{th} century A.D.) of Egyptian origin showed the possibility to detect dyes using Ag nanoparticles that were produced and immobilized *in situ* via the laser photoreduction of a silver nitrate aqueous solution in contact with the fiber.[25] We demonstrate here that the linen threads were able to uptake the Ag colloidal nanoparticles and instantly provide SERS signal. To the best of our knowledge, this is the first analysis of canvas painting supports by SERS, using Ag colloidal nanoparticles.

Experimental

Sampling

Due to the large dimensions of the canvas, analyses were carried out on samples taken during the first stages of restoration. A number of 20 single linen threads, ranging in size between 0.5 and 3 cm, were collected from different areas of the painting, highlighted in Fig. 1. These included both colored and plain fibers. Because of the limited number of colors in which the artwork was commissioned, the amount of pictorial material collected was considered more than sufficient for a complete characterization of the painting technique.

Instrumentation

FT-IR and FT-Raman spectra have been recorded using an Equinox 55 Bruker spectrometer with an integrated FRA 106S Raman module. A Nd:YAG laser operating at 1064 nm line was employed for the excitation of the linen fibers. The laser power was set to 200 mW, and 1000 scans were accumulated. An attenuated total reflectance (ATR) MIRacle module with ZnSe contact crystal has been coupled to the Equinox 55 FTIR Bruker spectrometer for the recording of ATR-FT-IR absorbance spectra in the 4000–650 cm^{-1} range. The spectral resolution was 2 cm^{-1}, and 40 scans were accumulated for each sample. The spectral data have been processed using Origin 8.0 software.

SERS and Raman spectroscopy were performed at the Scientific Investigation Laboratory of the Restoration Department of the University of Art and Design, Cluj-Napoca. Spectra were acquired using a Bruker Senterra Raman spectrometer, with a 50x Olympus

Figure 1. Restorer's sketch of 'The Crucifixion' canvas, showing the graphical documentation of the composition and specimen sampling points in bold (indicated with the letter N and numerals from 1 to 20).

microscope objective and a CDD detector. The excitation wavelength was 785 nm, obtained using a diode laser. The spectral resolution was 3–5 cm^{-1}. Measurements were taken collecting five to ten scans with an integration time ranging between 10 and 25 s, depending on the sample type and color (higher integration times were required for plain linen and white colored threads). The output laser power was set to the lowest possible value within these experimental conditions, 1 mW, in order to avoid sample damage. In the case of SERS measurements, spectra were obtained directly on the fiber,[18,25] without any prior preparation of the samples. Namely, fibers were placed on clean glass microscope slides, and one aliquot of a few micro liters of hydroxylamine-reduced Ag colloids was added. SER spectra were recorded after 2 min, before the complete evaporation of the colloid, as suggested by Van Elslande *et al.*[26] Reproducibility of the method was verified by performing measurements in different points and from different fibers.

Ag- colloid solutions were prepared according to the Leopold-Lendl procedure, described in detail elsewhere.[27] The Ag colloid was prepared by pippetting 10 ml of silver nitrate solution (10^{-2} M) to 90 ml of a hydroxylamine hydrochloride solution (1.67×10^{-3} M) containing 3.33×10^{-3} M sodium hydroxide, under continuous stirring.

Scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDS) data were acquired on a Jeol JSM 5510 LV instrument equipped with an energy dispersive detector (Oxford Instruments). SEM analysis was conducted in the backscattered mode, at an acceleration voltage of 25 kV. The instrument allows identification of elements heavier than boron. For a small number of imaging studies (e.g. plant fiber identification), samples had to be gold coated.

For the solid-state ^{13}C-NMR analysis, high-resolution ^{13}C-NMR signals of colored and uncolored fiber were collected on a Bruker Avance DRX 600 NMR spectrometer. Carbon spectra were recorded at 150.86 MHz ^{13}C Larmor frequency, using the standard CP/MAS pulse sequence. The spinning frequency of the sample was

Journal of RAMAN SPECTROSCOPY

$\nu_R = 14$ kHz, the applied ^1H 90^0 pulse length was 3.8 μs and the signal was acquired under two-pulse phase-modulated ^1H decoupling at 70 kHz by averaging 10.000 scans with a recycle delay of 3 s.

