DOI: 10.1002/anie.200905131

Historic Materials

The Nature of the Extraordinary Finish of Stradivari's Instruments**

Jean-Philippe Echard,* Loïc Bertrand,* Alex von Bohlen, Anne-Solenn Le Hô, Céline Paris, Ludovic Bellot-Gurlet, Balthazar Soulier, Agnès Lattuati-Derieux, Sylvie Thao, Laurianne Robinet, Bertrand Lavédrine, and Stéphane Vaiedelich

Antonio Stradivari is probably the most renowned musical instrument maker. He is known for the violins that he made in Cremona from around 1665 to his death in 1737. His work is considered to be the apogee of the Cremonese violin-making tradition, which began with Andrea Amati in the mid-16th century. In particular, the exceptional finish of his instruments has fascinated musicians, violin makers, historians, and chemists since the beginning of the 19th century. Many contradictory hypotheses have been raised about Stradivari's finishing technique,[1–8] but the evidence obtained has not yet allowed a clear understanding of his process.

We previously described the difficulties in studying samples from Stradivari's instruments, which led to only a very limited number of investigations.[9] Important work carried out over the past decades on individual instruments led to the identification of the elemental composition of the materials in the coatings,[5,10,11,12] which were sometimes correlated to inorganic compounds,[13,14] or to the description of the layer structure of the varnish.[13] In particular, two studies of Cremonese instruments indicated the presence of a layer that may contain pozzolona.[13,14] However, the organic component remains uncharacterized. This component could typically be derived from animal parts (such as albumin, casein, and collagen derivatives from cartilage, bones, and skin, i.e., animal glue, propolis) or plants (oils rich in unsaturated fatty acids, i.e., siccative oils, polysaccharidic, and terpenic exudates—gums and resins, respectively, or fossil amber).[6–8] An in-depth understanding has been hampered by the lack of a comprehensive microscale analysis method on a group of instruments rather than on individual ones. In an earlier work, we identified fatty acids from aged siccative oils and diterpenoid biomarkers of *Pinaceae* sp. resins on three Stradivari instruments. On a late Stradivari violin, we found vermilion (mercury sulfide) embedded in a medium composed of a siccative oil and larch (*Larix decidua* Mill.) resin.[15–17] However, these results gave only a partial understanding of the materials and techniques used by Stradivari to varnish his instruments. In particular, they provide no information on the stratigraphy of the varnish. We concluded that, because of the complex and heterogeneous nature of the materials, such individual analyses would not be fully representative of the instrument maker's working techniques, and could lead to uncertain conclusions because of possible restoration or later additions.[17]

We have determined the composition of the materials and stratigraphy of varnish samples from five instruments made by Antonio Stradivari. The samples came from four violins: a "Long Pattern" model, possibly from 1692; the "Davidoff", dated 1708; the "Provigny", dated 1716; the "Sarasate", dated 1724, which stands apart from the others in style,[18] and the head of a viola d'amore, dated around 1720. These instruments are undisputed representative examples of Stradivari's work.[18,19] The head of the viola d'amore can be considered as having one of the best-preserved of Stradivari's varnishes. The instruments have been in the collections of the Musée de la musique for at least a century. During this time, they were well documented and have been played and handled much less than musicians' instruments.

To overcome the difficulties associated with the investigation of the microscale chemical composition of varnishes, we used complementary spectroscopic techniques to determine the chemical composition of each of the varnish

