

Revealing the invisible: using surface-enhanced Raman spectroscopy to identify minute remnants of color in Winslow Homer's colorless skies

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The fading of pigments in items of importance to cultural heritage, such as paintings, works of art on paper, and textiles, is a ubiquitous problem. Tools currently available that can detect and identify organic colorants in severely degraded works of art are rare, given the heavy deterioration and restricted availability of the sample. Recently, however, surface-enhanced Raman scattering (SERS) spectroscopy has shown great promise in detecting and identifying mass-limited samples. The art conservation field has seized upon the opportunity opened up by this powerful analytical technique to enable the identification of microscopic amounts of organic molecules used as artists' colorants in complex matrices, such as biomaterials (i.e. dyed natural textiles, linseed oil biofilms present in oil paintings, etc.), a possibility that was previously precluded due to interfering fluorescence and small sample size. Here, we report SERS spectra recorded directly on single particles of red lake pigments from an important historical watercolor by the American master Winslow Homer (1836–1910) that suffered some degree of fading. The accurate colorant identification provided by SERS, enhanced by comparison with reference samples of historical watercolors, has thus enabled important discoveries regarding the materials and intended meanings behind artworks from one of the most influential American watercolor painters. Copyright © 2011 John Wiley & Sons, Ltd.

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Introduction

In recent years, surface-enhanced Raman scattering (SERS) spectroscopy has experienced a powerful renaissance, both in terms of a deepened fundamental understanding of the interactions between the nanostructured noble-metal substrates and model analytes,^[1,2] and in terms of its applications, ranging from biomedicine^[3,4] to biowarfare^[5] to art conservation.^[6–8] While in the past few years successful reports of SERS identification of artists' colorants on textile fibers have been published,^[9–12] positive identification of these colorants on single grains of pigment in paintings, watercolors, or pastels from historical artworks has remained largely elusive until recent years^[13]; this is a consequence of the extreme complexity of these matrices as well as their aging and potential admixture with extraneous materials, in particular those used in conservation treatments.

Identifying natural organic colorants is exceedingly important for the conservation, interpretation, and long-term preservation of highly prized and culturally important historical artworks. Many analytical techniques have been developed for the detection and identification of such colorants, including Fourier transform infrared (FTIR)^[14] spectroscopy and Raman spectroscopy.^[15] Currently, the most commonly used methods for dye analysis are high-performance liquid chromatography (HPLC)^[16] and UV–vis spectroscopy.^[17] While HPLC has to date identified the largest number of natural organic colorants in artworks, it suffers from the requirement of large sample size (typically ~5 mm of fiber or 15 µg of sample).^[16] Unfortunately, such large amounts can rarely be

taken from precious art objects, particularly works of art on paper, which are characterized by a thin film of medium over the paper substrate. UV–vis spectroscopy has been successfully used to identify colorants that are typically hard to analyze using HPLC,^[18] such as the red lake pigments (i.e. madder, cochineal); however, its fingerprinting capabilities are limited, especially when the colorant is embedded in a complex matrix. Raman spectroscopy has been used to detect and identify many pigments and colorants,^[19–22] which typically have been limited to inorganic pigments due to the strong fluorescence of organic dyestuffs; however, recently Raman spectra of a large number of synthetic organic pigments have been published.^[23,24]

SERS satisfies many of the features of an ideal analytical technique to detect and identify colorants in artworks. The presence of a nanostructured noble-metal substrate leads to enhanced Raman signals, such that only very minute (sub-µg to pg) samples are required. In addition, the same noble-metal surface quenches the interfering fluorescence generated by the dye. These qualities of SERS for the analysis of dyes have attracted the attention of both museum conservators and scientists. Over

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the past several years, many groups have shown the applicability of SERS to detect and identify colorants of importance to art conservation, which have been the subject of recent extensive reviews.^[12,25] Unfortunately, to obtain SER spectra of colorants used in an actual historical object, the dye components would need to be separated from the object specimen. This typically requires extensive sample preparation and manipulation, such as harsh extractions in strong acid that invariably degrade the host material. While less harsh methods of extraction have recently been reported,^[26] these extractions typically result in less effective color removal from the substrate. In general, however, even in the case where the color removal is excellent, the very small size of sample taken from art objects often precludes such laborious procedures.