Results and discussion

As shown in Fig. 1, the canvas sampling revealed only white, blue-green, blue and uncolored threads. As such, investigation of the collected specimens was considered sufficient for a complete characterization of the painting technique. The threads' structural details are well resolved by the SEM images shown in the Fig. 2, where the optical microscopy image provided by the Raman microscope is given for comparison.

Figure 3 presents the FT-IR and FT-Raman spectra of plain linen threads, where main cellulose bands were observed, whereas Fig. 4 presents SERS spectra of the four sampling groups (uncolored linen, white, blue-green and blue, respectively).

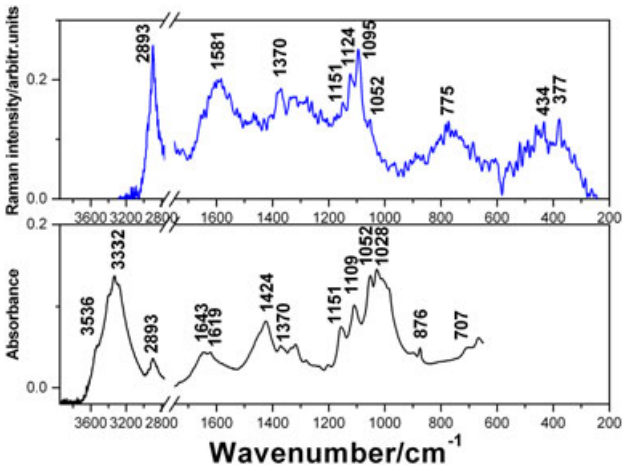

Figure 3. Attenuated total reflectance infrared spectrum (ATR-FT-IR) and FT-Raman spectrum ($\lambda_{exc} = 1064$ nm, 200 mW, 1000 scans) of plain linen threads, showing main cellulose bands. The glycoside dublet is visible at about 1100 cm^{-1}.

Pigments

All colored samples analyzed by μ-Raman spectroscopy, using the 785 nm laser excitation, exhibited a strong fluorescent background. Therefore, SERS was performed using the procedure described above. Main Raman bands observed and their assignment for pigment identification are summarized in Table 1 together with the results from SEM-EDS analyses, whereas the complete vibrational characterization of the linen threads is given in Table 2.

White areas have been found to contain lead white ($PbCO_3$ $Pb(OH)_2$), identified by its signature Raman band[28,29] at 1052 cm^{-1}(weak SERS band) and dolomite, giving a specific sharp band at circa 1093 cm^{-1}(Fig. 4). Surprisingly, the pigment on sample N20 exhibited some spectral features characteristic of titanium white (a band at 386 cm^{-1}).[15] Because of its distribution only within a restricted area of the painting, only in sampling point N20, where TiO2 was found on top of a very thin lead white layer (as indicated by SEM, result not shown here), titanium white was associated with previous undocumented restoration work.

Both green and blue areas have been found to contain lazurite ($Na_8[Al_6Si_6O2_4]S_n$), the mineral from which the natural ultramarine pigment is produced.[30] Its specific Raman bands at 549 or 554 in the SERS spectra of blue or green threads, respectively, (strong band indicating the S_3-symmetric stretch)[29,31] and 1632 cm^{-1} (with weaker features present at 277 and 1093 cm^{-1}) clearly differentiate this mineral from other blue pigments.[28] Results are confirmed by SEM-EDS data, which reveal the presence of traces

