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ARTICLE

Combined SERS and Raman Analysis for the Identification of Red Pigments in Cross-Sections from Historic Oil Paintings

Kristen A. Frano,[a] Hannah E. Mayhew,[a] Shelley A. Svoboda,[b] Kristin L. Wustholz[a]*

[a]Department of Chemistry, College of William and Mary, Williamsburg, Virginia 23187.
[b]Department of Conservation, Colonial Williamsburg Foundation, Williamsburg, Virginia, 23187

The analysis of paint cross-sections can reveal a remarkable amount of information about the layers and materials in a painting without visibly altering the artwork. Although a variety of analytical approaches are used to detect inorganic pigments as well as organic binders, proteins, and lipids in cross-sections, they do not provide for the unambiguous identification of natural, organic colorants. Here, we develop a novel combined surface-enhanced Raman scattering (SERS), light microscopy, and normal Raman scattering (NRS) approach for the identification of red organic and inorganic pigments in paint cross-sections obtained from historic 18th and 19th century oil paintings. In particular, Ag nanoparticles are directly applied to localized areas of paint cross-sections mounted in polyester resin for SERS analysis of the organic pigments. This combined extractionless non-hydrolysis SERS and NRS approach provides for the definitive identification of carmine lake, madder lake, and vermilion in multiple paint layers. To our knowledge, this study represents the first *in situ* identification of natural, organic pigments within paint cross-sections from oil paintings. Furthermore, the combination of SERS and normal Raman, with light microscopy provides conservators with a more comprehensive understanding of a painting from a single sample and without the need for sample pretreatment.

Introduction

The challenge of identifying natural, organic colorants in historic artworks has motivated recent applications of surface-enhanced Raman scattering (SERS) spectroscopy to study artists' materials.[1-14] Indeed, the combination of large electromagnetic and resonance Raman enhancements in SERS studies of chromophores has enabled the ultrasensitive identification of colorants in microscopic art samples. For example, several studies have demonstrated the detection of anthraquinone-based red lake pigments (e.g., carmine, madder) in microscopic samples from cultural heritage objects using extractionless non-hydrolysis SERS.[4,6,9,14,15] In this approach, Ag nanoparticles are added directly to dispersed paint samples without the need for pretreatment to extract the colorants from the paint matrix, which some organic pigments may require.[2] Although a single pigment grain is often sufficient to unequivocally identify organic colorants using extractionless non-hydrolysis SERS, a microscopic sample from the surface of a painting does little to provide conservators with contextual information regarding the stratigraphic structure of the painting

that is necessary to understand the artist's methodology and palette. In order to obtain a comprehensive understanding of the layers and materials present in a painting, cross-section sampling and analysis is often performed in the conservation setting.[16]

Cross-section sampling from paintings is a micro-destructive technique that is often rationalized by the large scope of information that can be gained from a microscopic (i.e., microns to millimeters) sample without visibly altering the artwork. In this approach, cross-section samples are mounted in a polyester resin, polished to reveal the paint stratigraphy, and then analysed using a variety of techniques. For example, cross-section analysis is often accomplished using optical microscopy,[16] attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR),[14,17-20] normal Raman scattering (NRS),[14,21-25] visible light imaging microspectroscopy (VIS-imaging),[26] and secondary ion mass spectrometry (SIMS).[27] Although these approaches, sometimes coupled with energy dispersive x-ray analysis (EDX) or micro-x-ray fluorescence (XRF), detect inorganic pigments as well as organic binders, proteins, and lipids, they do not enable the unambiguous identification of natural, organic colorants in cross-sections.

Here, we employ extractionless non-hydrolysis SERS with light microscopy and NRS for the identification of organic red lake colorants in mounted cross-sections from 18th and 19th century oil paintings. We previously demonstrated that extractionless non-hydrolysis SERS can successfully identify carmine lake in small, dispersed samples from oil paintings.[9] More recently, SERS was used for the analysis of red lake pigments (i.e., madder, kermes) in cross-sections from Italian 13th century polychrome statues and 16th century mural paintings.[28] Yet, in order to establish extractionless non-hydrolysis SERS as a versatile technique for paint cross-section analysis, investigations of additional colorants and binding media are required. In this work, reference cross-sections prepared from red pigments typical of the 18th century (i.e., carmine lake, madder lake, and vermilion) as well as actual art samples are examined. We investigate mounted cross-section samples obtained from two 18th century oil paintings in the Colonial Williamsburg Foundation's collection. The first, *Elizabeth Burwell Nelson*, is by Robert Feke, the first known American-born artist of European descent. A second painting, *Isaac Barré* by Sir Joshua Reynolds, was previously studied with extractionless non-hydrolysis SERS and found to contain carmine lake in small, dispersed samples obtained from the cheek and finger flesh.[9] Finally, we examine a 19th century example, *Young Woman in a Red Dress* by Gabriel de Cool. Ultimately, we demonstrate that extractionless non-hydrolysis SERS combined with light microscopy and NRS provides the ability to identify the red pigments carmine lake, madder lake, and vermilion in cross-section samples from 18th and 19th century oil paintings with pinpoint accuracy while maintaining sample integrity.

