

Leonardo under cover

Applying Raman spectroscopy for pigment identification in art

Jakob Thyr^[a], Lars Helldahl^[b], and Tomas Edvinsson^{*[a]}

[a] Dr, J Thyr, Professor, T, Edvinsson
Department of materials science and engineering
Uppsala University
Box 35, 75103 Uppsala, Sweden
E-mail: tomas.edvinsson@angstrom.uu.se

[b] Dr, L, Helldahl
Canus AB
Vasavägen 12, 582 20 Linköping, Sweden

Supporting information for this article can be found in the same archive as this posting

Abstract: The study of artwork is an interesting field that has undergone a major turn the last decades as new scientific analysis methods have been introduced and is becoming a significant part of the investigations. In this study we have employed Raman spectroscopy to analyse the pigments in an old painting of the Roman Emperor Domitian. The painting is of special interest since its creation is historically attributed to Tiziano Vecellio, more known as Titian, but it has recently been found to contain a signature that reads L daVinci. We here perform a rigorous pigment analysis of the painting and signature area to identify and classify the pigments by usage and the potential time of deployment. Microscopic cut outs from selected areas of the painting were analysed in a Raman microscope where 14 different pigments were identified. Out of these, 12 pigments were contemporary with Titian (1488/90-1567) and Leonardo da Vinci (1452-1519), one pigment, titanium white, was present during the Middle Ages but came into common use at a later time and one pigment, Prussian blue, is of newer origin. Complimentary X-ray imaging shows that at least one of the areas where Prussian blue was found has likely been altered at a later stage, providing an explanation for the presence of a modern pigment in an old painting. Special emphasis was also applied to resonant and non-resonant Raman response of Prussian green and blue, expressing different ratios of Fe^{2+} and Fe^{3+} states, valuable for identification and discrimination of the compounds in pigment identification and in the more recent field of battery research.

Introduction

Humans have always been fascinated by art. From the cave paintings of the upper Palaeolithic era^[1,2] up to the modern day's art galleries and digital art. It has been argued that the expression through art is inherent to humans as a species^[3]. Animals do not generally produce art. Exceptions exist, mostly involving domestic or captive animals trained by humans, though there are rare instances of creative behaviour observed in the wild.^[4] The original works of especially skilled or groundbreaking artist are extremely coveted, and many desire to possess such paintings. Due to the limited supply they therefore become very valuable. The sales in the art market reached a staggering 67.8 Billion dollar in 2002^[5]. The authorities in the art field, the art experts, previously had to rely mainly on the tools from the humanities when assessing paintings: Provenance, historical records, aesthetics and their own and other experts experience with similar

paintings. A complimentary scientific tool that has been used for over a century is X-ray imaging^[6]. As the field of science advances and the economic incentives increase more tools have become accessible and methods like X-ray fluorescence^[7], Raman spectroscopy^[8], FTIR spectroscopy^[9], carbon 14 dating^[10], DNA analysis^[11] and even X-ray spectroscopies at synchrotron facilities^[12] are now being employed in the difficult task of assessing art and they all give their contribution to the solutions of the puzzles. In this paper Raman spectroscopy has been used for investigation of an old painting of the Roman emperor Domitian, shown in figure 1.



Figure 1. Photograph of the painting of the Roman emperor Domitian taken by photographer Helena Christerdotter. The size of the painting is 133x102.5 cm

The painting in question was up for sale three times in the renowned Christies auction house in London in the years 1928 and 1929. In the catalogue at Christies it was listed as "Emperor Domitian, by Titian" and it remained unsold.

In 1939 it was again up for sale, now at an auction in Sweden. It was bought and has remained in the purchaser's family ever since. The current owner-generation discovered the presence of an interesting signature "L da Vinci", followed by the word "Pinxt" or "Pinxt" which is Latin for "Painted" a word conventionally found on medieval and Renaissance artwork. The possibility that the painting has been painted by one of the greatest masters of all times makes it very interesting from an art historical point of view. It is known that Titian painted a series of portraits of Roman emperors in the years 1536-1539. This is described in the book "Leonardo's Salvator Mundi and the Collecting of Leonardo in the Stuarts Court"^[13]. The portraits were brought from the palace of Mantua (current Mantova) in Italy to England in 1628 on the ship Margaret and were during the transit damaged by a mercury spill. At this time, it is mentioned that there were twelve portraits of emperors. Eleven of them were painted by Titian and one by another hand and it is specified that this portrait was the one from emperor Domitian. There is no consensus of who the painter of the twelfth portrait is but Anthony van Dyck, Giulio Romano and Bernardino Campi are mentioned as the painter in different sources^[13,14]. In 1651 the portrait series were purchased by the Spanish ambassador, Alonso de Cárdenas on behalf of the Spanish crown^[13]. The series of the twelve emperors was believed to have been destroyed in a fire in the old Alcázar in Madrid in 1734.^[14] Could the painting of Domitian that surfaced at Christies auction house in 1928 be one of the original twelve emperor portraits and is it possible that it was painted by Leonardo da Vinci? This hypothesis is complicated by the fact that da Vinci died 1519, 17-20 years before the supposed time of the completion of the series. On the other hand, it could potentially give an explanation why this portrait was not painted by Titian, where the series instead was completed with the other Emperors to complement an already existing painting portraying Emperor Domitian, historically denoted to be painted "by another hand". Visual inspection of the painting reveals a consistent shadowing where one for example can look at the eye, cheekbone, jaw, and left arm area, in connection with a delicate self-shadowing of the right arm where only the top surface is under illumination together with a fully lit right hand gripping a pole. Hands are among the most difficult objects to paint, especially in perspective, and it is therefore said that ancient paintings sometimes had a higher price if hands were to be drawn. Hands in paintings has also been highlighted, categorized, and investigated for their symbolical role.^[15,16] In the painting of the Roman emperor Domitian, the right hand is shown in perspective out-of-plane and shows a finger lock and strained knuckles in gripping a pole. This together with the delicate shadowing of muscles in the bruised left arm show that the painting has been drawn by a master in painting, with high skills in reproducing light-shadow effects and anatomic details. One can also note that the left hand is gripping a sword's hilt adorned with jewels in the lower right part of the painting, but in stark contrast, this hand is mostly hidden in shadows as if the money run out in the original commission. Apart from the visual appearance, the Domitian painting has been analysed by varying techniques, out of which Raman spectroscopy is one, in an attempt to investigate if this can be an authentic Leonardo da Vinci painting. Raman spectroscopy is here used for analysis and