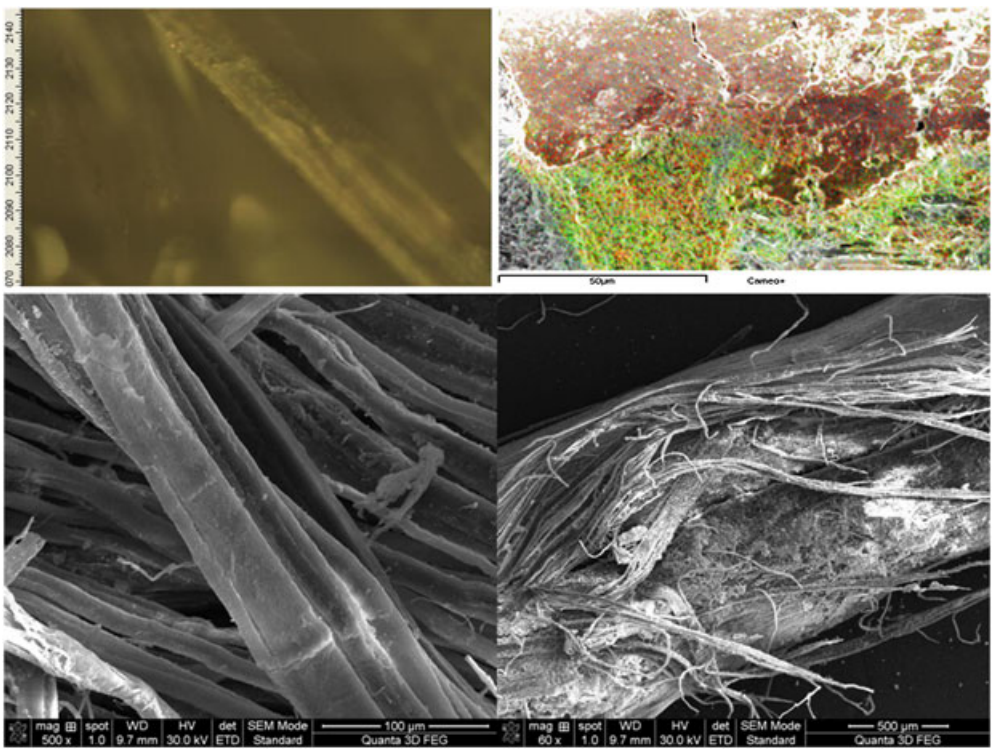

Figure 2. Scanning electron microscopy (SEM) images of a blue colored linen thread at 100 and 500 μm scale, respectively. Upper left: optical image from Raman microscope; upper right: SEM image combined with C (red), Pb (green) and S (blue) elemental maps (single maps shown on side) of the same sample.