Experimental

Materials, Synthesis, and Sample Preparation. Madder lake, carmine naccarat (lake prepared from aluminum mordant), vermilion, linseed oil, and charcoal black were obtained from Kremer Pigments. Flake white pigment was obtained from RGH Artists' Oil Paints. Reference paints of carmine lake, madder lake, vermilion and flake white were prepared in linseed oil on a marble slab with a glass muller. To generate reference cross-section samples, a preparation layer containing flake white and charcoal was applied to a primed wood panel (8" × 10"). Next, layers of carmine lake, madder lake, or a mixture of carmine and vermilion paint were added to create a stratified structure. After sufficient drying, a mastic varnish (Kremer) was applied. Cross-section samples from *Isaac Barré* (by Sir Joshua Reynolds, oil on canvas, 1766, 50-1/8 × 40-1/16 in.; CWF 2010-103), *Elizabeth Burwell Nelson (Mrs. William Nelson)* (by Robert Feke, oil on canvas, probably 1749-1751, 49-5/8 × 39-5/8 in.; CWF 1986-246), and dispersed samples from *Young Woman in a Red Dress* (by Gabriel de Cool, oil on canvas, 1890, 39 × 20-1/2in.; Private Collection) were investigated using SERS. Samples were obtained from oil paintings with surgical blades (Feather Safety Company). Glassware was base bathed, thoroughly rinsed, and then cleaned with aqua regia prior to use.
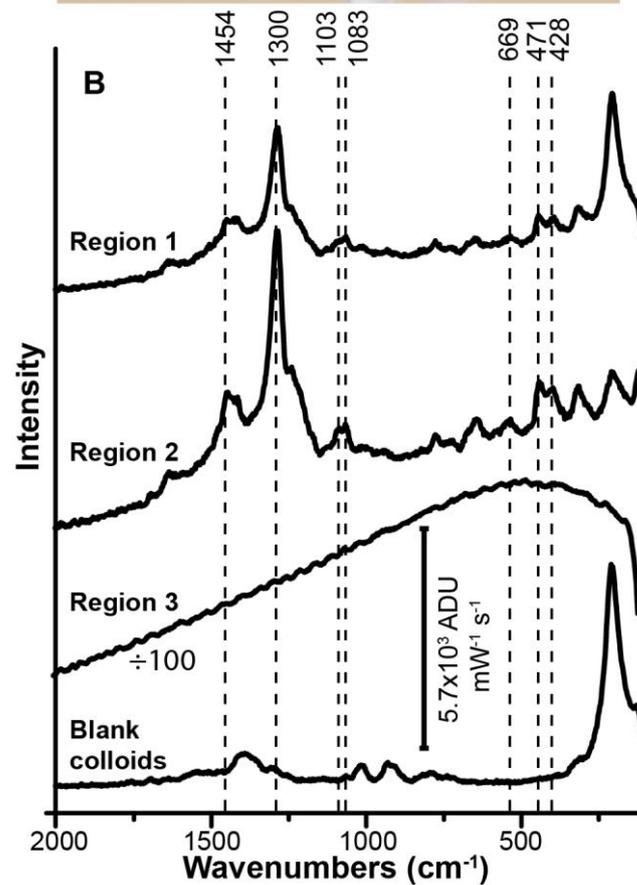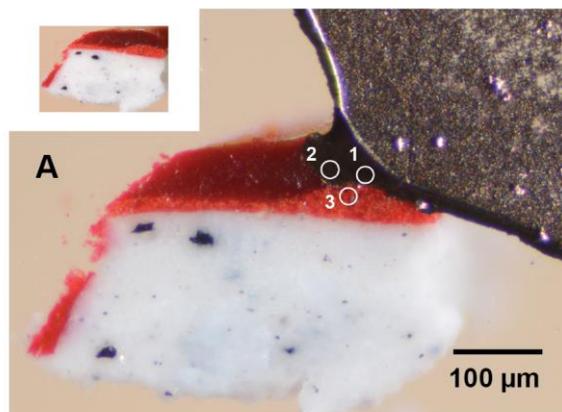

