

# Microanalysis of organic pigments and glazes in polychrome works of art by surface-enhanced resonance Raman scattering

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Communicated by Roald Hoffmann, Cornell University, Ithaca, NY, June 25, 2009 (received for review May 21, 2009)

Scientific studies of works of art are usually limited by severe sampling restrictions. The identification of organic colorants, a class of compounds relevant for attribution and provenance studies, is further complicated by the low concentrations at which these compounds are used and by the interference of the protein-, gum-, or oil-binding media present in pigment and glaze samples. Surface-enhanced resonance Raman scattering (SERRS) was successfully used to identify natural organic colorants in archaeological objects, polychrome sculptures, and paintings from samples smaller than 25  $\mu\text{m}$  in diameter. The key factors in achieving the necessary sensitivity were a highly active stabilized silver colloid, obtained by the reproducible microwave-supported reduction of silver sulfate with glucose and sodium citrate, and a non-extractive hydrolysis sample treatment procedure that maximizes dye adsorption on the colloid. Among the examples presented are the earliest so far found occurrence of madder lake (in a 4,000 years old Egyptian object dating to the Middle Kingdom period), and the earliest known occurrence in Europe of the South Asian dyestuff lac (in the Morgan Madonna, a 12<sup>th</sup> century polychrome sculpture from Auvergne, France).

archaeology | dyes

The discovery and exploitation of organic colorants as textile dyes and lake pigments is a distinguishing accomplishment of ancient civilizations. Tracing the use of organic colorants offers a way to follow trade routes, identify relations among archaeological objects, detect forgeries, and attribute works of art. The concentrations of organic colorants in artistic and archaeological objects are however very low, and sampling, when allowed, is limited to fragments a few hundred micrometers in diameter. The lack of analytical techniques of adequate sensitivity has thus significantly hindered ancient dye technology studies.

Historically, anthraquinone compounds from plants, such as alizarin and purpurin (in the Mediterranean basin found in the roots of madder and wild madder, *Rubia tinctorum* L. and *Rubia peregrina* L., respectively), and insects, such as kermesic acid (from kermes, *Kermes vermilio* Planchon), the laccaic acids (or lac dye, from *Kerria lacca* Kerr), and carminic acid (from cochineal, *Dactylopius coccus* Costa) have found wide use as mordant dyes for textiles, as lake pigments for painting in protein, gum or oil media, and as colorants for transparent glazes in oil painting (1–3) (Fig. 1).

While microanalytical methods for inorganic pigments abound, detection of dyes usually requires larger samples to be analyzed by high performance liquid chromatography (HPLC). The use of HPLC is common for archaeological and historical textiles (1), but more limited for paintings or polychrome objects due to the greater difficulty in obtaining a sufficiently large sample. Sampling of paintings or polychrome sculptures, when allowed, is limited to microscopic fragments—200  $\mu\text{m}$  or less—while it is generally possible to obtain a few millimeters of a thread from a textile. Non-invasive methods of analysis are limited to UV-visible absorption or fluorescence spectroscopy,

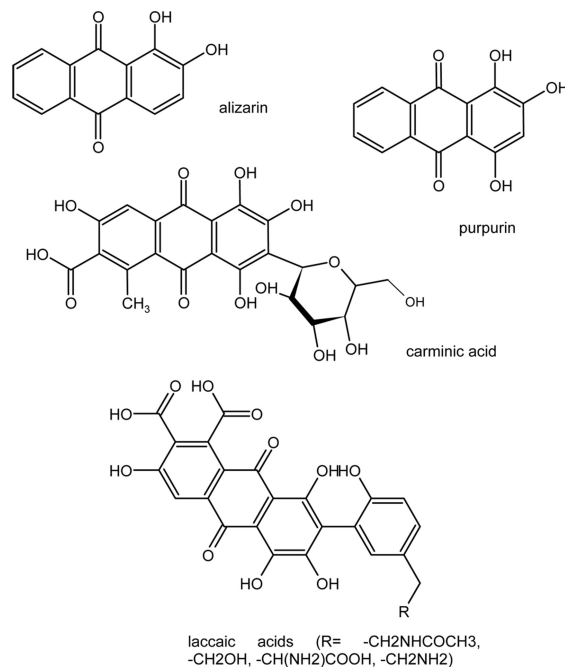


Fig. 1. The main anthraquinone dyes. Substitution of H for the sugar group at position 3 in carminic acid leads to kermesic acid.

carried out by means of fiber optic probes (4), and they are of limited use because of poor specificity.