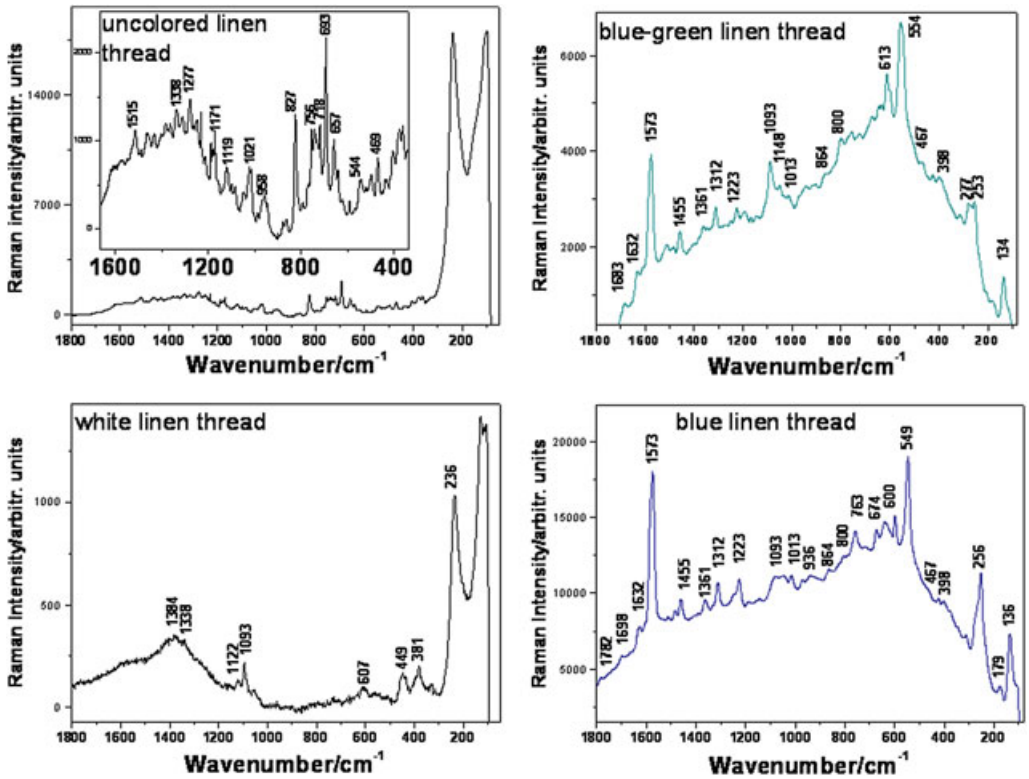

Figure 4. SERS spectra of the four representative threads: plain (uncolored, N7)-with a detailed insertion in the 400–1600 cm^{-1} range, white (N20), blue-green (N15) and blue (N18), respectively, as indicated on each spectrum. Excitation: 785 nm, 1 mW. This figure is available in colour online at wileyonlinelibrary.com/journal/jrs

Table 1. Selected results of SERS (Fig. 4) and SEM-EDS analysis

Sample color	Main SERS bands/cm^{-1}	Elements detected by SEM-EDS	Pigments identified
Green	134, 253, 277, 554, 613, 800, 1013, 1093, 1312, 1455, 1573, 1632, 1683	C, O, Si, S, Cl, Ca, Pb	Lazurite (main) Lead white,
		Na,Al[a]	Dolomite
		Mg, K, Cu, Br	Traces of indigo
Blue	136, 256, 280, 549, 600, 763, 1093, 1223,1249,1312,1361,1573, 1632, 1698	C; O,Si,S, Ca, Cl, Pb, Na, Mg, Br, Al	Indigo Lazurite, Dolomite
		K, Fe	
White	111, 236,381[b], 449, 607, 1093, 1122, 1338,1384	C, O, Si, S, Ca, Cl, Pb, Na, Mg, K	Dolomite, Lead white
		Ti[b]	Titanium white (isolated,
		Al	modern addition)

Comments: Trace elements are shown in italic. Raman bands presented are the main observed on all samples of the same color.
[a]Areas that contained Na had none or a very low Al content and vice versa.
[b]Titanium was detected only in specimens scraped off one area, on the surface of the fibers.

of Mg, K, Pb, Fe and Cu (the last two, in a quantity below 0.5%), thus indicating a natural source.

In dark blue areas, the vibrational spectra exhibited additional features, which were indicative of the use of a new pigment to darken the overall tone. SER spectra show a sharp Raman band at 1575 cm^{-1}, which was attributed to the indole ring vibration of indigo, while three weak intensity bands at 1223, 1312 and 1361 cm^{-1} were assigned to vibration modes of C–H and N–H groups.[26,29,32,33] In this case, the SERS technique allowed quenching the fluorescence of the linen substrate and enabled the identification of both organic and inorganic pigments on the same sample Fig. 4). We noted the similar SERS spectral feature in the 1200–1700 cm^{-1} spectral range for both blue and blue-green threads. Unlike citrate-reduced Ag nanoparticles, the hydroxylamine reduced Ag colloidal system does not exhibit any interference bands.[34] As a result, all observed bands were attributed to organic species within the sample. Additional information, provided by element mapping in SEM-EDS investigations (Fig. 2), supports the finding: a carbon-based pigment is indeed deposited on top of an inorganic (light colored) layer containing mainly O, Si and Pb. Solid-state NMR investigations confirmed the presence of an organic dye on blue and green (traces) colored linen samples.