To circumvent the problematic issue of dye extraction, researchers have recently focused their effort on a direct approach for obtaining SERS of microscopic quantities of art sample, typically using colloidal silver to deliver the SER active moiety to the analyte of interest. Leona *et al.* reported a successful approach wherein hydrofluoric acid was used to pretreat (hydrolyze) dyed fibers in order to remove the colorant from the mordant, and using this approach they elucidated the major colorant (berberine) in a severely degraded 11th century Byzantine textile.^[27] Chen *et al.* produced SERS spectra of organic colorants from a silver nanoparticle-treated dyed fiber taken from a mock artwork.^[28] Jurasekova *et al.* extended this to *in situ* on-fiber detection of weld dyes on dyed reference fibers using photoreduced silver nanoparticles.^[9] Recently, we have investigated the applicability of *in situ* on-fiber SERS to samples taken from actual historical textiles, successfully reporting direct identification of highly fluorescing colorants such as cochineal and lac dye on these samples.^[6] Reports of SERS analysis of single pigment particles are rare: only recently did Van Elslande *et al.* report direct nonextractive, nonhydrolysis SERS on pigment grains taken from a Grecian archeological site, allowing the identification of the colorants 6,6'-dibromoindigo and purpurin.^[29] Leona, in the most comprehensive study to date, described SERS identification of colorants on Egyptian leather, Medieval polychrome wood sculptures, and a 16th century easel painting, using stabilized colloids after HF pretreatment.^[13] Our work extends this on-specimen methodology to the analysis of 19th century pastels^[30] and to watercolors, the results of which are highlighted in this article. These results have shown that, while true noninvasive SERS on art objects has remained elusive, such microdestructive analysis can provide valuable information regarding the identity of dyes contained in artworks on severely mass-limited samples, information which is crucial for the correct interpretation and long-term preservation of works of art.

Winslow Homer's Watercolors

Winslow Homer (1836–1910) was a renowned American printmaker and painter who revolutionized the art of watercolor painting. Chiefly self-taught, Homer painted nearly 700 watercolors in less than three decades (1873–1905), firmly establishing himself as one of the most influential figures in the history of watercolors. These masterful watercolors portray scenes on varied landscapes, such as civil war battlefields, serene farmlands, and rocky oceanic coastlines.^[31] His mastery of this medium is considered unparalleled in 19th century American artwork. During his lifetime, Homer closely followed the scientific color theories set

out by Chevreul's treatise entitled *De la Loi du contraste simultané des couleurs et de l'assortiment des objets colorés* (1839), and as a result he was very careful to choose exactly the right colors to maximize visual impact.^[32] Such dramatic coloration depended greatly on the pigment that was used and its inherent properties, as well as the way in which the pigment was applied. Unfortunately, the photochemical degradation of some pigments over time has shifted the color balance of Homer's creations, leading the viewer in some cases to overlook the original intention of the piece.

Understanding which pigments Homer chose to use, how he used these pigments to create his masterpieces, and how some of these pigments may have changed with time constituted a major research effort at the Art Institute of Chicago, in preparation for a 2008 exhibition, for which the pigments contained in 29 of Homer's artworks were examined with various analytical techniques.^[32,33]

Experimental

Preparation of citrate-reduced colloids

Silver nitrate (99 + %) and sodium citrate were purchased from Sigma Aldrich (St. Louis, MO, USA). Citrate-reduced silver colloids were prepared using the standard Lee and Meisel technique,^[34] having a peak absorption wavelength of ~500 nm and a full-width at half-maximum (FWHM) of ~100 nm. After cooling, the colloidal nanoparticles were centrifuged 10 times (relative centrifugal force 36 000g, 15 min per cycle) to concentrate the colloid. The colloids prepared this way were stable at room temperature (stored in the dark) for up to 3 weeks.

Surface-enhanced Raman scattering spectroscopy

For these studies, a Jobin-Yvon Horiba Labram 300 confocal Raman microscope was used, which was equipped with an Andor multichannel air-cooled open electrode charge coupled device detector (CCD: 1024 × 256), a BXFM open microscope frame (Olympus), a holographic notch filter, and an 1800 grooves/mm dispersive grating. A He–Ne laser (632.8 nm) was used in conjunction with an appropriate neutral density filter such that the power at the sample was kept at 5 μW. The slit size was 200 μm, and the laser light was focused onto the sample (and scattered light was collected back) using a 100× objective (N.A. 0.9). After careful examination of the artwork (Fig. 1) under a high magnification stereomicroscope, a representative area of the sky was selected for sampling (Fig. 2a) and a few remaining pigment grains (protected by the paper fibers at the upper left corner of the watercolor) were sampled using a tungsten needle. Approximately 5–15 pigment grains were removed and placed on a clean glass microscope slide. An area of the slide containing several pigment grains was then visualized using the microscope (Fig. 2(b)), and the color of each grain documented. A small volume (2 μl) of the colloid paste described above was applied on top of these grains and allowed to dry. Once dry, SERS spectra were recorded for each pigment grain. In this study, SERS spectra were recorded for seven pigment grains. To establish a reference database for the Homer watercolor, SERS spectra were collected in a similar manner from paintouts of actual watercolor washes contained in a Winsor and Newton (W&N) catalog published in 1887 (Fig. S1, Supporting Information).^[35] Such paintouts constitute an excellent reference for identifying pigments in Homer's artwork, since he was known to use watercolors produced by this manufacturer and the paintouts