---

[*] J.-P. Echard, B. Soulier, S. Vaiedelich
Laboratoire de recherche et de restauration
Musée de la musique, Cité de la musique
221 avenue Jean Jaurès 75019 Paris (France)
Fax: (+33) 1-44-84-46-41
E-mail: jpechard@cite-musique.fr
Homepage: http://www.citedelamusique.fr/lab
Dr. L. Bertrand, Dr. L. Robinet
IPANEMA, Synchrotron SOLEIL
BP 48 Saint-Aubin, 91192 Gif-sur-Yvette cedex (France)
E-mail: loic.bertrand@synchrotron-soleil.fr
Homepage: http://www.synchrotron-soleil.fr/ipanema
Dr. A. von Bohlen
Institute for Analytical Sciences (ISAS), Dortmund (Germany)
J.-P. Echard, Dr. A. Lattuati-Derieux, S. Thao, Prof. B. Lavédrine
Centre de Recherche sur la Conservation des Collections
MNHN-CNRS-MCC, Paris (France)
Dr. A.-S. Le Hô
Laboratoire du Centre de Recherche et
de Restauration des Musées de France
(LC2RMF) UMR171, CNRS and MCC, Paris (France)
Dr. C. Paris, Dr. L. Bellot-Gurlet
Laboratoire de Dynamique, Interactions et Réactivité (LADIR)
UMR 7075, CNRS and Univ. P. et M. Curie Paris 6, Thiais (France)
B. Soulier
Staatliche Akademie der Bildenden Künste
Institut für Technologie der Malerei, Stuttgart (Germany)

[**] We thank Dr. P. Dumas and Dr. C. Sandt (SMIS, SOLEIL synchrotron), D. Jaillard, (CCME Univ. Paris-Sud), Dr. M.-A. Languille (IPANEMA, SOLEIL), and Dr. E. van Elslande (C2RMF). We acknowledge the essential collaboration of T. Maniguet, curator (Musée de la musique), for authorizing the sampling of the musical instruments. Dr. B. H. Berrie, Dr. M. Spring, Prof. P. Laszlo, and Prof. T. Blundell carefully reread the manuscript. Part of this work was supported by the European Commission FP6 IA-SFS transnational programme.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200905131.

layers.[9,20] Samples that contained both wood and varnish were taken from carefully chosen areas. Cross sections were prepared using a protocol optimized to allow the preservation of the spatial arrangement of the wood and the varnish layers. When possible, each cross section was examined using the same combination of analytical techniques. A thorough observation was performed by using optical microscopy. The chemical composition of each varnish layer was spatially resolved using synchrotron radiation micro-FTIR spectroscopy (SR–FTIR) and micro-Raman confocal spectroscopy (MRS). Field-emission cathode scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM–EDX) was used to obtain elemental information, in particular to characterize the inorganic fraction in the varnish layers. In complement to the above-mentioned methods that are non-destructive to the sample, the specific molecular composition of each layer was determined using pyrolysis gas chromatography/mass spectrometry (PyGC–MS).

Optical microscopy studies show that the varnish stratigraphy can be described as a two-layer system: The lower layer partially fills the upper wood cells and the upper lies above the wood (Figure 1).

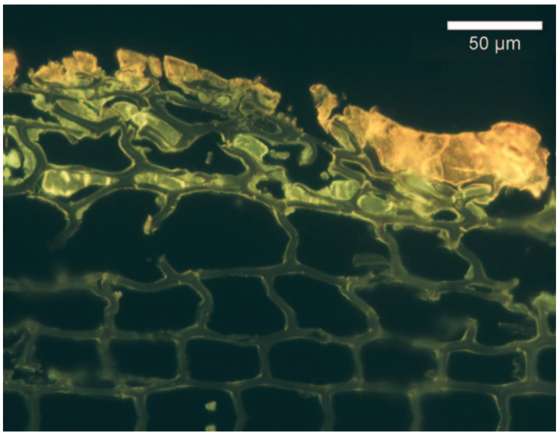

Figure 1. Cross-sectional view of Stradivari's "Provigny" varnish under 450–490 nm illumination. From below: wood cells, lower layer (slightly colored material impregnating wood cells), upper layer (tinted).