Journal of RAMAN SPECTROSCOPY

Table 2. Vibrational bands/cm^{-1} of uncolored linen fibers and their proposed assignment

SERS	FT-Raman	ATR-FT-IR	Tentative band assignment[14, 38–43]
361			skeletal deformation, aromatic ring
378	377	-	δ(CCC), symmetric, ring deformation
-	434	-	δ(CCO), δ(CCC), ring deformation
469	464	-	δ(CCO), δ(CCC), ring deformation, skeletal bending
497	-	-	aromatic ring deformation + other modes (δ(COC) glycosidic linkage)
544	523		δ(COC) glycosidic linkage
590	-	-	CO rocking (in CHO) + other modes
640	-	-	ring deformation
657	-	-	-
693	687	-	ring deformation
-	-	707	-
718		-	aromatic ring twisting?
756	775	-	aromatic ring breathing
827	-	-	aromatic CH twisting
862	-	-	aromatic CH deformation
-	-	876	
958	958	-	ρ(CH_2)
1021	-	1028	C–O stretching (in CHOH)
-	1052	1052	νCO, 2° alcohol groups
1098	1095	-	ν(COC), asymmetric, glycosidic link
-	-	1109	C-C ring vibrational stretching
1119	1124	-	ν(COC), symmetric, glycosidic link,
-	1151	1151	ν(COC) ring breathing
1171	-	-	ν(CC) ring breathing, asymmetric
1230	1231	-	aromatic CH in plane bending?
-	1261	-	δ(COH) out of plane?
1277	1276	-	δ(CH_2), δ(HCC), δ(HCO), δ(COH)
1310	1313	1313	δ(CH_2) twisting
1338	-	-	aliphatic O–H bend
1363	-	-	aromatic ring breathing + C–O stretch
1383	1370	1370	CH_3 deformation (in OCH_3)
-	-	1424	CH_3 bend + ring stretch
1433	1432	-	CH_2 in-plane bending
1463	1466	-	CH_3 bend + ring stretch
1515	-	-	δ(COH), 1° and 2° alcohol groups
-	1581	-	Aromatic ring stretch
-	-	1619	ν(C=C)
-	-	1643	ring stretching-aromatic lignin
-	2893	2893	ν(CH_2) symmetric and asymmetric
-	-	3332	-
-	-	3536	-

The solid-state ^{13}C-NMR spectra recorded on blue-green colored fibers feature chemical shifts specific of indigo, besides typical cellulose and lignin resonances (Fig. 5). Thus, the signal at 177.19 ppm could be attributed to the carbonyl 3(C = O) resonance of indigo (possibly accompanied by dehydroindigo), whereas the one at 112.47 ppm is indicative of 9(C_4) and 7(C–H) chemical shifts.[35,36] Other peaks can be related to the structure of the canvas support, such as the acetyl methyl group of hemicellulose at 19.74 ppm, several cellulose signals at 104.51 ppm (C1), 64.54 ppm (C6), peaks between 72 and 74 ppm (C2, C3 and C5 carbons), at 83.34 ppm (C4). Lignin signals can be observed at 105.31 ppm (guaiacyl and syringyl units), 74.58 ppm and 61.58 ppm.[37]

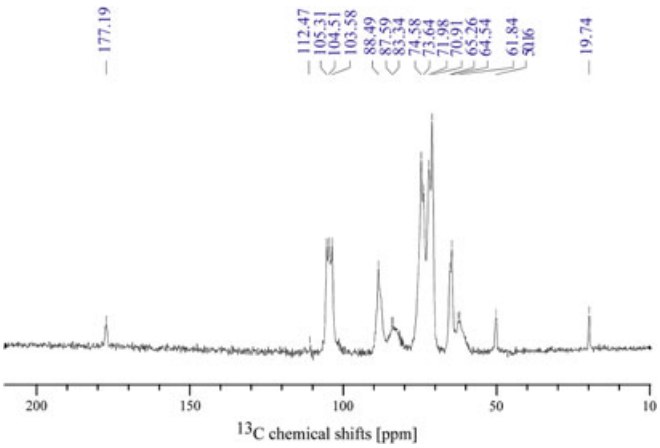

Figure 5. Solid –state ^{13}C-NMR spectrum of a blue colored linen thread (signals from 60 to 110 ppm are due to the presence of cellulose). This figure is available in colour online at wileyonlinelibrary.com/journal/jrs

The findings are surprising, because most of the artists of the period had already switched to the new, cheaper, widely available Prussian blue pigment.[15] However, the absence of a synthetic Fe-containing pigment does have direct implications on the dating of the painting, now undoubtedly determined as the first half of the 19th century.