Figure 1. Winslow Homer watercolor 'For to Be a Farmer's Boy' 1887, 355 × 509 mm (14 × 20 in.) (lower edge trimmed), gift of Mrs George T. Langhorne in memory of Edward Carson Waller, AIC 1963.760. Top panel shows the watercolor as it appears today, with a red box highlighting the corner where sampling was performed. The bottom panel is a digital rendering of how the painting most likely appeared just after its completion, taking into account which colorants remain on the artwork, as determined using SERS.

from this catalog are of similar age to those contained in the works of art. Upon analysis, however, it was found that four of the eight W&N watercolor samples (scarlet madder, pink madder, madder lake, rose madder) had very complicated SERS spectra, possibly as a result of contamination of the sample or degradation. As a result of this, only the four watercolor samples, which provided reliable SERS spectra (Indian purple, madder carmine, purple madder, burnt carmine), were used for comparison with the Homer

watercolor sample. SERS spectra (Figs S2–S5) and tabulated values of peak positions (Fig. S6) for these four W&N watercolors can be found in the Supporting Information.

FTIR spectroscopy

A Bruker Tensor 27 FTIR spectrophotometer with a mid-IR global source coupled to a Hyperion 2000 automated FTIR microscope with liquid nitrogen cooled mid-band and broadband mercury cadmium telluride (MCT) detectors (covering the range 7000–600 and 10 000–450 cm^{-1} , respectively) was used. A few remaining burgundy-colored pigment grains from the sky in the painting were analyzed in transmission through the microscope after compression in a diamond anvil cell, at a resolution of 4 cm^{-1} (256 scan acquisition).

Digital reconstruction of painting

To create a digital reconstruction of Homer's original color scheme for his watercolor 'For to Be a Farmer's Boy', spectrophotometric measurements were taken of unfaded watercolor washes from the W&N book containing the pigments identified with SERS. A SpectroEye spectrophotometer (GretagMacbeth, New Windsor, NY, USA) with 45°/0° geometry was used, operating over the range 380–730 nm with 10 nm resolution. CIELAB coordinates were calculated using the CIE 1976 standard 2° observer and illuminant C.^[36] Adobe Photoshop was then used to apply three superimposed layers of semitransparent colors reproducing the L*, a*, b* values calculated from each watercolor wash in the sky of 'For to Be a Farmer's Boy'. The extent of new color application was determined based on stereomicroscopic investigation of the artwork. Although Homer undoubtedly modulated the application of watercolor washes in the sky, no remaining trace evidence illuminating the artist's intention and application technique was found, and hence it was decided to produce the reconstruction with a homogeneous distribution of color.

Results and Discussion

In the present work, SERS was used for the detection of colorants in samples taken from a Homer watercolor entitled 'For to Be a Farmer's Boy', shown in the upper panel of Fig. 1. In this artwork, the sky appears to be colorless, noticeably void of brilliant colors that Homer typically employed for his evocative depictions of skies and seas. Only under magnification were some microscopic particles of pigments visible, trapped in the paper fibers (Fig. 2(a,b)). Precise

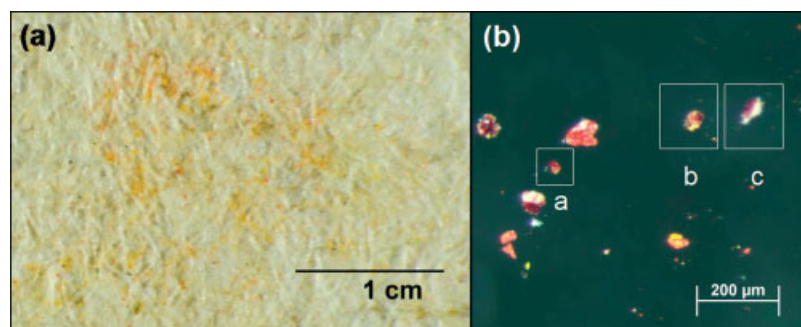


Figure 2. Photomicrograph of (a) area at upper left corner of watercolor highlighted in the red box shown in Fig. 1, where pigment grains illustrated in (b) were sampled from. SERS spectra are presented for each labeled grain in Figs 3–6.