identification of the colour pigments used in the painting and it is a well-established analysis technique for pigments identification^[7,8,17,18]. Some paint pigments have been used since antiquity, some natural pigments came into use in later years and for some synthetically produced pigments there is even a well-defined timepoint where the pigment was invented or where it first came into use. This timeline of pigments provides valuable information to draw conclusions about the time period in which the painting was produced. The Raman spectroscopy measurements provide information about bonds in molecules and thus detailed *chemical* information, not only which elements are present and is therefore suitable for determining which pigments that are present in the painting. The analysis technique is not suitable for distinguishing between a natural mineral and the corresponding synthetically made pigment of the same compound, unless there are naturally occurring contamination compounds found in a natural pigment. It is quite common that a natural pigment has been superseded by its synthetically made analogue, either because of availability, lower cost or because a higher quality could be achieved. Many of the old pigments are therefore still used today, and detection of naturally occurring contamination compounds and/or carbon dating of century old soot particles are the most available routes to date these pigments. Older paintings on the other hand, could also have gone through restorations or improvements by more or less skilled, later artists which adds further complications when dating art.

Experimental methods

For Raman spectroscopy measurements two Micro-Raman systems were used: One Invia Reflex (Renishaw) with 532 nm (green) excitation wavelength and a 2400 lines/mm grating and one Invia Qontor with 785 nm (near infrared) and 405 nm (violet-blue) excitation wavelengths and combined with a 1200 and 2400 lines/mm gratings respectively. The spectral resolution was 2 cm⁻¹ for 532 nm, 3 cm⁻¹ for 785 nm and 6 cm⁻¹ for the 405 nm wavelength, measured as the FWHM of an atomic emission peak. The objectives used for measurement were Leica N-plan 100x, 50x and 20x and for image capture also a 5x objective. Each measurement session was started by verifying the instrument calibration by ensuring that the main peak of an internal Si sample was at 520.5 cm⁻¹ Raman shift. To have access to several different laser wavelengths is a great advantage when measuring complex samples like pigment and binder mixtures used in paintings. By switching to a different wavelength, it is often possible to avoid sample fluorescence, which is one of the main obstacles to obtain clear and well resolved Raman spectra. For the very first measurements, a macro sampling arm with a low magnification focusing objective was used. This enabled focusing directly on the painting that was placed next to the spectrometer. The macro sampling arm approach, which is further mentioned in the supporting information, was abandoned due to lack of precision when choosing points of analysis, high sample fluorescence and the low signal associated with the low magnification objective. Instead, micro sized cut-outs that could be analysed directly under the Raman microscope were sampled from selected locations from the painting. Working under a microscope enables the use of high magnification objectives, x50 and x100. These have high numerical apertures and are therefore more efficient in collecting the Raman light. These objectives also

allow for much more spatially resolved information making it possible to focus on individual pigment grains, thus avoiding fluorescence from neighbouring grains.



Figure 2. The different sampling locations marked on the painting.

Table 1. Sample location denotation, description, and dominating colour

Sample location	Description	Major colour
A	Dark background	Black
B	Dark leaf of laurel wreath	Green
BA	Light leaf of laurel wreath leaf	Green
C	Ear,	Pink, skin coloured
D	Chin	Pink, skin coloured
E	Hairband	Red
F	Textile cloak	Light brown
G	Arm in shadow	Dark brown
H	Armour	Gray
I	Jewel on sword pommel	Blue
J	L daVinci signature	Black
K	Domitiano letters	Gold/Brown
L	Arm, illuminated	Yellow, skin coloured

The sampling locations were chosen in a way that included many different colours, thus increasing the probability of identifying many pigments. The sample locations and their notations are shown in figure 2 and described in table 1. At each location several samples were taken and thoroughly analysed by multiple spectra from each sample. Before the cut-outs were taken the sampling locations were cleaned to remove layers of soot and fat, which inevitably are deposited on surfaces exposed to indoor atmospheres due to older days candlelight and wood fires used for heating. Paintings are also protected by a layer of varnish. These layers on top of the pigments block the laser light used in Raman to reach the pigments, as well as give fluorescence and Raman signals of their own. Cleaning in these cases was done with a mixture of $\frac{3}{4}$ Gum Turpentine and $\frac{1}{4}$ Ethanol applied with a non-linting cotton swab. This solution has proven to be safe for older paintings, before 17th century. Then there is no risk that the solvent mixture dissolves any old pigments. This can happen with organic pigments synthesised later, during the 17:th and 18:th centuries and therefore it was important to check that the cotton swabs did not become coloured during the cleaning. The spectra obtained from the measurements were compared to and matched against reference spectra originating from measured reference compound, Raman databases, or from literature sources. When comparing with reference spectra one has to be aware that many references do not provide spectral information below 100 cm^{-1} Raman shift. This is highly likely due to a limitation of the instruments used to acquire the spectra. Namely the cut off of the Rayleigh filter. Most commonly the filter cut off is at approximately 100 cm^{-1} from the laser line. Some pigments, especially inorganic pigments with heavy atoms, do have peaks below 100 cm^{-1} Raman shift. Since the instruments used in this study had better Rayleigh filter cut off, 85 cm^{-1} and 45 cm^{-1} for the 532 nm and 785 nm laser wavelengths respectively, it was also possible to detect low shift Raman peaks, which increase the ability to identify pigments with heavy elements as evident from the results presented in this work. To improve readability, a single spectrum selected from the many acquired, one that was clear and representative of the measurement location, is displayed, unless multiple spectra are necessary to illustrate variation. Complimentary UV-VIS-NIR optical characterisation of reference compounds of Prussian blue and Prussian green was done by dissolving a small amount of the pigment in ethanol and measuring the UV-VIS NIR absorption in liquid phase in a 1x1 cm PMMA cuvette using an Ocean optics HR2000+ optical spectrometer coupled with fibre optics to a combined halogen deuterium light source from Mikropack (DH-2000-BAL). Absorbance was measured and pure ethanol was used as blank.