Canvas support

The SERS spectrum of plain linen fibers was obtained for the first time. The spectrum is displayed in Fig. 4. The bands were assigned taking into account available literature data and the comparison with complementary FT-Raman and ATR-FT-IR spectra (Fig. 3) of the same linen fiber. Although cellulose does not produce a SERS spectrum,[38] addition of the Ag colloids proved to quench background fluorescence and enabled observation of specific cellulose peaks even with 785 nm excitation, with low integration times. Photobleaching of the fibers[39] was not required prior to signal acquisition. SERS bands observed were in agreement with results obtained by means of ATR-FT-IR and FT-Raman investigations. Several marker bands of the polysaccharide[14,39–42] could be observed: the δ(CCC) ring deformations at 434 and 469 cm^{-1}, the ρ(CH_2) broad band at ~958 cm^{-1}, as well as the ν(COC) glycoside doublet at 1100 cm^{-1}. The marker bands visible in SERS correspond to analog vibrations in the FT-Raman spectrum: the glycosidic ring deformation, for example, appears at a Raman shift of 434 cm^{-1}, whereas the glycosidic doublet has the asymmetric link vibration at 1095 cm^{-1} and the symmetric one at 1124 cm^{-1}. However, no prominent bands of the FT-Raman spectrum could be associated to lignin, except for the band at 2893 cm^{-1} (CH stretching, Fig. 3). Vibrations observed in the ATR-FT-IR spectrum are also more informative about the cellulose and hemicellulose compounds.

As previously noted by Agarwal and Reiner,[38] lignin in wood samples is highly absorbed on silver colloids. The same behavior applies to lignin-related vibration modes in linen. When applying hydroxylamine-reduced Ag colloids directly on linen fibers, we observed specific Raman bands for phenol and aromatic ring modes between 300 and 1600 cm^{-1}. Some of the most representative bands were the ring deformation at 693 cm^{-1}, the aromatic CH twisting at 827 cm^{-1} and the lignin–cellulose complex at 1277 cm^{-1}. A summary of the SERS bands of linen and a tentative assignment of the vibrations, based on literature data, is shown in Table 2.

The possibility of identifying lignin in vegetal fibers in a fast, straight-forward procedure has immediate applications in artwork diagnosis. As underlined by other authors, the fiber type in canvas-supported cultural heritage can be identified on the basis of its specific vibrational spectroscopic features.[43] By using Ag colloids to induce SERS, one could differentiate lignin-containing fibers such as flax or jute from non-containing ones, such as cotton. Also, because of the low acquisition times and good quality of the signal obtained, SERS analysis of linen could easily be applied for *in-situ* investigations.

As interaction between Ag nanopraticles and linen constituents is limited to specific structures, and therefore only certain bands are enhanced, no assessment of the degradation state of the canvas could be made at this point from an analysis of the SERS spectrum.

The lack of any significant signals from a binding medium (with exception of the large SERS band at circa 238 cm^{-1}, present in all samples, and indicative of Ag–N binding, possibly caused by the presence of a small amount of animal glue), suggests a water-based technique such as watercolor or gouache, which employ a very small amount of water-soluble organic binder and render the support more flexible as compared to other traditional painting techniques like oil or tempera. The use of such a painting technique, as well as traditional pigments, suggests a tradition in producing large cult paintings that would withstand high mechanical stress.

Conclusions

We reported for the first time SERS spectra of colored and plain linen fibers from an Italian canvas dating from the early century. A SERS signal has been obtained upon instant nanoparticle incubation on the fiber, within a 25 s acquisition time and with high signal-to-noise ratio. The observed bands have been assigned and discussed in correlation with solid-state ^{13}C-NMR, SEM-EDS and ATR-FT-IR analyses, allowing to get insight into the painting technique of a valuable Italian cultural heritage canvas. The use of short integration times while showing accurate results demonstrates the advantages of the SERS technique over FT-Raman investigations of aged natural fibers. We demonstrate here that linen threads were able to uptake the Ag colloidal nanoparticles and instantly provide SERS signal. Although further research is still required in understanding how signal ratios for known ageing markers change when SERS is employed, the scattering effect enables a more complex diagnosis of historic textiles and canvas supports, allowing simultaneous observation of lignin and cellulose bands.