identification of such pigments was seen as key to 'recognizing the implicit emotional, narrative, and symbolic content' of the artist's work.^[32]

The challenge for any spectroscopic method used to study artwork is to work with the minute amount of sample that can be taken from a precious artwork such as this. Figure 2(b) shows a photomicrograph of pigment grains taken from the painting shown in Fig. 1 (top panel). A few pigment grains typically constitute the amount of sample that is available from a work of art on paper, if sampling is permitted at all. The inherent sensitivity of SERS makes it a likely candidate for analyzing such small samples, and recent work in this laboratory on pastel samples indicated that even in the presence of a complex matrix, such as binders and fillers, the dyestuff components can still be detected and identified.^[30]

Figures 3–5 show the SERS spectra collected for the grains labeled in the photomicrograph in Fig. 2. Three distinctly colored red/purple grain types were observed. Grain 'a' is an example of pigment grains which had a uniform reddish purple color. The SERS spectrum of this and similarly colored lake pigment grains shows bands that share common spectral features with those of a variety of lake pigments whose main chromophore is carminic acid. In Fig. 3, representative spectra of 19th century watercolor reference washes of cochineal, burnt carmine, and Indian purple (a pigment prepared by W&N by precipitating cochineal with copper sulfate) are illustrated alongside the unknown Homer pigment. Variability in the spectra is due to the sensitivity of the SERS spectrum of carminic acid to changes in chemical environment, as has been demonstrated at different sample pH values,^[37] and is expected in the presence of different complexing metal ions. In particular, while the band at 1426 cm^{-1} is characteristic for cochineal and is observed in all the spectra of the different lake pigments in Fig. 3, the most intense band in the spectrum, which is found at 1297 cm^{-1} for cochineal, is shifted to 1302 cm^{-1} for Indian purple and the unknown pigment grain. Broadening and shifting to higher wavenumbers of the 1297 cm^{-1} band has been correlated to incremental deprotonation of the hydroxyl groups of the carminic acid moiety, causing further electronic delocalization.^[37] An ionized carminic acid moiety is undoubtedly the species engaged in complexation with the CuSO_4 of Indian purple or other substrates, such as alumina or calcium carbonate, that are materials commonly used to prepare lake pigments. The Indian purple SERS spectrum also contains bands at ~ 1218 , ~ 806 , and 460 cm^{-1} , which are also present in the spectrum of grain 'a'. On the other hand, the sharp band at 1497 cm^{-1} has also been observed by Whitney *et al.* in other samples of carminic acid and cochineal carmine lake manufactured by Weber, and so it should not be considered specific to Indian purple.^[38] Thus, on the basis of the spectral evidence discussed above, it is concluded that grain 'a' is most likely composed of Indian purple. Other grains contained in the sample were observed to have a mixture of yellow, reddish purple, and bright red coloring (exemplified by grain 'b'); SERS spectra recorded for these grains (Fig. 4) identified the pigment as Indian purple mixed with vermilion (HgS), evidenced by strong bands at 340 and 251 cm^{-1} in Fig. 4)^[19] In addition, along with Indian purple and vermilion, chrome yellow (PbCrO_4) was observed at a different site on grain 'b' as shown in Fig. 5, evidenced by the very sharp bands at 842 and 356 cm^{-1} . Finally, some grains had a deep burgundy color, an example of which is identified as grain 'c'.

Figure 6 shows the SERS spectra obtained for pigment grain 'c', with the major bands labeled. Comparison with recorded W&N

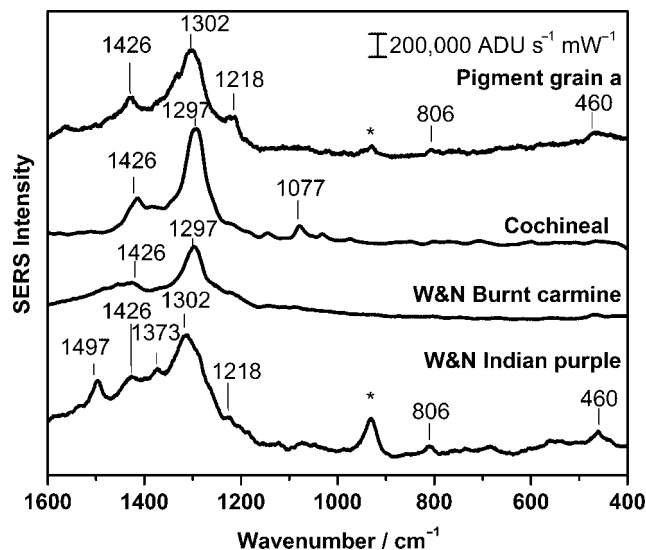


Figure 3. SERS spectra recorded for pigment grain 'a', as identified in Fig. 2. Reference SERS spectra recorded for Winsor and Newton Indian purple, cochineal, and burnt carmine are shown as comparison (Laser $\lambda_{\text{ex}} = 632.8\text{ nm}$, Power = $5\ \mu\text{W}$, Acquisition time = 1 s). Asterisk indicates band due to citrate.