Results and Discussion

The results and conclusions drawn from the measurements are first presented per sampling location after which all results are summarized and discussed.

The dark background - location A

The first location analysed, A, is from the background of the painting. Raman spectra were collected from several points using 532 nm and 785 nm lasers. The 785 nm laser was most suitable and the spectra revealed several distinguishable Raman peaks. The measurements are presented in the figures 3a, and 3b. By

comparing the data with literature reference spectra, several pigments could be identified. This comparison shows that the three first peaks, at ~ 226 , 294 and 410 cm^{-1} correspond to red ochre^[17,19] and the peak at 1008 cm^{-1} is the strongest Raman peak from gypsum^[17,19]. Red ochre is a red pigment very similar to its synthetically made analogue Mars red, they both have chemical formula Fe_2O_3 . The difference is that red ochre also contains clay and silica. These are however weak Raman scattering compounds and may not be detected. A microscope image of a red ochre grain is shown in the supporting information, figure S2. The peak at 1049 cm^{-1} shown in figure 3b can be attributed to lead white, $(\text{PbCO}_3)_2\text{Pb}(\text{OH})_2$, labelled very strong, in Bell, et al^[17]. As mentioned earlier low wavenumber peaks are often not included in the reference spectra and they are therefore difficult to find matches for. Lead white, also named cerussite, is discussed further later in this paper. A wide peak at about 1220 cm^{-1} appears

in the spectrum in Figure 3a, but not in the spectrum in Figure 3b. This peak is likely to originate from an earth pigment and this will be discussed further together with the results from location H. From the above data, one can conclude that in point A in the painting, four different types of spectra were found: One is gypsum, which has historically been used both as a pigment and as a grounding material, the latter use being the most likely here since there is also a dedicated white pigment present. The second type is red ochre and the third is lead white. In most of the spectra acquired in this location Raman peaks from an unspecified earth pigment is found. To this group belongs umbra, sienna and green earth. All are traditional names and with varying composition from place to place. After grounding the canvas with gypsum, the pigments used would give a dull, dark-red hue with addition of white as background to the portrait in the painting.