Figure 1: (A) Reference cross-section containing oil paint layers of lead white, a mixture of carmine and vermilion, and pure carmine (shown with and without colloids). (B) SERS spectra from three different regions of the cross-section as well as bare Ag colloids, obtained at 632.8 nm excitation.

Silver nitrate (Alfa Aesar, 99.9+%) and sodium citrate (Fisher Scientific) were used to synthesize citrate-reduced Ag colloids.[29] The colloids were centrifuged (Eppendorf, MiniSpin, 1 mL aliquots with ~0.9 mL of supernatant removed) for two cycles at a relative centrifugal force of 12 000 g at 15 min per cycle to concentrate the colloids and remove excess citrate. Consistent with previous extractionless non-hydrolysis SERS studies, microscopic dispersed art samples were placed on clean glass
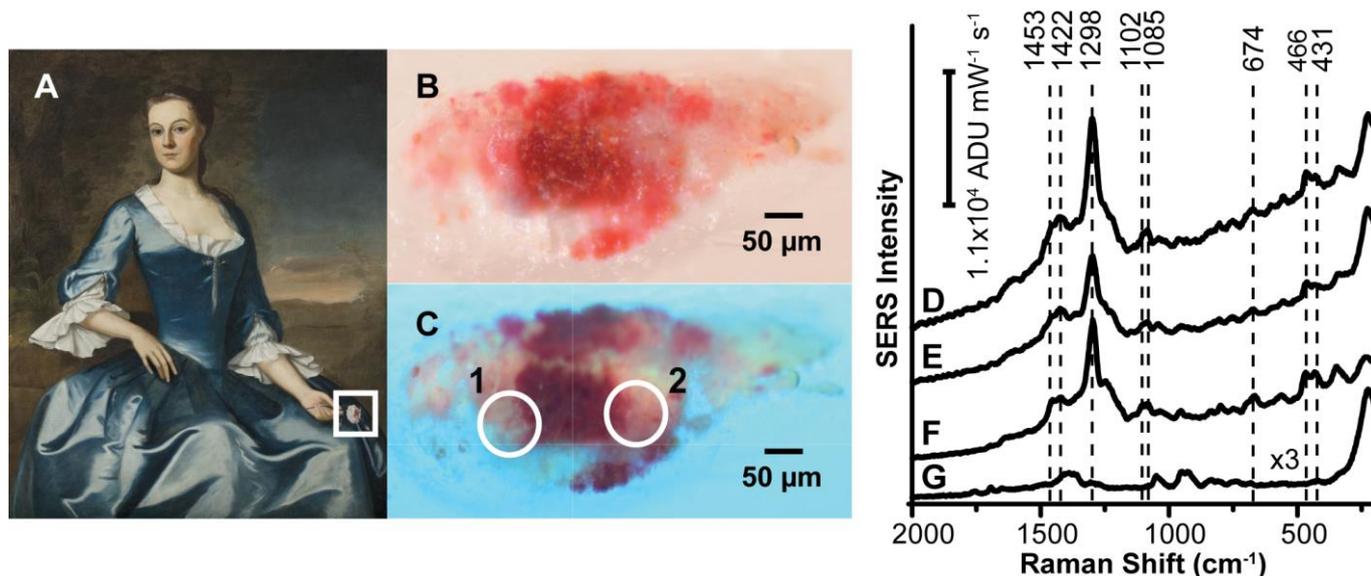
Figure 2. (A) *Elizabeth Burwell Nelson* by Robert Feke, probably 1749-1751. Rose bud sample imaged in (B) white and (C) UV light. SERS spectra from (D) region 1 and (E) region 2 of the sample obtained using 632.8 nm excitation. SERS spectra of (F) a reference carmine-containing cross-section mounted in polyester resin and (G) blank Ag colloids applied to the polyester resin block. Peaks attributed to carmine lake are highlighted.

coverslips and coated in 0.75 µL of Ag colloids for SERS analysis.[9] Using a surgical microscope (Zeiss, OPMI 1FC), approximately 0.25- 0.50 µL of Ag colloids were directly applied to specific regions of interest in the mounted samples. Samples were allowed to dry before SERS measurements (~20 minutes). SERS spectra were monitored across the cross-section samples using a manual translation stage (Nikon TiU) in order to examine the distribution of colorants and SERS intensities.