The material that partially fills the upper wood cells barely rises above the wood surface. This material penetrates to an approximate depth ranging between 10 and 30 µm into the spruce soundboards ("Davidoff" and "Provigny" samples, Figure 1) and between 30 and 100 µm into maple (viola d'amore and "Long Pattern"), depending on the orientation of the medullar rays in the wood. This layer appears to be homogeneous under an optical microscope, and has an intense whitish fluorescence under UV light. No inorganic compounds were detected from SEM-EDX analyses, thus indicating the organic nature of the layer. Infrared absorption bands associated with the O–H, C–H, and C=O stretches dominate the FTIR spectra (Figure 2). The shoulder around 2958 cm^{-1} is characteristic of the CH_3 asymmetric stretch of long aliphatic chains. The rather broad ν(C=O) band is centered between 1725 and 1715 cm^{-1}. These features can be interpreted as those of a partially oxidized and hydrolyzed drying oil.[21] The absence of amide I and amide II bands, around 1650 cm^{-1} and 1550 cm^{-1} respectively, rules out protein materials such as egg, casein, or animal glue as significant components of this layer. Similarly, neither the band around 1040 cm^{-1} (ν(C–O–C)) nor a sharp doublet at 1470/1460 cm^{-1} (CH_2/CH_3 bending modes), which are characteristic of gums and waxes, respectively, were observed.

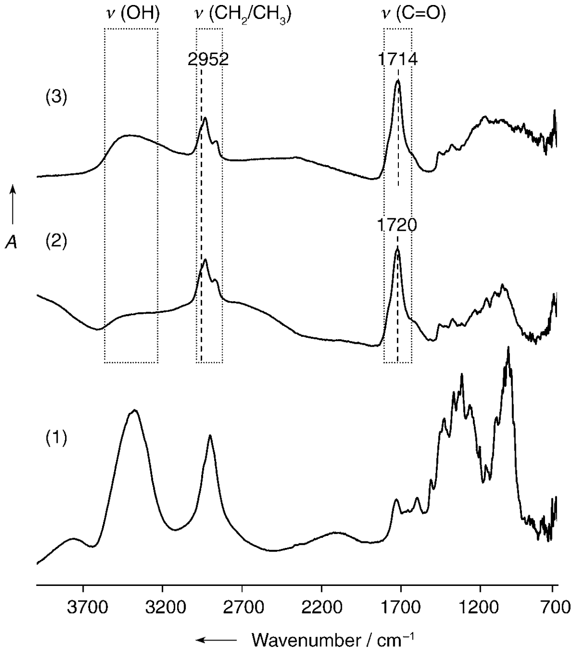

Figure 2. Typical microfocused SR–FTIR spectra obtained on point analyses of the "Provigny" varnish stratigraphy. 1) Wood, 2) lower layer, 3) upper layer. Note the $\nu_{as}(CH_3)$ shoulder around 2952 cm^{-1}.

The upper coating layer is 10 to 30 µm thick on all the instruments. This layer appears homogeneous under an optical microscope and fluoresces yellow under UV light. In samples from four instruments, red particles were observed. The upper varnish of the "Provigny" violin contains translucent red particles, the diameter of which ranges between 1 and 10 µm, and their MRS spectra are typical of anthraquinone dyes.[22] The closest match within our set of reference spectra is carminic acid, which suggests the use of a cochineal insect dyestuff (Figure 3 a).[23] SEM-EDX spectra show that these grains are aluminum- and oxygen-rich, which indicates a red lake pigment on an alumina substrate.[24] At the time, this lake was synthesized by precipitating carminic acid with the hydrated alumina that results from the in situ reaction between an alkali and alum, which, according to Kirby et al, was usually the potash alum $AlK(SO_4)_2\cdot 12\,H_2O$.[24] The upper layer of the "Davidoff" and the viola d'amore exhibits more opaque red pigments, in addition to the previously mentioned red lake pigments. The diameter of the opaque particles ranges between 1 and 5 µm and SEM-EDX showed that they are iron- and oxygen-rich. The particles were identified as iron oxides (hematite Fe_2O_3, magnetite Fe_3O_4) by MRS