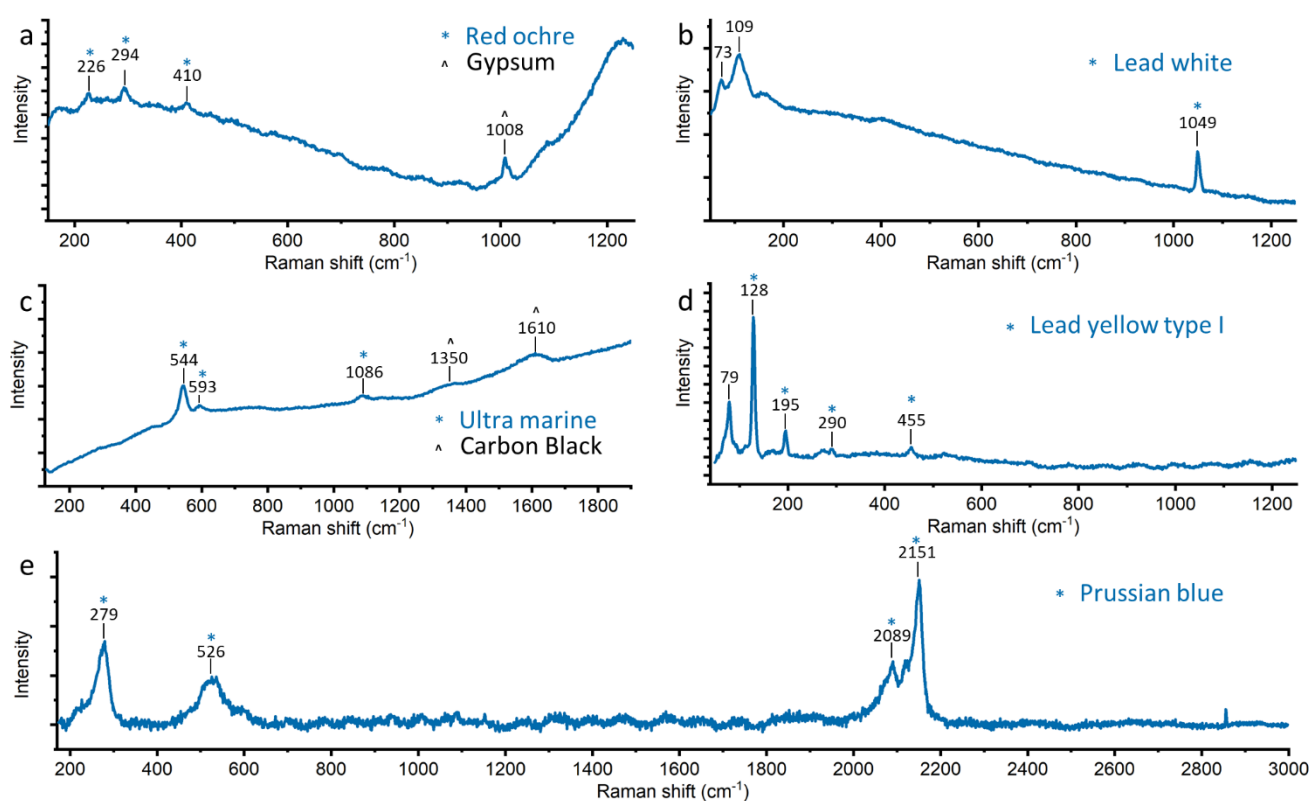


Figure 3. (a) Raman spectrum collected from a sample taken from location A. The three peaks at 226, 294 and 410 cm^{-1} indicate the presence of red ochre, Fe_2O_3 . (b) Spectrum obtained from a white grain in location A. The peak at 1049 cm^{-1} indicate the pigment white lead, $(\text{PbCO}_3)_2\text{Pb}(\text{OH})_2$. (c) Spectrum of ultramarine acquired from location B. The peaks at 1350 cm^{-1} and 1620 cm^{-1} originates from carbon black. (d) Spectrum from lead yellow type 1 acquired from a yellow point in a sample from location B. (e) Spectrum of Prussian blue obtained from a sample from location B. This spectrum laser has been baseline subtracted and cosmic ray peaks have been removed. Spectra 3a, b, d and e were acquired with a 785 nm laser and the spectrum 3c was acquired using a 405 nm laser.

The leaves of the laurel wreath – locations B and BA

The reason for sampling material from two different leaves in the laurel wreath is that they did not look the same. The leaf at location B seemed to be more superficial and had a different hue. The leaf at location BA was slightly lighter in appearance. It was therefore suspected that the BA and B leaves might be different, a suspicion that later was confirmed. It is known that only five green pigments were available in medieval times. Four of these are pigments based on chromium, none of them is found here. The fifth one is terra vert. Spectra acquired from a sample taken from a dark green area of the wreath at location B are a good

match to spectra from the green pigment Terra Vert reported by Bell et al^[17]. However, titanium white, TiO_2 in the anatase polymorph, can display peak positions that closely resemble those of the other pigment. We find it likely that the terra verte sample analyzed by Bell contains a small proportion of anatase, and that the reported spectrum represents a mixture of terra verte and anatase signals. One can also note that reference spectra of terra verte display considerable differences^[17,20]. TiO_2 came into common use as an art pigment in the 19th century but there are some evidence for use also in ancient artwork^[21]. A comparison

with literature is given in table 2, and the spectrum is shown in figure S3 of the Supporting Information.

Table 2. Comparison of peak positions sample vs. reference

Origin	Raman peak positions (intensity)								
Sample	95	142	393	513	639	704		1002	
BB4	(m)	(s)	(m)	(w)	(m)	(ww)		(ww)	
Terra vert ^[17]		145	399	510	635	685	820	1007	1085
		(s)	(ww)	(w)	(m)	(m)	(ww)	(m)	(m)
Titanium white ^[21]		142	395	514	639				
		(vs)	(w)	(w)	(m)				

A sample taken at a larger depth, also in location B, showed a spectrum, shown in figure 3c, which was identified as originating from ultramarine, a pigment that is made from the mineral lapis lazuli and has been used since ancient time. The small peak at 593 cm⁻¹ is relatively strong compared to the main peak, but one reference^[18] mentions that the peak at 593 cm⁻¹ appears more clear when the spectrum is acquired with a shorter wavelength laser, as has been done in the current study. The spectrum in figure 3c also contains the two wide peaks at 1350 cm⁻¹ and 1620 cm⁻¹ which are the signature peaks for amorphous carbon, which is also used as a pigment under the names carbon black, lamp black and ivory black.

The third pigment identified in location B is lead tin yellow type 1 (Pb₂SnO₄), also known as lead stannate.^[17,22] The peak at 79 cm⁻¹ in the lead yellow type 1 spectrum, shown in figure 3d, is not mentioned in any of the cited references. Peaks below 100 cm⁻¹ are in fact often missing in published reference spectra due to the limitation of the edge filter cut-off which was previously explained in the experimental section and for at least one of the references it is evident that the data does not extend down to this peak.

The fourth pigment identified in area B was Prussian blue. This is a blue pigment that was first invented in 1704^[17] and is therefore not contemporary with Titian or da Vinci. Figure 3e shows the spectrum of Prussian blue; the spectral range has here been extended to also include the strong peaks around 2100 cm⁻¹ to enable a clear identification.

In location BA no blue pigment was identified. The compounds identified in this location was lead yellow type 1 and chalk. In summary the laurel wreath in Domitian's hair has green colours that comes from the green pigment Terra vert or by mixing of yellow and blue pigments: lead yellow type 1 and ultramarine or the more recent pigment Prussian blue, which is also present in location B.

Prussian blue and Prussian green

In literature there have also been mentions of the use of Prussian green as pigment for paintings^[23,24] and, since the area B is clearly green when viewed by eye, the presence of Prussian green was a possibility that needed to be excluded. Prussian green is an analogue to Prussian blue with a different oxidation state ratio and