Conventional Raman spectroscopy, while useful for the non-invasive analysis of inorganic pigments (5), is not suitable for the identification of organic dyes: with the notable exception of indigo, natural dyes are generally fluorescent even at 785 nm excitation, and the resulting background obscures their Raman spectrum. The problem is compounded by the fact that organic colorants have very high tinting power, and they are likely to be found in works of art in extremely low concentrations.

The large enhancement of the amplitude of Raman scattering encountered when organic molecules with delocalized electron systems are adsorbed on metal nanoparticles (6, 7) points to surface enhanced Raman scattering (SERS) as a possible solution to the problem of identifying very low concentrations of organic dyes in microscopic samples.

SERS was first used to this end by Guineau (8) in 1987, when he obtained SERS spectra of alizarin extracted from madder dyed textile samples. The samples' size was not however remarkably smaller than required for HPLC. Recent work has shown

Author contributions: M.L. designed research, performed research, contributed new reagents/analytic tools, analyzed data, and wrote the paper.

The author declares no conflict of interest.

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significant improvements, but most of the applications have been in textile analysis (9–11). The work conducted on historical textiles has demonstrated the possibility of detecting anthraquinone dyes in historical textiles from fragments of a textile fiber measuring a few hundred micrometers in length. Samples of this size are still too large for paintings, prints, and drawings. Further obstacles to the SERS analysis of samples from polychrome objects, drawings and paintings are the additional dilution of the dye in the sample volume due to the presence of a paint binder (a pigment dispersing and film-forming vehicle, such as a drying oil, a polysaccharide gum, or a protein such as collagen or casein) and the possible interference of the binder with the adsorption of the dye on the SERS support (particularly in the case of proteins). To date the SERS identification of dyes in paintings or polychrome objects other than textiles has not been possible. The only exception to the predominance of textile analyses in the published work is the identification of purpurin in a pink powder, thought to be a cosmetic, from the excavation of a first century Roman site in Germany (12); in this case however the colorant was a pure lake, without any binder.

To improve on the analytical performance of SERS in the analysis of microscopic samples with complex matrices we singled out 3 areas of investigation: 1) using excitation matching the plasmon resonance of the silver colloid to the dyes' optical absorption, to obtain surface-enhanced resonance Raman scattering (SERRS); 2) obtaining a reproducible, stable, and highly sensitive SERRS support; and 3) chemically treating the sample before analysis to maximize the dyes' diffusion into the colloid drop and their adsorption onto the SERRS support.

## Results and Discussion

The optical absorption of anthraquinone dyes of artistic interests peaks in the vicinity of 450 nm. This is a convenient range for both Ar<sup>+</sup> laser sources and silver nanoparticle supports. For practical reasons we decided to use 488-nm excitation.

With the exception of earlier work on pure anthraquinones using nanosphere lithography Ag nanoparticles (13), and silver nanoisland films (14, 15), solution reduced Ag colloids [primarily Lee-Meisel (16) citrate reduced colloids] have been the SERS support of choice for analysis of dyes of artistic interest. The chief advantage of nanosphere lithography nanoparticles, the tunability of their plasmon resonance has been offset by a strong carbon background (11). Lee-Meisel colloid is easy to prepare and quite effective for SERS, but its stability and reproducibility is limited. The colloid has a wide particle size range and contains larger particle aggregates: its  $\lambda_{\max}$  is generally around 425 nm and its FWHM is larger than 165 nm. Munro et al. (17) succeeded in preparing an approximately monodisperse Ag colloid ( $\lambda_{\max}$  about 404 nm and FWHM below 60 nm) by refining Lee and Meisel's procedure. The role of various parameters such as silver to citrate molar ratio, reagent mixing rate, and stirring and heating rates have been thoroughly reviewed in the literature (18–20). In the course of this study experiments at 488 nm excitation with a freshly prepared polydisperse Lee-Meisel citrate reduced colloid ( $\lambda_{\max}$  425 nm and FWHM of 165 nm) on reference samples of madder lake showed that Raman resonance leads to a significant increase in sensitivity. The stability of this colloid proved to be an issue, as the results could not be reproduced a few days after the preparation of the colloid. A batch of colloid prepared with careful monitoring of stirring, mixing, and heating parameters, had considerably lower particle size dispersion ( $\lambda_{\max}$  406 nm and FWHM 56 nm), and it performed reproducibly for several months. Subsequent attempts at repeating the synthesis however proved unsuccessful, and this approach was abandoned.