Cross-Section Analysis. Cross-sections were mounted in a plastic tray with polyester resin (Ward's Bio-Plastic), resulting in approximately 12.7 mm × 12.7 mm × 12.7 mm (~2500 mm^3) sample cubes. Cubes were ground down on a belt grinder (Wilton, 335 grit) to an approximate size of 12.7 mm × 9.5 mm × 3.1 mm (374 mm^3), and then finely polished with bonded abrasive cloths (Micro-Mesh, Inc., 320-12,000 grit). Cross-section samples were examined with a microscope (Nikon Eclipse E600) under white light (OPELCO, fiber optic halogen source) and UV illumination (100 W Hg lamp) at 10× magnification and imaged with a camera (Nikon D7000). To remove Ag colloids from the cross-section samples and expose a fresh surface of paint, samples were polished again using 1500 grit bonded abrasive cloth.

SERS Measurements. SERS studies were performed on an inverted microscope (Nikon, TiU) coupled to a 1/3 m imaging spectrograph (Princeton Instruments, SP2356) equipped with a CCD camera (Princeton Instruments, PIXIS: 100B- Excelon). For normal Raman and SERS measurements, excitation at 632.8 nm (chosen due to its success in previous SERS studies of red lakes)[9] from a HeNe laser (Research Electro-Optics, LHRP-1701) was filtered (Semrock, LL01-633-25) and focused to the

sample using a 20× objective (Nikon CFI, N.A.= 0.5). Scattering from the sample was collected through the objective, filtered (Semrock, LP02-633RS-25), and focused to the entrance slit of the spectrograph. Raman scattering was dispersed using a 600 g/mm grating blazed at 500 nm. The observed Raman frequencies were calibrated using a cyclohexane standard. A color camera (Edmund Optics, EO-0413C) was used to record images of the samples and to localize the exciting laser to specific regions of interest. In particular, those regions containing natural, organic pigments exhibited fluorescence upon examination with a microscope under UV illumination. Typical excitation powers (P_{exc}) of 10-20 µW and ~1 mW were used for SERS and normal Raman measurements, respectively. Acquisition times (t_{acq}) were varied from ~30-90 s for SERS measurements in order to maximize signal-to-noise ratios while avoiding molecular photobleaching.

Results and Discussion

Figure 1 presents a cross-section sample containing a preparation layer of lead white paint followed by applications of a paint mixture containing carmine lake and vermilion and a pure carmine lake overpaint. Approximately 0.25 µL of Ag colloids were added to one edge of the sample, enabling SERS measurements in various regions within the cross-section. In particular, SERS spectra of regions 1 and 2 exhibit major peaks at 1454 cm^{-1} (m), 1300 cm^{-1} (s), 1103 cm^{-1} (w), 1083 cm^{-1} (w), 669 cm^{-1} (w), 471 cm^{-1} (m), and 428 cm^{-1} (m), consistent with previous SERS studies of carmine (see Electronic Supplementary Information for table of discriminant peaks for all references and samples).[4,5,9] In region 3, an area not coated in nanoparticles, strong fluorescence from carmine is observed.

Although region 3 also contains the non-fluorescent colorant vermilion, the NRS signal from vermilion is overwhelmed by fluorescence from the organic colorant. These results demonstrate that by directly applying Ag colloids to a paint cross-section, SERS provides the ability to identify an organic pigment in multiple regions with pinpoint accuracy while maintaining the integrity of the stratigraphy within the sample.

To test the applicability of this SERS-based approach to identify pigments in cross-sections from a historic oil painting, we examined a cross-section sample obtained from the flower bud in *Elizabeth Burwell Nelson* by Robert Feke. Figure 2 presents a sample imaged in white and UV light. Although the sample lacks a defined paint-layer structure, the presence of a lake pigment is indicated by fluorescence under UV illumination (Figure 2C). Figures 2D and 2E present SERS spectra from regions 1 and 2 of the sample obtained using 632.8 nm excitation. Major peaks are consistent with the SERS spectrum of reference carmine lake paint mounted in polyester resin (Figure 2F) as well as previous SERS studies of carmine.[4,5,9] Figure 2G shows the SERS spectrum of blank Ag colloids on the polyester resin.