Acknowledgements

Ms. Gui would like to acknowledge financial support from the Q-DOC project, contract no. POSDRU/107/1.5/S/78534. Mr. Barbu-Tudoran would like to acknowledge financial support from the POSDRU contract no. 89/1.5/S/61104 and Dr. Aluas would like to acknowledge financial support from the POSDRU contract no. 89/1.5/S/60189. The support of Officina della Memoria and of the Soprintendenza BB.CC.AA. Caltanissetta is gratefully acknowledged.

References

[1] C. Ricci, I. Borgia, B. G. Brunetti, C. Miliani, A. Sgamellotti, C. Seccaroni, P. Passalacqua, *J. Raman Spectrosc.* **2004**, *35*, 616.
[2] S. Daniilia, E. Minopoulou, K. S. Andrikopoulos, I. Karapanagiotis, G. A. Kourouklis, *Anal. Chim. Acta* **2008**, *611*, 239.
[3] C. M. Franceschi, G. A. Costa, E. Franceschi, *J. Therm. Anal. Calorim.* **2011**, *103*, 69.
[4] E. Joseph, S. Prati, G. Sciutto, M. Ioele, P. Santopadre, R. Mazzeo, *Anal. Bioanal. Chem.* **2010**, *396*, 899.
[5] M. Cotte, P. Dumas, Y. Taniguchi, E. Checroun, P. Walter, J. Susini, *C. R. Physique* **2009**, *10*, 590.
[6] M. Abdel-Ghani, H. G. M. Edwards, R. Janaway, B. Stern, *Vibr. Spectrosc.* **2008**, *48*, 69.
[7] I. Petroviciu, F. Albu, A. Medvedovici, *Microchem. J.* **2010**, *95*, 247.
[8] I. Bonaduce, L. Carlyle, M. P. Colombini, C. Duce, C. Ferrari, E. Ribechini, P. Selleri, M. R. Tine, *J. Therm. Anal. Calorim.* **2011**. DOI 10.1007/s10973-011-1586-6
[9] K. Kerem Şerifaki, H. Böke, Ş. Yalçınb, B. İpekoğlu, *Mater. Charact.* **2009**, *60*, 303.
[10] M. P. Mateo, T. Ctvrtnickova, G. Nicolas, *Appl. Surf. Sci.* **2009**, *255*, 5172.
[11] M. L. Franquelo, A. Duran, L. K. Herrera, M. C. Jimenez de Haro, J. L. Perez-Rodriguez, *J. Mol. Struct.* **2009**, *924–926*, 404.
[12] M. Petrou, H. G. M. Edwards, R. C. Janaway, G. B. Thompson, A. S. Wilson, *Anal. Bioanal. Chem.* **2009**, *395*, 2131.
[13] M. Bicchieri, A. Sodo, G. Piantanida, C. Coluzza, *J. Raman Spectrosc.* **2006**, *37*, 1186.
[14] M. Christensen, M. Frosch, P. Jensen, U. Schnell, Y. Shashoua, O. F. Nielsen, *J. Raman Spectrosc.* **2006**, *37*, 1171.
[15] P. Vandenabeele, M. C. Christensen, L. Moens, *J. Raman Spectrosc.* **2008**, *39*, 1030.
[16] I. Osticioli, A. Zoppi, E. M. Castellucci, *J. Raman Spectrosc.* **2006**, *37*, 974.
[17] C. L. Brosseau, F. Casadio, R. P. Van Duyne, *J. Raman Spectrosc* **2010**. DOI 10.1002/jrs.2877
[18] M. Leona, J. Stenger, E. Ferloni, *J. Raman Spectrosc.* **2006**, *37*, 981.
[19] S. Bruni, V. Guglielmi, F. Pozzi, *J. Raman Spectrosc.* **2010**, *41*, 175.