is chemically very similar. Prussian blue is due to its recent use in battery chemistry a very well-studied compound. In solution it forms Fe³⁺ cations and hexacyanoferrate anions with a charge of -4, an octahedral arrangement and a central iron in the Fe²⁺ oxidation state. Figure 4 shows its chemical structure(a), the octahedral arrangement of the hexacyanoferrate ion (b) and the crystal structure (c) of Prussian blue. In Prussian green almost all iron is in the Fe³⁺ oxidation state but a small fraction on the C-bound site (hexacyanoferrate) remains in the Fe²⁺ state. Prussian green is much less studied and reference spectra were difficult to find in literature. One study was found which was inconclusive on whether the Raman spectra for Prussian green and blue differed^[25]. To add to the complexity the term Prussian green has in some cases been used to describe a mixture of Prussian blue and a yellow pigment^[24]. To resolve this ambiguity, reference compounds of Prussian blue and Prussian green were sourced and these reference samples were measured with two laser wavelengths to clarify whether there indeed was a difference in the Raman spectra of these two very similar pigments. For Prussian blue Sigma Aldrich Prussian blue, water soluble was used as a reference and for Prussian green, which is not a commercial product, a reference compound produced by almost complete oxidation of the precursor Prussian white was used. The dark green Prussian green pigment is seen in the pigment comparison in figure 5a. The results of the Raman measurements of the reference compounds are shown in figure 4d and 4e for the 532 nm and 785 nm laser respectively. For the 532 nm excitation working in resonance Raman mode (electronically exciting the compounds) there is a very pronounced difference as there is an extra peak occurring at 2176 cm⁻¹ for Prussian green that is not present in Prussian blue. The difference between Prussian blue and green is not equally clear in the case using non-resonant Raman at 785 nm, where instead analysis of peak shifts is required. When comparing the spectrum from Prussian green to the Prussian blue spectrum using 785 nm Raman laser, there is a downward shift for the lowest peak from 278 cm⁻¹ to 272 cm⁻¹ and a shift for the highest intensity peak from 2154 cm⁻¹ to 2148 cm⁻¹. To further characterize and compare the two reference compounds their optical properties were also studied. Figure 5 a show the two pigments smeared out on white paper (a), dissolved in ethanol solution (b) and their optical absorption in the UV-VIS-NIR region (c). The Raman spectrum from the Prussian blue analogue found in the green leaf (B) was acquired with 785 nm wavelength and matches Prussian blue. The presence of Prussian blue shows that the painting has been either painted or altered at a later date than what the provenance state. X-ray imaging has been carried out on this painting and the laurel wreath is one region of the painting where there are clear signs of alterations. In figure 6a there is a comparison between a photograph and an X-ray image of this part of the painting and it shows that not all laurel leaves are visible in X-ray, something that could indicate the use of pigments with different X-ray contrast. The titanium white could also originate from the alterations of this location.

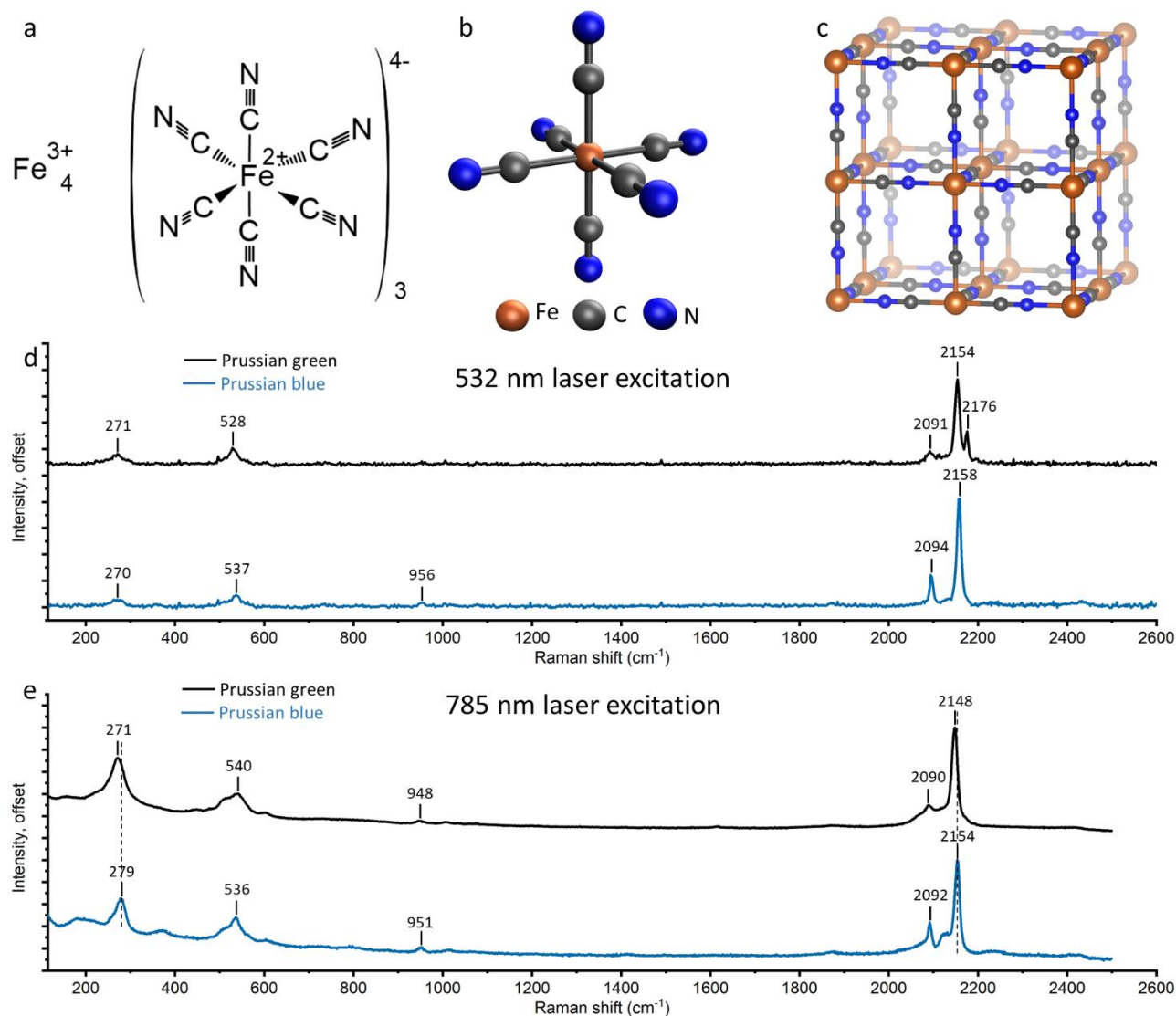


Figure 4. (a) Comparison of photograph (left) and X-ray image (right) of the laurel wreath, where some of the leaves visible in the photograph are absent in the x-ray image. The red arrow points at the leaf in location BA. Spectra from location C (b), Domitian's ear, matching the pigments of massicot and red ochre, from location E (c), the hair band, matching the pigment of cinnabar from location F (d), textile on shoulder, matching the pigment of cinnabar white lead and yellow ochre and spectra from location G (e), arm in shadow matching yellow ochre. Pigment grains of cinnabar (f) and yellow ochre (g), as viewed in the microscope using a 50x objective.