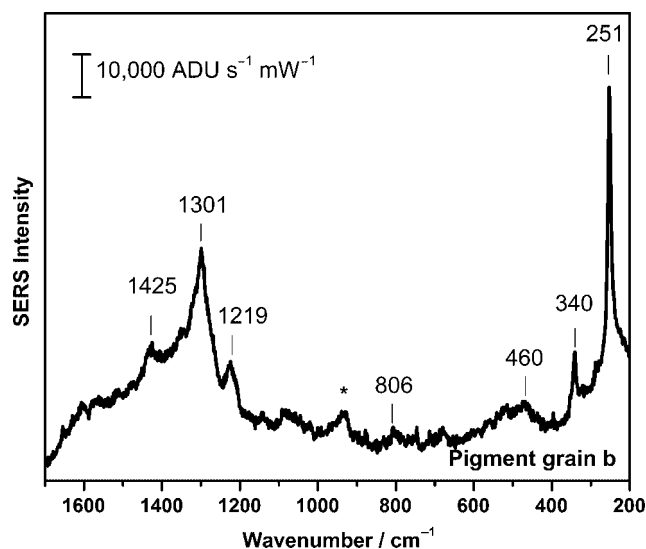


Figure 4. SERS spectrum recorded on an area of pigment grain 'b', as identified in Fig. 2 (Laser $\lambda_{\text{ex}} = 632.8\text{ nm}$, Power = $5\ \mu\text{W}$, Acquisition time = 1 s) showing co-presence of Indian purple and vermilion. Asterisk indicates band due to citrate.

watercolor reference spectra did not produce a conclusive match, thus illustrating the need for extensive databases of SERS spectra for historical artist pigments. Some bands in the SERS spectra in Fig. 6 are indicative of the presence of Indian purple (bands at 1428 , 1302 , 1222 , and 806 cm^{-1}). Additional bands in this spectrum suggest the presence of a second component, possibly a madder-based pigment. Complementary FTIR measurements performed on a few additional grains of remaining pigments after compression in a diamond anvil cell produced spectra that matched very well with those of various shades of reference madder samples from the W&N watercolor book (Figs 7 and S8 (Supporting Information)) as well as published data.^[39] It is to be noted that FTIR has very low sensitivity to the analysis of lake

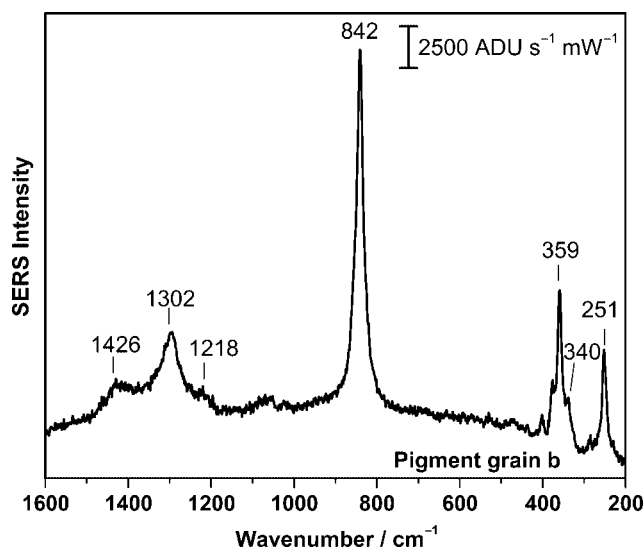


Figure 5. SERS spectrum recorded for another site on pigment grain 'b', as identified in Fig. 2 (Laser $\lambda_{\text{ex}} = 632.8$ nm, Power = $5 \mu\text{W}$, Acquisition time = 1 s) showing co-presence of Indian purple with chrome yellow and vermillion.