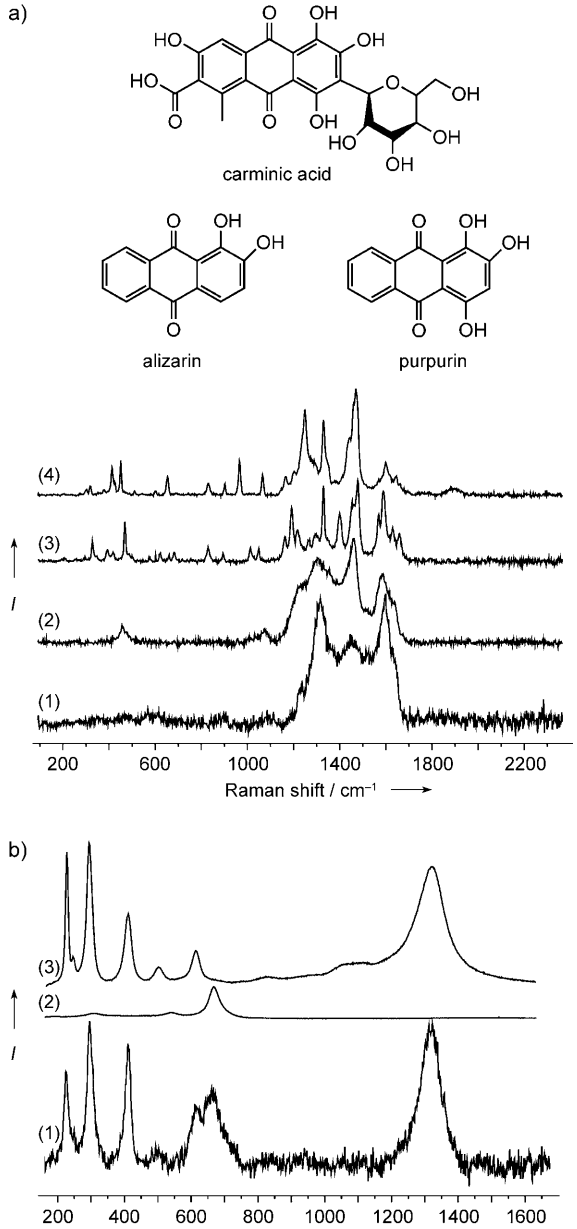

Figure 3. a) MRS spectra (excitation 458 nm, baseline-subtracted) from 1) a "Provigny" red particle (acquisition time 5×60 s), and reference compounds: 2) carminic acid (2×120 s), 3) alizarin (2×150 s), 4) purpurin (2×150 s). Differences in the relative band intensities between (1) and (2) could be due to the dye interaction with aluminum or the surrounding medium. b) Comparison of MRS spectra from 1) a "Davidoff" red particle (excitation 514 nm, acquisition time 300 s, baseline-subtracted) with reference spectra for 2) magnetite and 3) hematite underlines the presence of iron oxides.

(Figure 3b).[25] Clay minerals and quartz were not detected, thus suggesting the use of quite pure or refined ochre rather than a native earth pigment.[26]

It was possible to examine the upper layer of the "Provigny" and the viola d'amore by using SR–FTIR. The FTIR signature of this layer is very similar for both instruments and shows little difference from those of the lower layer (Figure 2). The main distinction observed was a greater variability in the position of the ν(C=O) band, with maxima that range between 1730 and 1695 cm^{-1}. Bands in the range 1730–1710 cm^{-1} were ascribed to degradation products of the original triglycerides, and bands below 1710 cm^{-1} suggest the presence of resinous acids in the upper layer.[27] As for the lower layer, the absence of the characteristic bands excludes the presence of protein compounds, gums, or waxes as main constituents of this layer.