The use of microwave radiation can alleviate heat transfer and reagents mixing problems, as the solution is heated at a fast rate without temperature gradients. Decoupling the reducer/

stabilizer system can also lead to better control of the reaction: the combined use of citrate as a protective agent and formaldehyde as a reducer in the microwave synthesis of Ag colloids starting from silver nitrate has been explored by Yin et al. (21), although the optical properties of the resulting colloids have not been investigated. We obtained excellent results by reducing silver sulfate with glucose in the presence of sodium citrate using a high power microwave digestion system. The resulting colloid was clear amber-yellow, had  $\lambda_{\max}$  401 nm and FWHM of 50 nm.

To reduce the amount of citrate in competition with the analyte for adsorption on the nanoparticles, a small aliquot of the colloid was centrifuged before use, and the supernatant removed and replaced with ultrapure water. The activated colloid was found to react immediately in the presence of an anthraquinone dye, forming aggregates of silver nanoparticles (as observed by optical microscopy) and giving excellent SERRS spectra. The colloid produced by microwave-supported reduction gave excellent results with anthraquinone dyes solutions and with test samples of lake pigments and glazes, and it was used for all further analytical work.

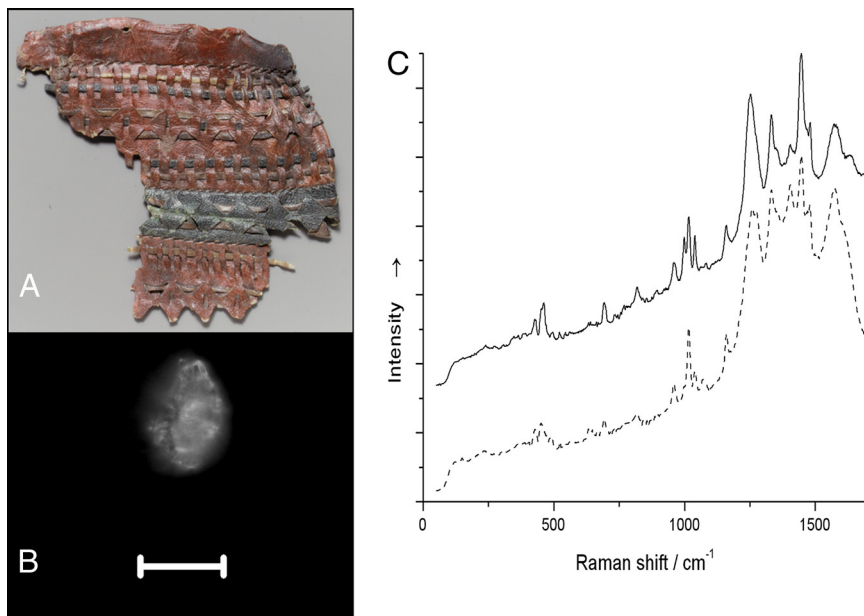
Compared with colloids prepared by conventional heating, the colloid obtained by microwave supported reduction gave superior results with samples more closely approaching the complexity of actual samples from works of art. While the two colloids did not differ radically in their performance with a madder lake sample without any binding medium (with the caveat that the polydisperse Lee-Meisel colloid was tested immediately after synthesis), only the glucose reduced colloid detected carminic acid in samples in which a cochineal lake had been dispersed in protein and in linseed oil.

As the anthraquinone dyes are typically used as complexes of aluminium (22, 23) or other metal salts adsorbed on alumina and/or clays, a mild hydrolysis procedure developed for the analysis of textiles (9) was used for the pigment and glaze samples studied here. Samples obtained from works of art were briefly exposed to HF vapor in a microchamber at room temperature (buffered HF gel—commercially available as a glass etching agent—was used). Silver colloid was added directly to the treated samples and the Raman spectra acquired immediately following the onset of colloid aggregation, using a 20 $\times$  microscope objective. Reference spectra were obtained from lakes and glazes of the anthraquinone dyes prepared in the course of this study using traditional methods, starting from the natural dyestuffs.

The better performance of the colloid described above can be explained by its narrow particle size range and by the absence of the aggregates found in classical Lee Meisel colloids. The monodisperse colloid is predominantly formed of nanoparticles with plasmon resonance in the vicinity of the dyes' optical absorption and of the laser excitation wavelength. In addition, as dye molecules adsorb on the surface of the Ag nanoparticles, interparticle repulsion decreases and aggregates form. This results in a broadening of the colloid plasmon resonance to better match both the anthraquinones' optical absorption range and the excitation laser wavelength.