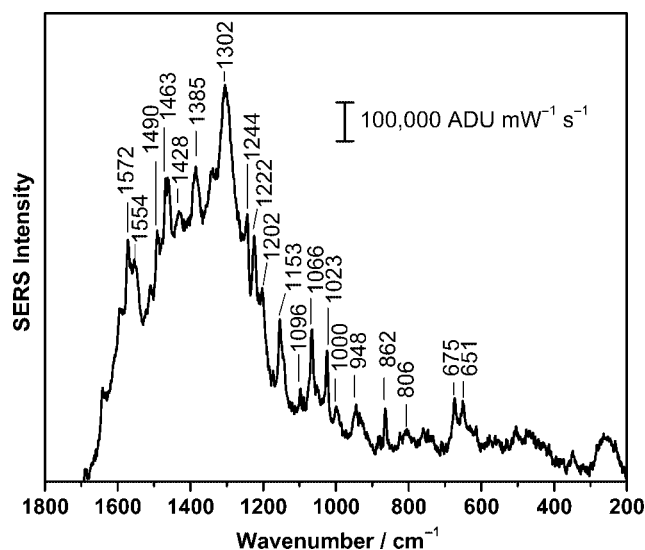


Figure 6. SERS spectra recorded for pigment grain 'c', as identified in Fig. 2 (Laser $\lambda_{\text{ex}} = 632.8$ nm, Power = $5 \mu\text{W}$, Acquisition time = 1 s).

pigments, especially when present in complex matrices,^[40] so only the major components are detected in the most favorable cases (i.e. when binding media and extender interferences are low, as is the case for watercolors), as opposed to SERS, where any dye molecule in close proximity of a 'hot spot' will be detected, resulting in an ensemble-average signal that can carry various spectral contributions. Although the FTIR spectrum of madder lake shows few bands due to the dye chromophore, which on the other hand, is the enhanced component in the SERS, its broad spectral features offer valuable information on the technique of manufacture of the specific lake pigment. The spectrum is in fact a combination of bands characteristic of the chromophores of madder (with key band assignments, characteristic of anthraquinones including $3401 \text{ cm}^{-1} = \nu(\text{O-H})$, $2919 \text{ cm}^{-1} = \nu(\text{C-H})_{\text{ring}}$, $1620 \text{ cm}^{-1} = \nu(\text{C=C})_{\text{ring}}$, $\nu(\text{C=O})$, $1423 \text{ cm}^{-1} = \nu(\text{OH})$, $\nu(\text{CH})_{\text{ring}}$, $1075 \text{ cm}^{-1} = \nu(\text{C-OH})$)^[41] as well as broad features related to the use of amorphous hydrated alumina as lake substrate. In fact, as discussed in the literature, broad peaks in the O-H stretching region (3400 cm^{-1}) and deformation (centered at 1650 cm^{-1}) can be related to the presence of an amorphous aluminum hydroxide substrate.^[42] Al-O vibrations below 900 cm^{-1} , approximately centered at 600 cm^{-1} , are also present in the spectra and are related to crystal lattice vibrations.^[43] Interested readers can find SERS spectra recorded for additional pigment grains in Fig. S7 (Supporting Information), as well as a comparative FTIR spectrum for Indian purple lake in Fig. S9 (Supporting Information). The latter is clearly distinguishable from the FTIR spectrum of madder lake and, in comparison, has a larger proportion of spectral features from the chromophore carminic acid still visible in the spectrum due to the different substrate used (CuSO_4) for preparation of the lake pigment.

These results indicate that in Homer's painting 'For to Be a Farmer's Boy' the 'colorless' sky once depicted a vibrant autumn sunset, with organic madder and cochineal-based purples and reds, in addition to inorganic vermillion and chrome yellow. Molecular identification of the specific colorants present in the lake pigment particles allowed researchers to select two swatches

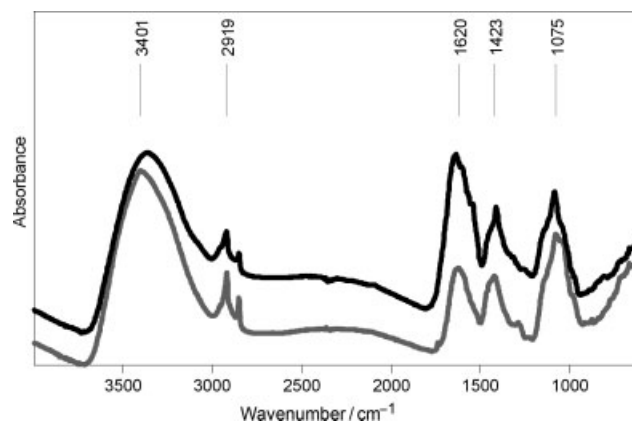


Figure 7. FTIR spectra recorded on a pigment grain of similar deep burgundy color to pigment grain 'c' (gray curve). A reference for purple madder is also reported for comparison (black curve).