Typical fatty acid PyGC–MS profiles for aged drying oils in the lower layer confirm its oily nature (Figure 4). In particular, azelaic and suberic acids are markers of aged siccative oils, as they are the final products of the autoxidation of long-chain unsaturated fatty acids.[21] In the upper layer, diterpenoids that result from the oxidation of abietane- and pimarane-type molecules are observed in addition to the fatty acids. These diterpenoids are biomarkers for oxidized *Pinaceae* sp. resins.[28]

It is striking that the five instruments showed such similar layer structures and binding media composition, despite the fact that the date of their manufacture is spread over three decades. A siccative oil was first applied to the wood for probable use as a sealant, with no fillers or pigments. This result contrasts with previous studies where a mineral-rich layer was reported.[13,14] A single slightly tinted oil-resin layer was then applied to the instruments. Although it has been hypothesized that protein materials, gums, or fossil amber were used in the finishing process, neither of these were found on any of the examined instruments.

The second essential result from this investigation concerns the coloring agents incorporated into the coating. No pigment was detected in the "Long Pattern" violin. On a later instrument, the "Sarasate", we previously identified a red pigment, vermilion.[15] We have now identified two additional types of red pigments in Stradivari's varnishes: an anthraquinone lake with an alumina substrate (probably cochineal lake) and iron oxides (see the Supporting Information). Red iron oxides and vermilion were artists' pigments that were widely used at the time Stradivari produced his instruments.[26,29] All three instrument varnishes from Stradivari's "Golden Period" (ca. 1700–1720) are colored with red lake pigments. Central American cochineal (*Dactylopius coccus* L. Costa) is the most likely source of the red dye: it was readily available at the turn of the 18th century, when it had almost totally replaced the other insect sources of red dyestuffs such as kermes (*Kermes vermilio* Planch.), Polish (*Porphyrophora polinica* L.) and Armenian (*P. hamelii* Brandt) cochineals.[30] Furthermore, Central American cochineal lake pigments have been found in many 16th to 18th century European paintings.[23]

Analyses were performed on instruments that had completely different histories before entering the collections of the Musée de la musique. Nonetheless, the results obtained from all the studied instruments provide a consistent picture of how the instruments were coated. It is highly unlikely that old "touching up" on all the instruments would have been so similar. This hypothesis therefore supports our conclusion that these findings represent Stradivari's own varnishing materials and methods.