In order to apply this SERS approach to a cross-section with a defined layer system, we examined a sample from *Isaac Barré* by Sir Joshua Reynolds. Figure 3 presents a cross-section from the coat region of the painting imaged in both white and UV light. The cross-section from the sitter's coat reveals a preparation layer, a paint layer containing non-fluorescent colorants, and a paint layer containing a red lake pigment as evidenced by fluorescence under UV illumination. Figure 3D shows the SERS spectrum of the spot (region 1) indicated in Figure 3B. At this location, major peaks consistent with carmine lake and linseed oil (i.e., ~870 cm^{-1}) are observed, as well as peaks attributed to the resin (i.e., ~1640 cm^{-1} and ~1700 cm^{-1}) and adsorbed citrate.[4,9,30] The detection of carmine lake is consistent with previous extractionless non-hydrolysis SERS measurements of disperse samples from the sitter's fleshtones.[9] Although these results demonstrate that carmine lake can be identified in the paint cross-sections from historic oil paintings, they do not provide the spatial distribution of colorants. To examine the potential for SERS as a spatial mapping tool, spectra were recorded in a variety of locations within the nanoparticle spot on the cross-section. Inhomogeneous SERS intensities for carmine lake were observed across the cross-section, indicating that the signal originates from localized pigment-containing areas in the sample and that carmine lake is not readily dissolved in the colloids to produce homogeneous intensities.

Although these results demonstrate the first *in situ* SERS-based detection of carmine lake in a cross-section from an oil painting, attempts to repeat the results presented in Figures 2 and 3 more than one week after the application of Ag colloids were unsuccessful. It is possible that interactions between the polyester resin and Ag nanoparticles eventually render the samples SERS inactive due to nanoparticle diffusion through the resin matrix. In order to investigate the reproducibility and future viability of cross-section samples, we used a polishing cloth to gently remove Ag nanoparticles and expose a fresh paint layer. White light microscopy revealed that although some residual
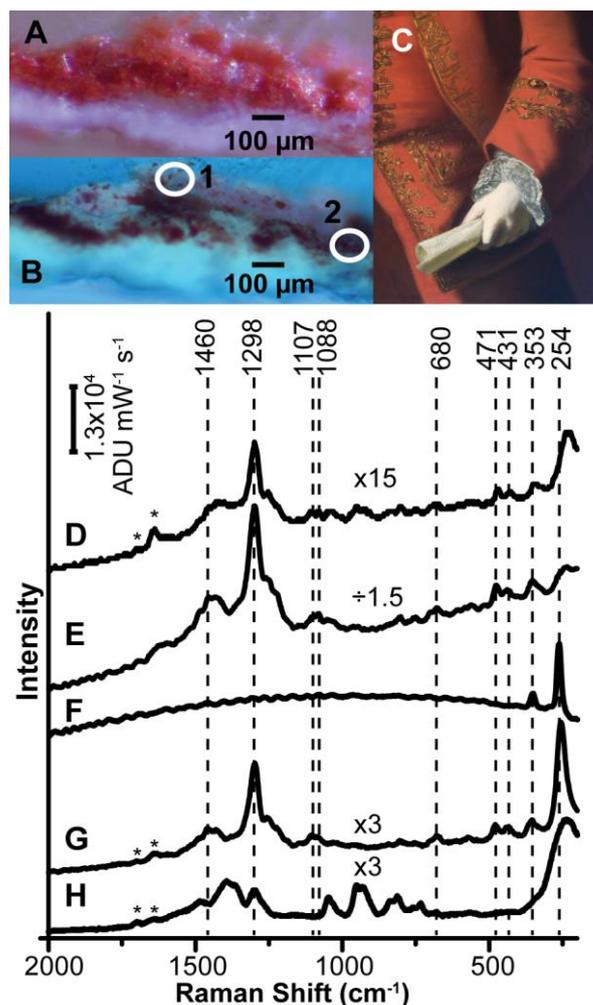

Figure 3: (A) Painting cross-section imaged in white and (B) UV light from the (C) detail of coat in the *Portrait of Isaac Barré* by Sir Joshua Reynolds, 1766; (D) SERS spectrum from *Portrait of Isaac Barré* cross-section; (E) SERS spectrum of same cross-section sample after colloids were removed by polishing and reapplied; (F) Raman spectrum from area containing vermilion in *Portrait of Isaac Barré* after colloids were removed; (G) Reference carmine and vermilion containing cross-section mounted in polyester resin; (H) SERS spectrum of blank Ag colloids applied to a polyester resin cube.

colloids remain on the sample after repolishing, the integrity of the cross-section layers is maintained. After repolishing, Ag nanoparticles were reapplied to the newly-exposed paint layer. Figure 3E shows the SERS spectrum of region 1 in the repolished cross-section. Remarkably, SERS peaks from carmine lake are readily observed following Ag nanoparticle removal, repolishing, and reapplication.