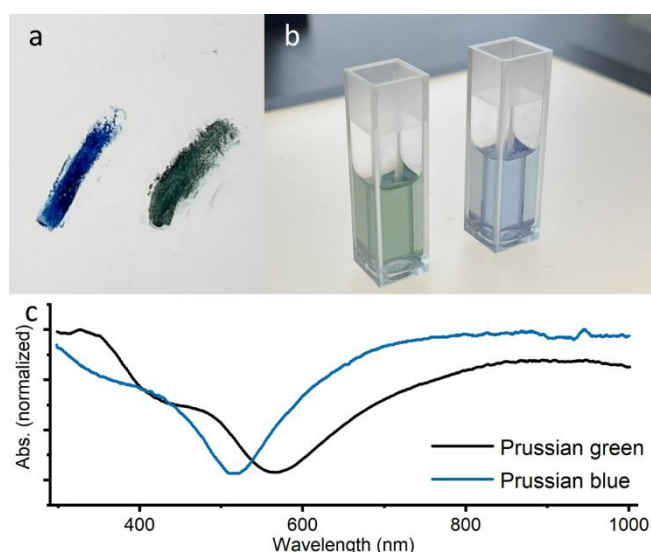


Figure 5. The optical properties of Prussian blue and Prussian green. Comparison of solid pigments on a white sheet of paper (a), pigments dissolved in ethanol (b) and the optical absorption of the two pigments measured in solution (c).

The tip of the ear – location C

The pinkish skin coloured area at the tip of Domitian's ear was analysed and three different pigments were identified. Figure 6b shows two spectra obtained from this location. The first spectrum corresponds well to the pigment massicot, PbO of orthorhombic structure, matched against a spectrum from Costantini et al.^[26] There are however rather large variations in reported peaks for lead oxide pigments, which complicates assignments. This is likely due to compositional variations in the lead oxide but could also be due to that some of the lead oxides are sensitive to laser heating from the Raman laser and undergo phase transitions^[26]. An example of such variations in reported peaks for pigments is shown in the supporting information, table S1. Variations in peak positions in lead pigments will be further discussed later in connection to sample H. The second spectrum in figure 6b was identified as the pigment red ochre (Fe_3O_4). The spectrum has been matched against several references. One of them being a comprehensive list of contemporary art pigments published by Elias Brenner in 1680^[27,28], containing a chart of actual pigment samples. The pigments in the book of Brenner are unique in two ways. First, these are truly old pigments, produced about 340 years ago, which have undergone the same aging processes as contemporary paintings. Secondly the Raman raw data from the Brenner study, which was available through one of the authors, was obtained using the same Raman spectrometer as in our study, thus eliminating differences in spectra quality. Fe_3O_4 has been used since ancient times under the name red ochre but there is

also a synthetically produced analogue called Mars red. Since the chemical compound is identical, it is not possible to distinguish between the natural red ochre and the synthetic Mars red, unless the previous contains some impurity, and differences between spectra reported in literature are assumed to mainly originate from differences in the measurements rather than variations of the pigments. From this we draw the conclusion that the colour of the human skin of the ear is achieved by mixing massicot or similar lead oxide-based pigments with red ochre.

The chin – location D

Due to a huge sample fluorescence that completely overshadowed the Raman signal, no pigments could be identified in location D. Fluorescence is a much stronger light emitting process than Raman scattering and this complication is reported to occur frequently.^[29]

The hairband – location E

The red pigment of the hair band was determined to be cinnabar. The spectra were very clear and easy to identify^[17]. Figure 6c shows a cinnabar spectrum with the peaks denoted and figure 6f shows a photograph of the corresponding pigment grain acquired through the microscope. Cinnabar, also known as mercury sulphide (HgS) has been used as a pigment since ancient times.

Textile on shoulder – location F

Two samples were taken from location F. In these samples three pigments were identified cinnabar, lead white and yellow ochre. Yellow ochre is a natural pigment that consist of an iron oxide hydroxide ($\alpha\text{-FeO(OH)}$) and is in mineralogy called goethite. Its synthetically produced analogue is called Mars yellow and has been produced since the middle of the 19th century^[17]. As previously mentioned in the case of red ochre, Raman spectroscopy is not ideal for distinguishing between natural and synthetic pigments with identical chemical compounds. The old document from 1680 made by the painter Elias Brenner mentioned above mentions that yellow ochre consists of goethite, clay and silica, with no ratio between the components given. Spectral features from these additives were however not seen in the spectra obtained from the samples from the Domitian painting but neither were they detected in analysis of the yellow ochre in the pigment chart in Brenner's own document. This is likely due to that clay and silica have weak Raman signals compared to goethite. Figure 6d shows the spectra of pigments found in location F. These spectra were matched against literature^[22] and databases^[17,19,30].

Arm in shadow – location G

Part of emperor Domitian's upper arm lies in shadow and has a dark brown colour. One pigment was clearly identified in this location: yellow ochre which was matched against a spectrum database^[17]. In figure 6e the spectrum and the corresponding pigment grain is shown in figure 6g.