An additional sensitivity increase may originate from the role played by the dye in the aggregation of the colloid. Because aggregation is driven by the adsorption of dye molecules on the silver nanoparticles surface, it results in more efficient trapping of the dye molecules in SERS hot spots, thus resulting in higher SERS efficiency.

Finally, the HF pretreatment increases the mobility of the dye molecules, by breaking down the lake pigment and by partially attacking the organic binding medium. This maximizes the concentration of the dye in the colloid drop, with an evident analytical advantage. The treatment is a non-extractive gas-solid hydrolysis of the dye-metal complex and of the aluminium hydrate inorganic support of the lake. There are no analyte losses due to dilution or adsorption on the walls of a container: the



**Fig. 2.** Analysis of Egyptian painted leather quiver fragment. (A) Fragment of a quiver; Accession No. 28.3.5; Middle Kingdom, around 2124–1981 BC (H. 11 cm; W. 13 cm). MMA 1911–1912, Tomb MMA830, Thebes, el-Khokha, Upper Egypt; Rogers Fund, 1928. (B) Polarized reflected light photograph of sample removed from red painted area before HF treatment (Scale bar, 20  $\mu\text{m}$ ). (C) SERS spectrum of sample from Middle Kingdom leather quiver. Solid line, spectrum of sample from red painted area; dashed line: spectrum of a second C. BC pink pigment from Corinth, Greece, previously identified by HPLC as a madder lake (mostly purpurin). Spectra were normalized and vertically shifted for ease of comparison, but no smoothing or baseline correction was used.

sample is recovered after treatment as a solid, and it can be treated with the colloid without transfer to a different support.

The spectra obtained from HF treated lakes of anthraquinone dyes are more detailed and more intense than in the absence of the treatment, as evident by comparison of the data presented here with those of earlier studies (12).

Three examples of the application of this procedure to the analysis of works of art are particularly remarkable. The visual examination of a red and green polychrome leather fragment (Fig. 2A), originally part of a quiver, excavated in the Metropolitan Museum campaign of 1911–12 in Egypt (Tomb MMA 830, el-Khokha, Upper Egypt, Thebes) and dated to the Middle Kingdom, around 2124–1981 BC, suggested that the red translucent paint on the leather was probably due to an organic dye. Analysis of a scraping of the red glaze (Fig. 2B), following the protocol outlined above, resulted in the spectrum in Fig. 2C. The correspondence with madder lake is evident [a detailed analysis of the SERS spectrum of alizarin was conducted by Cañamares et al. (24)].

The discovery of madder lake in the 4,000 years old object is so far the earliest evidence in human history for the complex chemical knowledge necessary to extract a colorant from a plant or insect source, and to precipitate it as a solid pigment forming a lake. The object analyzed predates by at least 7 centuries the earliest previous indication for the use of madder in Egypt (25).

While madder was the principal dye plant in the Mediterranean and one of the most important dyestuffs in the whole world, deeper crimson shades can be obtained with insect dyes. Before the availability of the New World dyestuff cochineal, kermes, and other insect dyes were popular in Europe (26), and far more common than madder in the preparation of glazes—translucent red or crimson paints prepared by dispersing lake pigments in oil. An example of the use of organic glazes is given by the painting “St. John the Baptist Bearing Witness,” from the workshop of Francesco Granacci, Florence (ca. 1510). SERS analysis of a 50- $\mu\text{m}$  fragment of the red glaze revealed the presence of kermes, a result consistent with the position of this anthraqui-

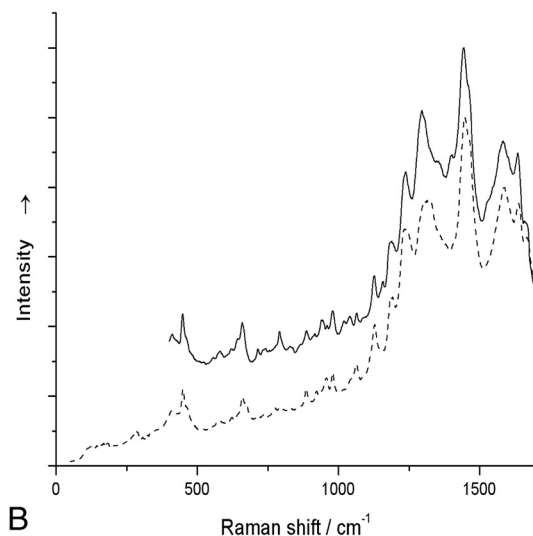
none dye as the main colorant for red glazes in Europe before the introduction of cochineal from the New World (Fig. 3).