White light microscopy of the cross-section (Figure 3A) indicated the presence of a red inorganic colorant in the sitter's coat. In order to identify the inorganic pigment, both SERS and NRS measurements were performed on these non-fluorescent regions. NRS measurements of the non-fluorescent, red regions

in the cross-section (e.g., region 2 indicated in Figure 3B) demonstrate the presence of vermilion (Figure 3F).[31,32] However, corresponding SERS measurements, performed after the addition of Ag colloids, did not exhibit peaks due to vermilion. Poor SERS signals from vermilion may be attributed to modest resonance Raman enhancement or insufficient adsorption of the inorganic colorant to the nanoparticle substrate. Indeed, previous SERS studies of the inorganic pigment Prussian blue demonstrated the need for sample pretreatment with acid in order to solubilize the pigment, thereby increasing SERS enhancement.[8] Ultimately, the combination of white light microscopy with NRS and SERS provides for the unambiguous detection of carmine lake and vermilion in different regions of the cross-section from this historic oil painting. To our knowledge, this data represents the first example of SERS-based identification of colorants in an oil painting cross-section in localized regions within multiple paint layers and without the need for sample pretreatment. Furthermore, the SERS substrate is removable via polishing to reveal a fresh layer of paint and a cross-section for further analysis.
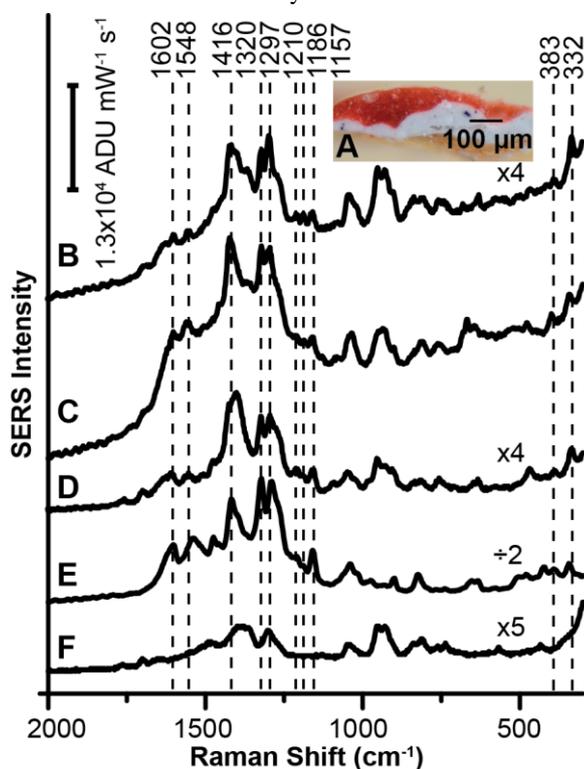

Figure 4. (A) Reference cross-section sample containing madder lake imaged in white light. (B) Corresponding SERS spectrum of A. (C) SERS spectrum of a dispersed paint sample from *Young Woman in a Red Dress* by Gabriel de Cool (1890). SERS spectra of reference madder lake (D) paint and (E) pigment. (F) SERS spectrum of blank Ag colloids applied to a polyester resin block.

To establish that this SERS-based method is successful for organic pigments beyond carmine lake, we investigated samples containing another ubiquitous red lake pigment: madder lake. Figure 4A displays a reference cross-section sample containing