[20] A. V. Whitney, R. P. Van Duyne, F. Casadio, *J. Raman Spectrosc.* **2006**, *37*, 993.
[21] F. Casadio, M. Leona, J. R. Lombardi, R. P. Van Duyne, *Acc. Chem. Res.* **2010**, *43*, 782.
[22] K. Chen, M. Leona, K. Vo-Dinh, F. Yan, M. B. Wabuyele, T. Vo-Dinh, *J. Raman Spectrosc.* **2006**, *37*, 520.
[23] B. Doherty, B. G. Brunetti, A. Sgamellotti, C. Miliani, *J. Raman Spectrosc.* **2011**, *42*, 1932.
[24] S. Bruni, V. Guglielmi, F. Pozzi, *J. Raman Spectrosc.* **2011**, *42*, 1267.
[25] Z. Jurasekova, E. del Puerto, G. Bruno, J. V. García-Ramos, S. Sanchez-Cortes, C. Domingo, *J. Raman Spectrosc.* **2010**, *41*, 1455.
[26] E. Van Elslande, S. Lecomte, A. S. Le Ho, *J. Raman Spectrosc.* **2008**, *39*,1001.
[27] N. Leopold, B. Lendl, *J. Phys. Chem. B* **2003**, *107*, 5723.
[28] L. Burgio, R. J. H. Clark, V. S. F. Muralha, T. Stanley, *J. Raman Spectrosc.* **2008**, *39*(10), 1482.
[29] T. D. Chaplin, R. J. H. Clark, D. Jacobs, K. Jensen, G. D. Smith, *Anal. Chem.* **2005**, *77*, 3611.
[30] N. Eastaugh, V. Walsh, T. Chaplin, R. Siddall, The Pigment Compendium: A Dictionary of Historical Pigments, Elsevier, Amsterdam, **2004**.
[31] C. M. Schmidt, M. S. Walton, K. Trentelman, *Anal. Chem.* **2008**, *81*, 8513.
[32] A. Amat, F. Rosi, C. Miliani, A. Sgamellotti, S. Fantacci, *J. Mol. Struct.* **2011**, *993*, 43.
[33] H. Ajiki, F. Pozzi, L. Huang, L. Massa, M. Leona, J. R. Lombardi, *J. Raman Spectrosc.* **2011**. DOI 10.1002/jrs.3066
[34] M. V. Cañamares, J. V. Garcia-Ramos, S. Sanchez-Cortes, M. Castillejo, M. Oujja, *J. Colloid Interface Sci.* **2008**, *326*, 103.
[35] R. Giustetto, K. Seenivasan, F. Bonino, G. Ricchiardi, S. Bordiga, M. R. Chierotti, R. Gobetto, *J. Phys. Chem. C* **2011**, *115*, 16764.
[36] A. Domenech, M. T. Domenech-Carbo, M. Sanchez del Rıo, S. Goberna, E. Lima, *J. Phys. Chem. C* **2009**, *113*, 12118.
[37] M. Bardet, M. F. Foray, S. Maron, P. Goncalves, Q. C. Tran, *Carbohydr. Polym.* **2004**, *57*, 419.
[38] U. P. Agarwal, R. S. Reiner, *J. Raman Spectrosc.* **2009**, *40*, 1527.
[39] K. Kavkler, A. Demsar, *Spectrochim. Acta A* **2011**, *78*, 740.
[40] E. Marengo, M. C. Liparota, E. Robotti, M. Bobba, M. C. Gennaro, *Anal. Bioanal. Chem.* **2005**, *381*, 884.
[41] H. G. M. Edwards, N. F. Nikhassan, D. W. Farwell, P. Garside, P. Wyeth, *J. Raman Spectrosc.* **2006**, *37*, 1193.
[42] P. Adapa, C. Karunakaran, L. Tabil, G. Schoenau, *Agricultural Engineering International: the CIGR Ejournal*, **2009**, *1081*(11). http://www.cigrjournal.org/index.php/Ejounral/article/viewFile/1081/1151
[43] P. Garside, P. Wyeth. *Stud. Conserv.* **2003**, *48*(4), 269.