An important insect dye from south Asia, lac, appears to have reached Europe by the Middle Ages, according to commercial records dating from 1222 (27, 28). The historical document mentions that lac dye was imported into Southern Europe by Catalan or Provençal traders who procured it in Northern Africa (where presumably Muslim traders received it from India). Until now however, the use of this colorant in European art was not documented before the 15<sup>th</sup> century (26). It is therefore relevant that the SERS method presented here allowed us to examine microscopic samples (about 50  $\mu\text{m}$  in diameter) from an important polychrome wood sculpture in the collection of the Metropolitan Museum of Art, depicting the Virgin and Child in Majesty (the Morgan Madonna, acc. 16.32.194, gift of J. Pierpont Morgan, 1916; Fig. 4).

The sculpture, decorated with red glazes over inorganic red pigment layers to obtain different shades of red, was found to contain lac [a detailed analysis of the SERS spectrum of lac was conducted by Cañamares and Leona (29)]. The date of the work, 1150–1200, predates by a few decades the commercial records, but the connection to Provençal trade is reinforced, as the sculpture was housed in a church in Auvergne, a region bordering Provence.

The importance of materials analysis in establishing relationships between works of art is underscored by the concurrent SERS identification of lac dye in another French Romanesque polychrome sculpture at the Metropolitan Museum of Art. The Cloisters’ Montvianeix Madonna (1967.153), an example of Virgin and Child in Majesty originally made for the Chapel of Saint-Victor in Montvianeix, in the Puy-de-Dôme, has long been thought to be by related stylistically to the Morgan Madonna (30, 31). A recent examination of the Montvianeix Madonna (32) highlighted technical similarities between the two sculptures and suggested that samples be taken for dye analysis from areas that appeared to have the same purple glazing as found in the Morgan Madonna. The identification of lac dye, a colorant that would





**Fig. 3.** Analysis of a painting by the workshop of Francesco Granacci. (A) St. John the Baptist Bearing Witness (detail). St. John the Baptist Bearing Witness. Accession no. 1970.134.2; workshop of Francesco Granacci, Florence (ca. 1510). 75.6 × 209.6 cm. Purchase, Gwynne Andrews, Harris Brisbane Dick, Dodge, Fletcher, and Rogers Funds, funds from various donors, Ella Morris de Peyster Gift, Mrs. Donald Oenslager Gift, and Gifts in memory of Robert Lehman, 1970. (B) SERRS spectrum of red glaze sample from St. John the Baptist Bearing Witness. Solid line, spectrum of sample from red glaze; dashed line: spectrum of a reference sample of kermesic acid. Spectra were normalized and vertically shifted for ease of comparison, but no smoothing or baseline correction was used.

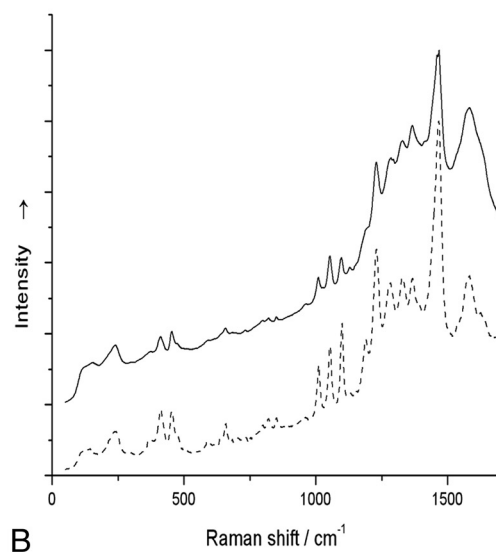
have been extremely rare in Europe in the 12<sup>th</sup> Century in two stylistically related sculptures from the same region is a very strong hint for their origin in the same workshop.

The result of the SERRS analysis of the 2 polychrome sculptures makes the Morgan Madonna and the Montvianeix Madonna the earliest examples to date of European works of art employing a South Asian dyestuff, underscoring the global trade

connections in the period between the Crusades and the Spanish *reconquista*.