of color from the W&N watercolor book, which then formed the basis of digital reconstruction. This information is relevant because correlating the microscopic color of a few remaining pigment particles with the macroscopic hues of watercolor swatches is not straightforward and could lead to arbitrary results for the digital recolorization. Figure 1 shows a comparison of how the Homer watercolor appears now (upper panel) and a digital rendering of what it may have looked like when it was first completed (lower panel). The digital rendering is a result of combining the newfound information highlighted in this article, along with art historical and conservation knowledge of how the sky should have looked, based on observation of skies in unfaded watercolors by the same artist.

Conclusions

This paper reports the ultrasensitive SERS identification of colorants in the watercolors of Winslow Homer, providing important clues to resolve the enigma of the colorless sky in the artist's 'For to Be a Farmer's Boy'. Thus, this study presents the first ever direct SERS spectra taken on 19th century

watercolor pigment grains obtained from an actual artwork, further expanding the areas of application for SERS in cultural heritage research. Additionally, important 19th century watercolor red lake pigment references have also been characterized, demonstrating differences in the SERS spectrum of the same chromophore (namely carminic acid) when prepared as a lake pigment with different procedures and materials (i.e. co-precipitated with different metal salts or as a free acid). Although it can be considered a relatively novel technique in the cultural heritage scientist's toolbox, SERS is quickly becoming an established method for the minimally invasive analysis of artworks of great cultural value. Information gained from such studies will provide answers to important questions postulated by those in charge of the interpretation and preservation of such items. As further studies continue to be conducted on this application of SERS, it is hoped that eventually this tool can be used to noninvasively examine artworks. It is anticipated that colorant identification based on this approach will become nearly universal, advancing our knowledge of their photochemical and thermal degradation mechanisms and leading to a new level of understanding of the materials used in art without the need to remove large samples from such precious items.

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Supporting information

Supporting information may be found in the online version of this article.