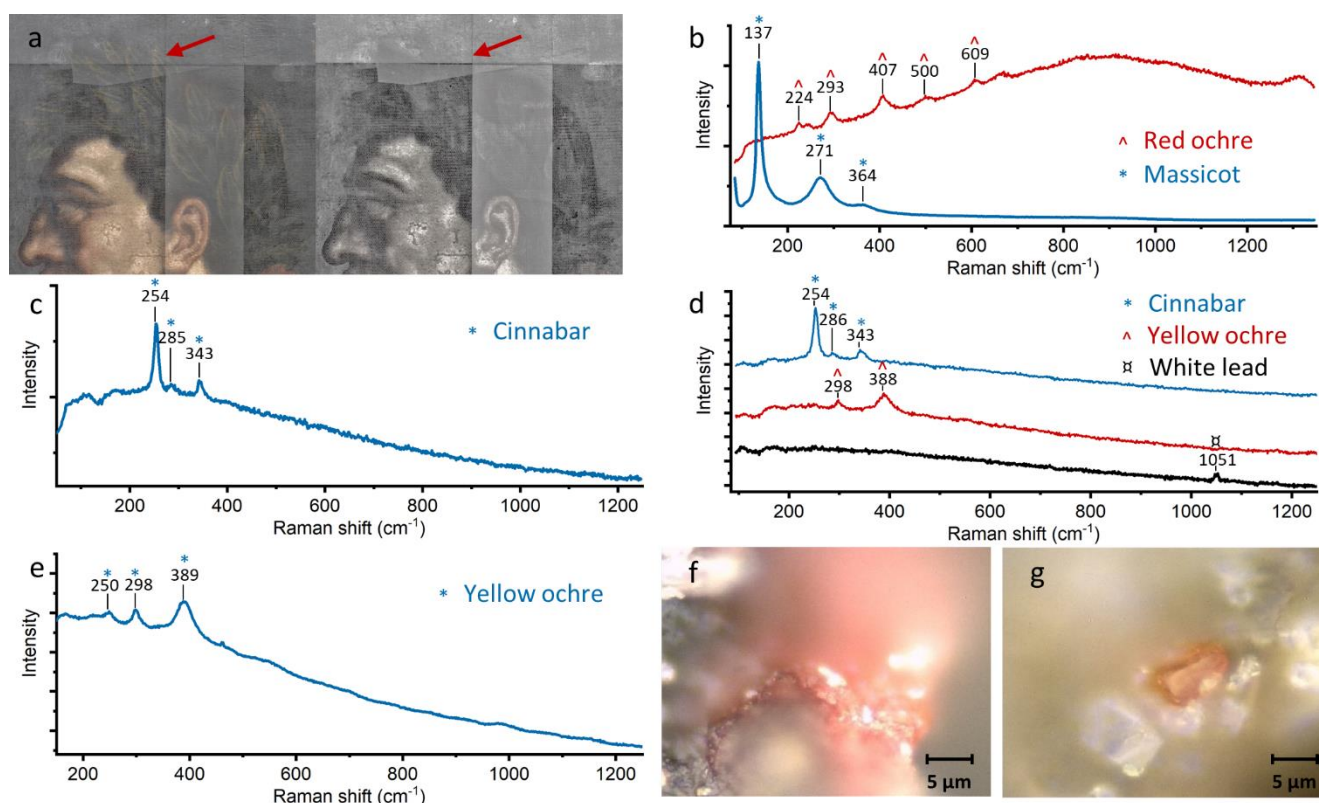


Figure 6. (a) Comparison of photograph (left) and X-ray image (right) of the laurel wreath, where some of the leaves visible in the photograph are absent in the x-ray image. The red arrow points at the leaf in location BA. Spectra from location C (b), Domitian's ear, matching the pigments of massicot and red ochre, from location E (c), the hair band, matching the pigment of cinnabar from location F (d), textile on shoulder, matching the pigment of cinnabar white lead and yellow ochre and spectra from location G (e), arm in shadow matching yellow ochre. Pigment grains of cinnabar (f) and yellow ochre (g), as viewed in the microscope using a 50x objective. Spectra in 6b is acquired with 532 nm laser and spectra in 6c, d and e is acquired with 785nm laser.

Armour – location H

For analysis of Domitian's armour, a clean area with a metallic appearance was chosen. Several pigments were identified in samples taken from this location of the painting. Firstly, spectra from cinnabar, lead white, massicot and carbon black were found, these are shown in figure 7a. A spectrum, acquired in location H, that exhibits peaks from the pigment, azurite^[31] is shown in the supporting information figure S4. Azurite is a mineral that was the most commonly used blue pigment in medieval artwork due to its availability and that it was less expensive than the more exclusive ultramarine^[32]. For massicot there were very good matches with references for several of the spectra acquired but there were also spectra similar to massicot but with small variations of the peak positions. This is shown in figure 7b. The different positions between these peaks are real (see the details of the lowest peak in the insert in figure 7b – the reproducibility of the instrument is better than 0.1 wavenumbers and the accuracy of the instrument is better than 0.5 wavenumbers, which is checked every analysis session against a silicon sample as a standard procedure. Hence these variations must be in the composition. In the spectra seen the peak position of the strongest peak varies within a range from 135 cm⁻¹ to 143 cm⁻¹. A mix of two discrete phases would give a mixture of two discrete but separate spectra. The gradual drift in peak positions that is seen in the samples from the Domitian

painting rather indicates several intermediate spectra or a mixture of non-stoichiometric phases and possibly even ongoing reactions due to ageing. Lead oxides have been used throughout history as red, yellow, and white pigments. In a paper by Burgio^[33] an interesting study of compositions and phases existing during reduction of the mineral plattnerite (PbO₂) is presented. Specially interesting is the dependence on the wavelength of light, and power used in Raman microscopy. Lasers in the wavelength range 400 – 600 nm combined with high power facilitate progressive reduction of lead oxides. At excitation with longer wavelengths, the red and infrared regions, these compounds are more stable. Most measurements in our own study were conducted using a 785 nm laser for which the reduction effect was less pronounced. Plattnerite is a weak Raman scatterer, it has been used as a pigment, but not so frequently, and it is the starting point as the most oxidised compound. The intermediate compounds red lead (Pb₃O₄, red) and litharge (PbO) and the final stable oxidation state massicot (PbO) are all pigments in art. In table 3 these four lead compounds are listed together with their Raman peak positions, structure and colour. It is noteworthy that even though the peak positions for the intermediate phases show some variation between different references, the most stable phase, massicot, appears with defined peak positions, similar in all the references.