### Conclusions

Surface-enhanced resonance Raman scattering can be routinely applied to the identification of organic colorants in works of art from samples as small as 25 μm. Lake pigments embedded in



**Fig. 4.** Analysis of the Morgan Madonna. (A) The Morgan Madonna. Virgin and Child in Majesty; Accession No. 16.32.194; 1150–1200 CE; (H. 79.5 cm; W. 31.7 cm; D. 29.2 cm). Auvergne, France; Gift of J. Pierpont Morgan, 1916. (B) SERRS spectrum of sample from the Morgan Madonna. Solid line, spectrum of sample from red glaze; dashed line: spectrum of a reference sample of lac dye glaze in hide glue. Spectra were normalized and vertically shifted for ease of comparison, but no smoothing or baseline correction was used.

paint medium and colorants dispersed in oil glazes were easily identified thanks to the improvement in sensitivity obtained with a microwave reduced monodisperse silver colloid and a non-extractive hydrolysis sample pretreatment procedure.

The fact that results of remarkable archaeological and historical significance were obtained in a rapid and unobtrusive way and after a brief and by no means exhaustive survey of a single (albeit large) collection is a clear demonstration of the potential of the technique. The few examples reported here are likely to be joined by several others as this technique is applied to a larger number of objects, and the dates of first occurrence here noted for madder and lac will probably be superseded by earlier dates.

## Materials and Methods

**Silver Colloid Synthesis and Characterization (Conventional Heating).** One hundred milliliters of a  $10^{-3}$  M silver nitrate (Aldrich) solution were brought to a boil under agitation in a 250-mL conical flask wrapped in aluminium foil. Two milliliters of a 1% w solution of sodium citrate (Aldrich), also at boiling, were added to the silver nitrate solution at once. The solution was kept simmering under agitation and in reflux (using a Pyrex funnel as a simple condenser) for approximately 1 h. Heating was then discontinued but the solution was left on the hotplate under agitation until it slowly cooled to room temperature ( $\approx 45$  min).

**Silver Colloid Synthesis and Characterization (Microwave Heating).** One hundred milligrams silver nitrate (Aldrich) were dissolved in 5 mL cold ultrapure water and 10%  $\text{H}_2\text{SO}_4$  was added dropwise to precipitate silver sulfate. The precipitate was washed twice with ultrapure water, and then dissolved in 580 mL ultrapure water to give a  $0.5 \times 10^{-3}$  M solution. Twenty-five milliliters of the silver sulfate solution were added to a pressure resistant Teflon microwave vessel (CEM Ultimate Digestion Vessel UDV 10, CEM Corporation), together with 2 mL of a 1% w solution of glucose (Sigma) and 1 mL of a 1% w solution of sodium citrate (Aldrich). The resulting solution was shaken vigorously for a few seconds to mix the reagents, and heated to 120 °C for a total of 60 s (a 30-s isotherm followed by two 15-s isotherms, with 1-min intervals between isotherms to sample the colloid and perform UV-Vis measurements), using a CEM MDS-2100 microwave digestion system with temperature and pressure monitoring. The stock colloid was kept refrigerated and in the dark. To prepare the colloid for use, 1 mL was centrifuged for 5 min at  $16,060 \times g$  RCF (relative centrifugal force) with a Fisher Scientific Accuspin 400 centrifuge. Nine hundred fifty microliters of the supernatant were removed and replaced with 18 M $\Omega$  ultrapure water (Millipore Simplicity 185 water Purification system).

**Sampling and Sample Treatment.** Samples of approximately 25–50  $\mu\text{m}$  in diameter were obtained from the works of art using a tungsten needle and

placed in a sample holder obtained from the lid of a BEEM Embedding Capsule (Size 3). The sample holder was placed inside a micro chamber fashioned out of a BEEM Embedding Capsule (Size 00) held horizontally on a glass microscope slide. A hole pierced in the capsule lid allowed for a small HF leak ensuring vapor flow over the sample holder. HF saturation of the micro chamber was obtained by placing a small amount of glass etching gel (Velvet Etching Gel, Seppic/McKay Frosting Products) or a 10- $\mu\text{L}$  drop of HF (Fisher Scientific hydrofluoric acid solution, trace metal grade, A513–500) in the pyramidal bottom of the capsule before sample introduction. After 5–10 min at room temperature, the sample holder was removed and left to air out for 5–10 min. Finally, a 1- $\mu\text{L}$  drop of activated colloid was added directly to the sample in the holder.