References

- [1] P. Stiles, J. A. Dieringer, N. C. Shah, R. P. Van Duyne, *Ann. Rev. Anal. Chem.* **2008**, *1*, 601.
- [2] A. D. McFarland, M. A. Young, J. A. Dieringer, R. P. Van Duyne, *J. Phys. Chem. B* **2005**, *109*, 11279.
- [3] D. A. Stuart, C. R. Yonzon, X. Zhang, O. Lyandres, N. C. Shah, M. R. Glucksberg, J. T. Walsh, R. P. Van Duyne, *Anal. Chem.* **2005**, *77*, 4013.
- [4] D. A. Stuart, J. M. Yuen, N. Shah, O. Lyandres, C. R. Yonzon, M. R. Glucksberg, J. T. Walsh, R. P. Van Duyne, *Anal. Chem.* **2006**, *78*, 7211.
- [5] X. Zhang, J. Zhao, A. Whitney, J. Elam, R. P. Van Duyne, *J. Am. Chem. Soc.* **2006**, *128*, 10304.
- [6] C. L. Brosseau, A. Gambardella, F. Casadio, C. M. Grzywacz, J. Wouters, R. P. Van Duyne, *Anal. Chem.* **2009**, *81*(8), 3056.
- [7] M. Leona, J. Stenger, E. Ferloni, *J. Raman Spectrosc.* **2006**, *37*(10), 981.
- [8] K. L. Wustholz, C. L. Brosseau, F. Casadio, R. P. Van Duyne, *Phys. Chem. Chem. Phys.* **2009**, *11*, 7350.
- [9] Z. Jurasekova, C. Domingo, J. V. Garcia-Ramos, S. Sanchez-Cortes, *J. Raman Spectrosc.* **2008**, *39*, 1309.
- [10] C. Corredor, T. Teslova, M. V. Cañamares, Z. Chen, J. Zhang, J. Lombardi, M. Leona, *Vib. Spectrosc.* **2009**, *49*, 190.
- [11] M. Leona, J. R. Lombardi, *J. Raman Spectrosc.* **2007**, *38*(7), 853.
- [12] F. Casadio, M. Leona, J. R. Lombardi, R. P. Van Duyne, *Acc. Chem. Res.* **2010**, DOI:10.1021/ar10019q.
- [13] M. Leona, *Proc. Natl. Acad. Sci.* **2009**, *106*(35), 14757.
- [14] S. A. Centeno, J. Shamir, *J. Mol. Struct.* **2008**, *873*, 149.
- [15] G. Smith, R. J. H. Clark, *Rev. Conserv.* **2001**, *2*, 92.
- [16] J. Wouters, *Stud. Cons.* **1985**, *30*(3), 119.
- [17] I. Karapanagiotis, L. Valianou, S. Daniilia, Y. Chryssoulakis, *J. Cult. Herit.* **2007**, *8*, 294.
- [18] M. Montazer, M. Parvinezadeh, *J. Appl. Polym. Sci.* **2004**, *93*, 2704.
- [19] I. M. Bell, R. J. H. Clark, P. J. Gibbs, *Spectrochim. Acta, Part A* **1997**, *53*, 2159.
- [20] F. Schulte, K.-W. Brzezinka, K. Lutzenberger, H. Stege, U. Panne, *J. Raman Spectrosc.* **2008**, *39*, 1455.
- [21] P. Vandenaabeele, L. Moens, H. G. M. Edwards, R. Dams, *J. Raman Spectrosc.* **2000**, *31*, 509.
- [22] S. P. Best, R. J. H. Clark, R. Withnall, *Endeavour* **1992**, *16*, 66.
- [23] N. C. Scherrer, S. Zumbuehl, F. Delavy, A. Fritsch, R. Kuehnen, *Spectrochim. Acta A: Mol. Biomol. Spectrosc.* **2009**, *73*(3), 505.
- [24] P. Ropret, S. A. Centeno, P. Bukovec, *Spectrochim. Acta Part A* **2008**, *69*, 486.
- [25] K. Chen, M. Leona, T. Vo-Dinh, *Sens. Rev.* **2007**, *27*, 109.
- [26] X. Zhang, R. A. Laursen, *Anal. Chem.* **2005**, *77*, 2022.
- [27] M. Leona, J. Stenger, E. Ferloni, *J. Raman Spectrosc.* **2006**, *37*, 981.
- [28] K. Chen, K.-C. Vo-Dinh, F. Yan, M. B. Wabuyele, T. Vo-Dinh, *Anal. Chim. Acta* **2006**, *569*, 234.
- [29] E. V. Van Elslande, S. Lecomte, A.-S. Le Hô, *J. Raman Spectrosc.* **2008**, *39*, 1001.
- [30] C. L. Brosseau, K. S. Rayner, F. Casadio, C. M. Grzywacz, R. P. Van Duyne, *Anal. Chem.* **2009**, *81*(17), 7443.
- [31] W. H. Downes, *The Life and Works of Winslow Homer*, Lenox Hill Pub. & Dist. Co.: New York, **1974**.
- [32] M. Tedeschi, K. Dahm, J. Walsh, K. Huang, *Watercolors by Winslow Homer: The Color of Light*, The Art Institute of Chicago: Italy, **2008**.
- [33] F. Casadio, K. Dahm, in *Conservation Science*, (Eds: J. H. Townsend, L. Toniolo, F. Cappitelli), Archetype Publications: London, **2007**, p 197.
- [34] P. C. Lee, D. Meisel, *J. Phys. Chem.* **1982**, *86*, 3391.
- [35] J. S. Taylor, *A Descriptive Handbook of Modern Water-Colour Pigments*, Winsor and Newton: London, **1887**.
- [36] G. Wyszecki and W. S. Stiles, *Color Science: Concepts and Methods, Quantitative Data and Formulae*, (2nd Ed.) Wiley and Sons: New York, **1982**.
- [37] M. V. Cañamares, J. V. Garcia-Ramos, C. Domingo, S. Sanchez-Cortes, *Vib. Spectrosc.* **2006**, *40*(2), 161.
- [38] A. V. Whitney, F. Casadio, R. P. Van Duyne, *Appl. Spectrosc.* **2007**, *61*(9), 994.
- [39] F. Fliedner, *A Descriptive Handbook of Modern Water-Colour Pigments*, Winsor and Newton: London, **1887**.
- [40] W. G. T. Roelofs, P. B. Hallebeek, J. H. Hofenk de Graaf, R. F. S. Karreman, The analysis of natural dyestuffs and organic pigments: a comparative study into the possibilities and limits of various methods; Preprints of the ICOM Committee for Conservation, 8th Triennial Meeting, Sydney, Australia, 6–11 September, **1987**, 709.
- [41] G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, John Wiley & Sons, Ltd.: Chichester, **2001**.
- [42] J. Kirby, M. Spring, C. Higgitt, *Nat. Gall. Tech. Bull.* **2005**, *26*, 71.
- [43] V. C. Farmer, *The Infrared Spectra of Minerals*, (4th edn) (Ed.: C. Farmer) Mineralogical Society Monograph: London, **1974**.