madder lake. The corresponding SERS spectrum of the madder-containing cross-section is presented in Figure 4B. Major peaks are observed at 1602 cm^{-1} (w), 1548 cm^{-1} (w), 1416 cm^{-1} (s), 1320 cm^{-1} (s), 1297 cm^{-1} (s), 1210 cm^{-1} (w), 1186 cm^{-1} (w), 1157 cm^{-1} (w), 383 cm^{-1} (w), and 332 cm^{-1} (m), in excellent agreement with the SERS spectra of alizarin and purpurin, the main dye components of madder lake (see Electronic Supplementary Information), as well as previously published SERS spectra of madder lake.[2,33,34] To test the viability of this approach on a real art sample, a dispersed paint sample from *Young Woman in a Red Dress* by Gabriel de Cool (see Electronic Supplementary Information) was investigated using extractionless non-hydrolysis SERS. Figure 4C presents the SERS spectrum of a microscopic sample from the flower region, consistent with major peaks for madder lake. Indeed, the data in Figures 3B and 4C are consistent with the SERS spectra of reference madder lake paint and pigment (Figures 4D and 4E, respectively). These promising results demonstrate that extractionless non-hydrolysis SERS provides the ability to detect madder lake in oil paintings. Furthermore, the data suggests that this SERS methodology can be successfully applied to interrogate cross-sections from historic oil paintings containing madder lake.

Conclusion

The results presented here demonstrate that extractionless non-hydrolysis SERS can provide the direct identification of red lake pigments in cross-sections from historic oil paintings. By applying Ag colloids directly to mounted cross-sections, SERS delivers definitive identification of both organic (carmine lake, madder lake) and inorganic (vermilion) materials in specific regions within multiple paint layers, providing conservators with a more comprehensive knowledge of artist's materials in just a single sample and without the need for sample pretreatment. These results represent an important step toward developing SERS as a spatial mapping tool for the identification of organic pigments in painting cross-sections. Current work is underway to use this combined white light microscopy, NRS, and SERS approach to image both organic and inorganic colorants in cross-sections.

Notes and references

1   M. Leona, J. Stenger, E. Ferloni, *J. Raman Spectrosc.*, 2006, **37**, 981.

2   F. Pozzi, J. R. Lombardi, S. Bruni, M. Leona, *Anal. Chem.*, 2012, **84**, 3751.

3   K. L. Wustholz, C. L. Brosseau, F. Casadio, R. P. Van Duyne, *Phys. Chem. Chem. Phys.*, 2009, **11**, 7350.

4   C. L. Brosseau, K. S. Rayner, F. Casadio, C. M. Grzywacz, R. P. Duyne, *Anal. Chem.*, 2009, **81**, 7443.

5   C. L. Brosseau, A. Gambardella, F. Casadio, C. M. Grzywacz, J. Wouters, R. P. Van Duyne, *Anal. Chem.*, 2009, **81**, 3056.

6   C. L. Brosseau, F. Casadio, R. P. Van Duyne, *J. Raman Spectrosc.*, 2011, **42**, 1305.

7   H. E. Mayhew, D. M. Fabian, S. A. Svoboda, K. L. Wustholz, *Analyst*, 2013, **138**, 4493.

8   L. H. Oakley, D. M. Fabian, H. E. Mayhew, S. A. Svoboda, K. L. Wustholz, *Anal. Chem.*, 2012, **84**, 8006.

9   L. H. Oakley, S. A. Dinehart, S. A. Svoboda, K. L. Wustholz, *Anal. Chem.*, 2011, **11**, 3986.

10 M. V. Cañamares, J. V. Garcia-Ramos, C. Domingo, S. Sanchez-Cortes, *Vib. Spectrosc.*, 2006, **40**, 161.

11 F. Casadio, M. Leona, J. R. Lombardi, R. Van Duyne, *Accounts Chem. Res.*, 2010, **43**, 782.

12 Z. Jurasekova, E. del Puerto, G. Bruno, J. V. Garcia-Ramos, S. Sanchez-Cortes, C. J. Domingo, *J. Raman Spectrosc.*, 2010, **41**, 1165.

13 J. Arslanoglu, S. Zaleski, J. Loike, *Anal. Bioanal. Chem.*, 2011, **399**, 2997.

14 C. Daher, L. Drieu, L. Bellot-Gurlet, A. Percot, C. Paris, A. Le Hô, *J. Raman Spectrosc.*, 2014, DOI: 10.1002/jrs.4565 (Early View).

15 A. Idone, M. Gulmini, A. I. Henry, F. Casadio, L. R. Chang, L. Appolonia, R. P. Van Duyne, N. C. Shah, *Analyst*, 2013, **138**, 5895.

16 R. C. Wolbers, S. L. Buck, P. Olley, *In The Conservation of Easel Paintings*; J. H. Stoner, R. Rushfield, Eds.; Routledge: New York, NY, 2012, p 326.