**Raman Microscopy.** SERS spectra were obtained directly from the colloid drop covering the sample using a Bruker Senterra Raman microscope with 488 nm excitation, a 1,200 lp/mm holographic grating, a CCD detector, and power at the sample of 0.25 mW. A 20 $\times$  long working distance Olympus objective was used.

**Reference Materials.** Reference lakes and glazes of the anthraquinone dyes were prepared using traditional methods starting from the natural dyestuffs. Madder lake was prepared by Elena Phipps (Department of Textile Conservation, The Metropolitan Museum of Art) using the following recipe. Ten grams of ground madder root was soaked overnight in 200 mL distilled water; the solution was then heated for 30 min and filtered. A sodium carbonate solution (10 g in 200 mL distilled water) was then added to the madder root extract, and an alum solution (20 g aluminium potassium sulfate in 200 mL distilled water) was slowly added. After resting overnight, the precipitate was filtered, washed, and dried. As an additional reference for madder, a sample of a second century BC pink pigment from the excavation of the South Stoa at Corinth, kindly provided by Michele Marincola at the Conservation Center of New York University, found by HPLC to contain mostly purpurin, was also used. Kermesic acid was extracted from the insect by treating with 5 mL of ethanol the crushed body of 1 insect. The orange ethanol extract was evaporated, redissolved in water, and used to collect reference SERS spectra of kermes. Finally, a lac dye glaze was prepared by mixing a lac dye solution with hide glue in the presence of a small amount of calcium carbonate until a deep red translucent gel was obtained.

**ACKNOWLEDGMENTS.** I thank Elena Phipps (Metropolitan Museum of Art) for bringing the fragment of a quiver to my attention, Lucretia Kargere (Metropolitan Museum of Art—The Cloisters) for suggesting the analysis of the Morgan Madonna, and John Olmsted and John Lombardi for critical reading of the manuscript. This work was supported by the National Science Foundation, the Camille and Henry Dreyfus Foundation, the David H. Koch Foundation, and the Andrew W. Mellon Foundation.

- Hofenk de Graaff JH (2004) in *The Colourful Past* (Abegg-Stiftung, Riggsberg, and Archetype, London).
- Schwepe H, Winter J (1997) in *Artists' Pigments: A Handbook of Their History and Characteristics*, ed West Fitzhugh E (National Gallery of Art, Washington DC), Vol 3, pp 109–142.
- Schwepe H, Roosen-Runge H (1986) in *Artists' Pigments: A Handbook of Their History and Characteristics*, ed Feller RL (National Gallery of Art, Washington DC), Vol 1, pp 255–283.
- Leona M, Winter J (2001) Fiber optics reflectance spectroscopy: A unique tool for the investigation of Japanese paintings. *Stud Conserv* 46:153–162.
- Smith G, Clark RJH (2001) Raman microscopy in art history and conservation science. *Rev Conserv* 2:96–106.
- Jeanmaire DL, Van Duyne RP (1977) Surface Raman spectroelectrochemistry: Part I. Heterocyclic, aromatic, and aliphatic amines adsorbed on the anodized silver electrode. *J Electroanal Chem* 84:1–20.
- Fleischmann M, Hendra PJ, McQuillan AJ (1974) Raman spectra of pyridine adsorbed at a silver electrode. *Chem Phys Lett* 26:163–166.
- Guineau B, Guichard V (1987) Identification of natural organic colorants by resonance Raman microspectroscopy and by surface-enhanced Raman effect (SERS) (Identification des colorants organiques naturels par microspectrométrie Raman de résonance et par effet Raman exalte de surface (SERS)) in *ICOM Committee for Conservation: 8th Triennial Meeting, Sydney, Australia, 6-11 September, 1987. Preprints. Volume 2* (The Getty Conservation Institute, Marina del Rey), pp 659–666.
- Leona M, Stenger J, Ferloni E (2006) Application of surface-enhanced Raman scattering techniques to the ultra-sensitive analysis of natural dyes in works of art. *J Raman Spectrosc* 37:981–992.
- Leona M, Lombardi JR (2007) Identification of berberine in archaeological textiles by surface enhanced Raman spectroscopy. *J Raman Spectrosc* 3 8:853–858.
- Brosseau CL, Gambardella A, Casadio F, Grzywacz CM, Wouters J, Van Duyne RP (2009) Ad-hoc surface-enhanced Raman spectroscopy methodologies for the detection of artist dyestuffs: Thin layer chromatography-surface enhanced Raman spectroscopy and in situ on the fiber analysis. *Anal Chem* 81:3056–3062.
- Van Elslande E, Lecomte S, Le Hô A (2008) Micro-Raman spectroscopy (MRS) and surface-enhanced Raman scattering (SERS) on organic colorants in archaeological pigments. *J Raman Spectrosc* 39:1001–1006.
- Whitney AV, Casadio F, Van Duyne RP (2007) Identification and characterization of artists' red dyes and their mixtures by surface-enhanced Raman spectroscopy. *Appl Spectrosc* 61:994–1000.
- Whitney AV, Van Duyne RP, Casadio F (2005) in *Proceedings of SPIE, Vol. 5993 Advanced Environmental, Chemical, and Biological Sensing Technologies III*, eds Vo-Dinh T, Lieberman RA, Gauglitz G (SPIE, Bellingham), pp 117–126.
- Leona M (2005) in *Proceedings of SPIE, Vol. 5993 Advanced Environmental, Chemical, and Biological Sensing Technologies III*, eds Vo-Dinh T, Lieberman RA, Gauglitz G (SPIE, Bellingham), pp 127–134.
- Lee PC, Meisel D (1982) Adsorption and surface-enhanced Raman of dyes on silver and gold sols. *J Phys Chem* 86:3391–3395.
- Munro CH, Smith WE, Garner M, Clarkson J, White PC (1995) Characterization of the surface of a citrate-reduced colloid optimized for use as a substrate for surface-enhanced resonance Raman scattering. *Langmuir* 11:3712–3720.
- Henglein A, Giersig M (1999) Formation of colloidal silver nanoparticles: Capping action of citrate. *J Phys Chem B* 103:9533–9539.
- Pillai ZS, Kamat PV (2004) What factors control the size and shape of silver nanoparticles in the citrate ion reduction methods? *J Phys Chem B* 108:945–951.
- Dement'eva OV, Mal'kovskii AV, Filippenko MA, Rudoy VM (2008) Comparative study of the properties of silver hydrosols prepared by "citrate" and "citrate-sulfate" procedures. *Colloid J* 70:561–573.
- Hengbo Y, Yamamoto T, Wada Y, Yanagida S (2004) Large-scale and size-controlled synthesis of silver nanoparticles under microwave irradiation. *Mat Chem Phys* 83:66–70.