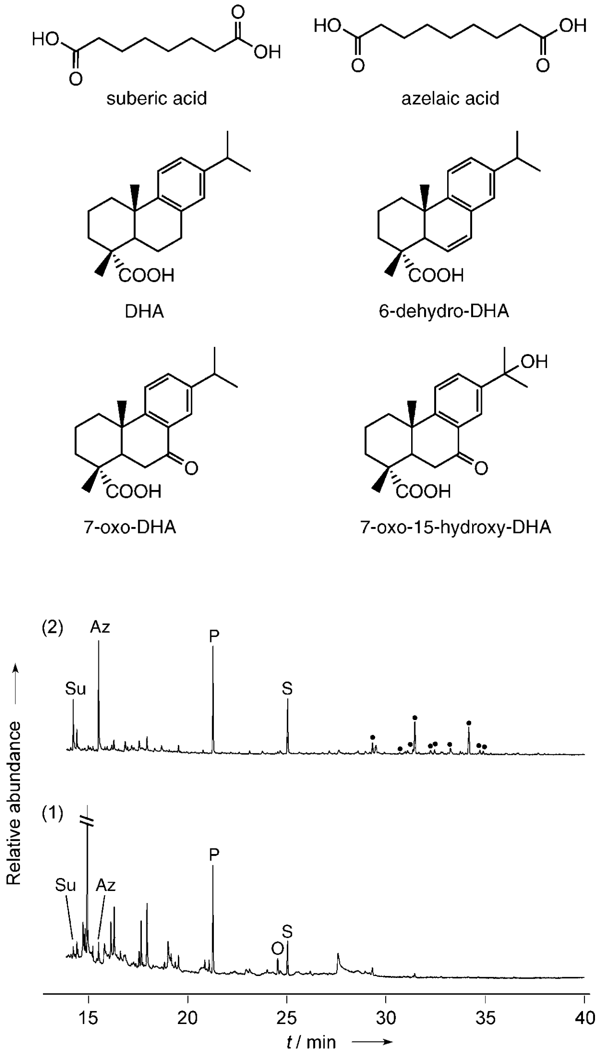

Figure 4. PyGC–MS total ion current chromatograms of the 1) lower and 2) upper layers of the "Long Pattern" varnish. Su (dimethyl suberate), Az (dimethyl azelate), P (methyl palmitate), O (methyl oleate), S (methyl stearate), ● diterpenoids (primarily methylated products of dehydroabietic acid (DHA), 6-dehydro-DHA, 7-oxo-DHA, 7-oxo-15-hydroxy-DHA). The peaks that are not marked have been identified as by-products of the methylation reagent and wood pyrolysis products.

Our results shed new light on the techniques Antonio Stradivari utilized to finish his violins. We have found that Stradivari employed common and easily available components that were commonly used among craftsmen and artists in the 18th century. Through the use of several red pigments, he sought a variety of tints for his instruments, which are still the most highly praised for their beautiful appearance. These conclusions are fundamental in re-establishing the historical status of Antonio Stradivari: he might not have possessed an unusual or "secret" ingredient, but he was an outstandingly skilled craftsman who had mastered the art of violin making, and in particular wood finishing.

Experimental Section

In situ visible and UV optical microscopy was performed using a Zeiss microscope (Axio Scope.A1, epifluorescence filter Fs05, 395–440 nm excitation). When necessary, the surface of the varnish was gently cleaned from fats and dust before sampling. Samples were sectioned to a thickness of 2 μm by ultramicrotomy (Leica EM UC6, Diatome Histo diamond knife) after wetting with water or isopropyl alcohol, and deposited on silver-coated low-emissivity microscope slides (MirrIR, Kevley Technologies).

FTIR spectromicroscopy of cross sections was performed using the two spectrometers (Nicolet Continuum and NicPlan, MCT-A detectors) at the SMIS beamline of the SOLEIL synchrotron. Data were collected in transflection mode (spectral range 4000–650 cm^{-1}, aperture 10×10 or 6×6 μm^2, 64 to 128 scans, spectral resolution 4 to 8 cm^{-1}).

Confocal Raman analyses were performed on a Horiba Jobin–Yvon HR800 dispersive spectrometer equipped with Edge filters (air-cooled Ar$^+$ laser, 458 and 514 nm excitation wavelengths, power: 30 μW at the sample with a spatial resolution close to 2 μm and a spectral resolution of ca. 3 cm^{-1} at 1000 cm^{-1}). The presented spectra are baseline-corrected to remove the intense fluorescence contribution exhibited by the samples.

Electron microscopy was carried out at a field-emission cathode SEM (FEI QUANTA 200F) with EDX detection (SDD, spectral resolution 123 eV at Mn$_{K\alpha}$) operated in low-vacuum mode. Elements with atomic number $Z \geq 4$ could be detected simultaneously.

Pyrolysis gas chromatography/mass spectrometry was performed with a Shimadzu GCMS-QP2010Plus/Frontier Lab PY-2020iD system using thermally assisted hydrolysis and TMAH methylation (25 wt% in methanol, Acros Organics) according to adapted protocol.[16,17]

Received: September 13, 2009

Keywords: diterpenoids · dyes/pigments · fatty acids · historic materials · natural products

[1] S.-A. Sibire, *La chélonomie ou le parfait luthier*, Minkoff, Geneva, **1984**, reprint of the **1823** edition.

[2] E. Mailand, *Découverte des anciens vernis italiens employés pour les instruments à cordes et à archets*, Lahure, Paris, **1859**.