17 M. Spring, C. Ricci, D. A. Peggie, S. G. Kazarian, *Anal. Bioanal. Chem.*, 2008, **392**, 37.

18 E. Joseph, S. Prati, G. Sciutto, M. Ioele, P. Santopadre, R. Mazzeo. *Anal. Bioanal. Chem.*, 2010, **396**, 899.

19 R. Sloggett, C. Kyi, N. Tse, M. J. Tobin, L. Puskar, S. P. Best, *Vib. Spectrosc.*, 2010, **53**, 77.

20 R. Mazzeo, E. Joseph, S. Prati, A. Millemaggi, *Anal. Chim. Acta*, 2007, **599**, 107.

21 C. Conti, C. Colombo, M. Matteini, M. Realini, G. J. Zerbi, *J. Raman Spectrosc.*, 2010, **41**, 1254.

22 D. Lau, C. Villis, S. Furman, M. Livett, *Anal. Chim. Acta*, 2008, **610**, 15.

23 C. L. Aibeo, S. Goffin, O. Schalm, G. van der Snickt, N. Laquiere, P. Eyskens, K. J. Janssens, *J. Raman Spectrosc.*, 2008, **39**, 1091.

24 P. Ropret, S. A. Centeno, P. Bukovec, *Spectroc. Acta Pt. A-Molec. Biomolec. Spectrosc.*, 2008, **69**, 486.

25 L. Burgio, R.J.H. Clark, L. Sheldon, G.D. Smith, *Anal. Chem.*, 2005, **77**, 1261.

26 J. van der Weerd, M. K. van Veen, R. M. A. Heeren, J. J. Boon, *Anal. Chem.*, 2003, **75**, 716.

27 K. Keune, J. J. Boon, *Anal. Chem.*, 2004, **76**, 1374.

28 A. Idone, M. Aceto, E. Diana, L. Appolonia, M. Gulmini, *J. Raman Spectrosc.*, 2014, DOI: 10.1002/jrs.4491 (Early View)

29 P. C. Lee, D. Meisel, *The Journal of Physical Chemistry*, 1982, **86**, 3391.

30 P. Vandenabeele,; M. Ortega-Aviles, D. T. Castilleros, L. Moens, *Spectroc. Acta Pt. A-Molec. Biomolec. Spectrosc.*, 2007, **68**, 1085.

31 L. Burgio, R.J.H. Clark, *Spectroc. Acta Pt. A-Molec. Biomolec. Spectrosc.*, 2001, **57**, 1491.

32 I. M. Bell, R. J. H. Clark, P. J. Gibbs, *Spectroc. Acta Pt. A-Molec. Biomolec. Spectrosc.*, 1997, **53**, 2159.

33 S. Bruni, V. Guglielmi, F. Pozzi, *J. Raman Spectrosc.*, 2010, **41**, 175.

34 S. Bruni, V. Guglielmi, F. Pozzi, *J. Raman Spectrosc.*, 2011, **42**, 1267.

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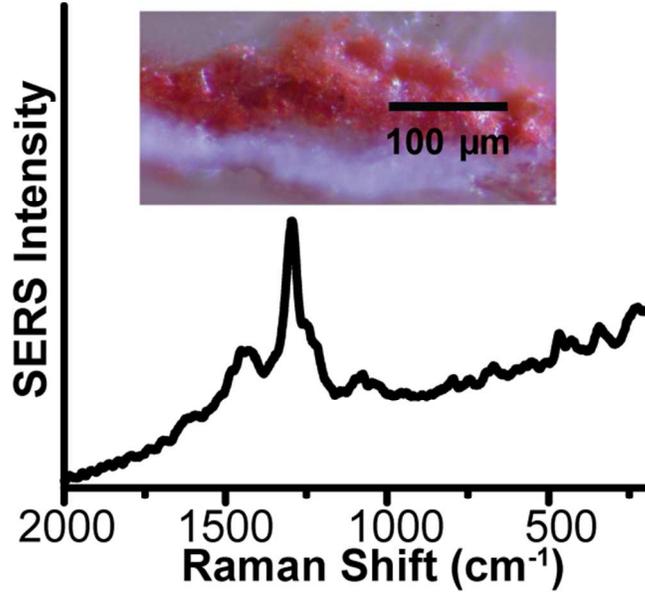
SERS and normal Raman approach to identify red pigments in cross-sections from historic oil paintings
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