22. Wunderlich CH, Bergerhoff G (1994) Structure and color of alizarin and purpurin lakes (Konstitution und farbe von alizarin- und purpurin-farblacken). *Chem. Ber* 127:1185–1190.
23. Soubayrol P, Dana G, Man PP (1996) Aluminium-27 solid-state NMR study of aluminium coordination complexes of alizarin. *Mag Reson Chem* 34:638–645.
24. Cañamares MV, Garcia-Ramos JV, Domingo C, Sanchez-Cortes S (2004) Surface-enhanced Raman scattering study of the adsorption of the anthraquinone pigment alizarin on Ag nanoparticles. *J Raman Spectrosc* 37:921–927.
25. Chenciner R (2003) in *Madder Red: A History of Luxury and Trade* (Routledge Curzon, London), p 23.
26. Kirby J, White R (1996) The identification of red lake pigment dyestuffs and a discussion of their use. *National Gallery Technical Bulletin* 17:56–80.
27. Eastaugh N, Walsh V, Chaplin T, Siddall R (2004) in *The Pigment Compendium: A Dictionary of Historical Pigments* (Elsevier Butterworth-Heinemann, Oxford and Burlington), p 214.
28. Depping GB (1830) in *A History of the Commerce between the Levant and Europe from the Crusades to the Founding of the American Colonies, Volume 1 (Histoire du Commerce entre le Levant et l'Europe depuis les Croisades jusqu'à la Fondation des Colonies d'Amérique. Tome 1)* (Treuttel et Wurtz, Paris. Reprinted by Elibron), p 144.
29. Cañamares MV, Leona M (2007) Surface-enhanced Raman scattering study of the red dye laccaic acid. *J Raman Spectrosc* 38:1259–1266.
30. Forsyth IH (1972) in *The Throne of Wisdom, Wood Sculpture of the Madonna in Romanesque France* (Princeton Univ Press, Princeton).
31. Little C (1987) Romanesque sculptures in North American collections. *Gesta* 81–82:153–155.
32. Kargère L (2002) in *The Montvianeix Madonna: Materials and Techniques in Twelfth Century Auvergne. 13th Triennial Meeting, Rio de Janeiro Preprints, ICOM-CC Conference* (James and James, London), p 507–512.