[3] C. Reade, *Cremona fiddles from the "Pall Mall Gazette"*, Kellow, Bridgewater, **1981**, reprint of the **1872** edition..

[4] G. Fry, *Italian violin varnish*, Virtuoso, Cape Coral, **1981** reprint of the **1904** ed..

[5] J. Michelman, *J. Franklin Inst.* **1949**, *247*, 569.

[6] G. Baese, *J. Violin Soc. Am.* **1986**, *8*, 49.

[7] W. M. Fulton, *Turpentine violin varnish*, **1988**.

[8] S. F. Sacconi, *I Segreti di Stradivari*, Libreria del convegno, Cremona, **1972**.

[9] J.-P. Echard, B. Lavédrine, *J. Cult. Heritage* **2008**, *9*, 420.

[10] B. H. Tai, *J. Violin Soc. Am.: VSA papers* **2007**, *21*, 119.

[11] P. A. Tove, D. Sigurd, S. Petersson, *Nucl. Instrum. Methods* **1980**, *168*, 441.

[12] A. von Bohlen, *J. Trace Microprobe Tech.* **1999**, *17*, 177.

[13] C. Y. Barlow, P. P. Edwards, G. R. Millward, R. A. Raphael, D. J. Rubio, *Nature* **1988**, *332*, 313.

[14] J. Nagyvary, J. M. Ehrman, *Naturwissenschaften* **1988**, *75*, 513.

[15] J.-P. Echard, *Spectrochim. Acta Part B* **2004**, *59*, 1663.

[16] J.-P. Echard, C. Benoit, J. Peris-Vicente, V. Malecki, J. V. Gimeno-Adelantado, S. Vaiedelich, *Anal. Chim. Acta* **2007**, *584*, 172.

[17] J.-P. Echard, S. Vaiedelich in *De la peinture de chevalet à l'instrument de musique: vernis, liants et couleurs*, Cité de La musique, Paris, **2008**, pp. 104–113.

[18] W. H. Hill, A. F. Hill, A. E. Hill, *Antonio Stradivari, his life and work (1644–1737)*, W. E. Hill & Sons, London, **1902**.

[19] C. Beare, B. Carlson, *Antonio Stradivari: The Cremona exhibition of 1987*, Beare, London, **1993**.

[20] J.-P. Echard, M. Cotte, E. Dooryhee, L. Bertrand, *Appl. Phys. A* **2008**, *92*, 77.

[21] R. J. Meilunas, J. G. Bentsen, A. Steinberg, *Stud. Conserv.* **1990**, *35*, 33.

[22] E. van Elslande, S. Le Comte, A.-S. Le Hô, *J. Raman Spectrosc.* **2008**, *39*, 1001.

[23] J. Kirby, R. White, *Natl. Gall. Tech. Bull.* **1996**, *17*, 56.

[24] J. Kirby, M. Spring, C. Higgitt, *Natl. Gall. Tech. Bull.* **2005**, *26*, 71.

[25] D. Neff, S. Reguer, L. Bellot-Gurlet, P. Dillmann, R. Bertholon, *J. Raman Spectrosc.* **2004**, *35*, 739.

[26] K. Helwig in *Artists' Pigments*, *Vol. 4* (Ed.: B. H. Berrie), National Gallery of Art, Washington, Archetype, **2007**, pp. 39–109.

[27] D. Scalarone, M. Lazzari, O. Chiantore, *J. Anal. Appl. Pyrolysis* **2002**, *64*, 345.

[28] K. J. van den Berg, J. J. Boon, I. Pastorova, L. F. M. Spetter, *J. Mass Spectrom.* **2000**, *35*, 512.

[29] R. J. Gettens, R. L. Feller, W. T. Chase in *Artists' Pigments*, *Vol. 2* (Ed.: A. Roy), National Gallery of Art, Oxford University Press, Washington, **1993**, pp. 159–182.

[30] R. L. Lee, *J. Mod. Hist.* **1951**, 23, 205.