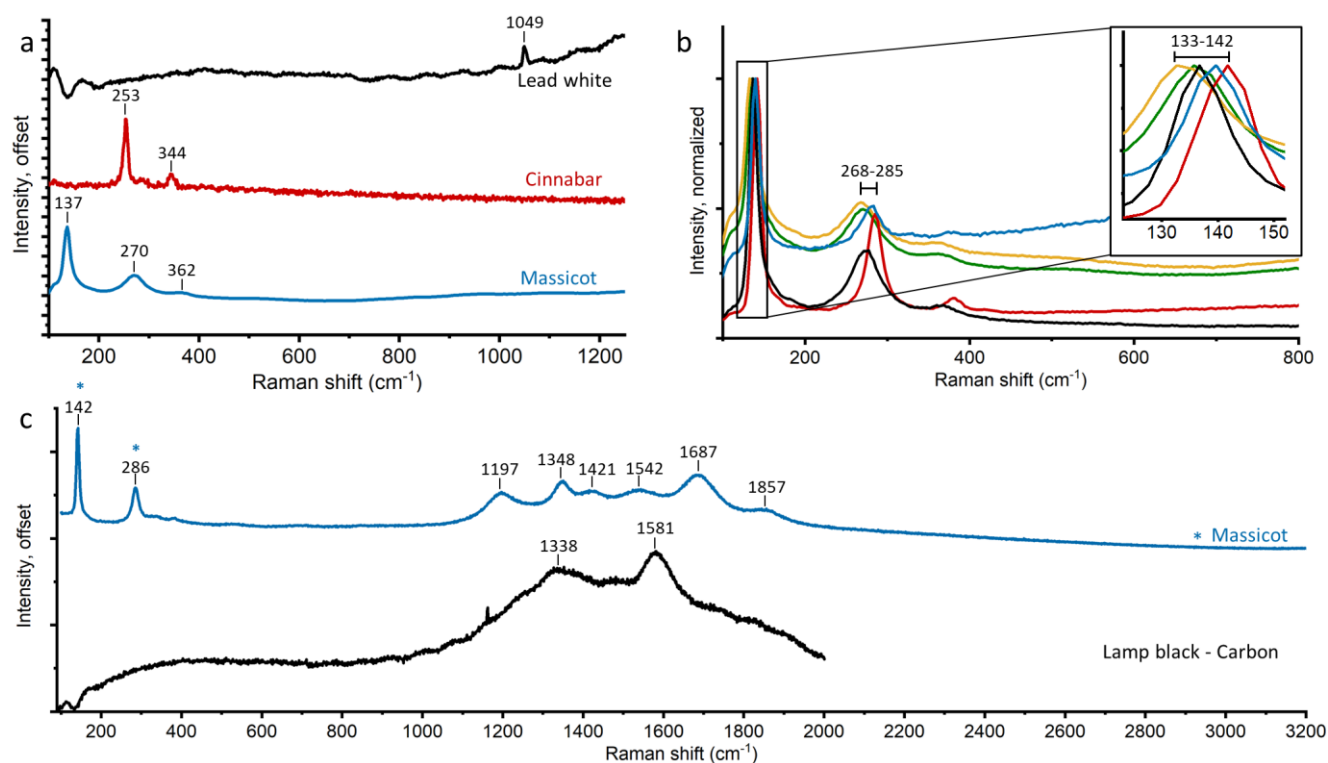


Figure 7. (a) Raman spectra from pigments identified in location H. (b) Comparison of lead oxide spectra from different points in sample location H the peak position variation is attributed to varying composition. (c) Extended range Raman spectra from location H showing peaks from massicot, an unidentified compound assumed to be an earth pigment (upper), and carbon black (lower). The massicot spectrum in 7a and the spectra in 7b were acquired with a 532 nm laser and the rest of the spectra with a 785 nm laser.

Table 3. Lead oxides pigments and their Raman peak positions

Compound	Colour	Structure	Raman peak positions (intensity)										
Plattnerite PbO ₂	black	tetragonal	-	-	-	-	-	-	-	424 (vw)	-	515 (w)	653 (vw)
Red lead Pb ₃ O ₄	red	tetragonal	65 (vw)	87 (vw)	122 (vs)	149 (m)	223 (w)	313 (w)	340 (w)	390 (w)	480 (w)	550 (s)	-
Litharge PbO	red	tetragonal	-	83 (w)	-	145 (vs)	-	285 (vw)	336 (w)	-	-	-	-
Massicot PbO	yellow	orthogonal	72 (vw)	87 (m)	-	143 (vs)	-	289 (s)	-	385 (w)	-	-	-

Reference data originate from the spectrum database of University College London^[17] and for the low wave number peaks from the article by Borgio^[33].

Figure 7c show two extended range spectra acquired from location H. One is of carbon black, which can be assumed to have been used to vary the light-dark impression. The other one has low wave number peaks matching massicot, but also a strong distinct signal within the region from 1000 cm⁻¹ to 1900 cm⁻¹, a region called the fingerprint region, where many organic molecules give peaks. The spectral features of this spectrum were consistent in several measurement points, indicating that it

originated from a homogenous, well-defined pigment. Although we were unable to find a match for this pigment it was noted that the only pigments exhibiting this type of behaviour with many wide peaks in the fingerprint region were earth pigments. Examples of earth pigments are sienna^[19]: terra vert^[20], and umbra^[19]: brown, green or grey pigments based on soils.

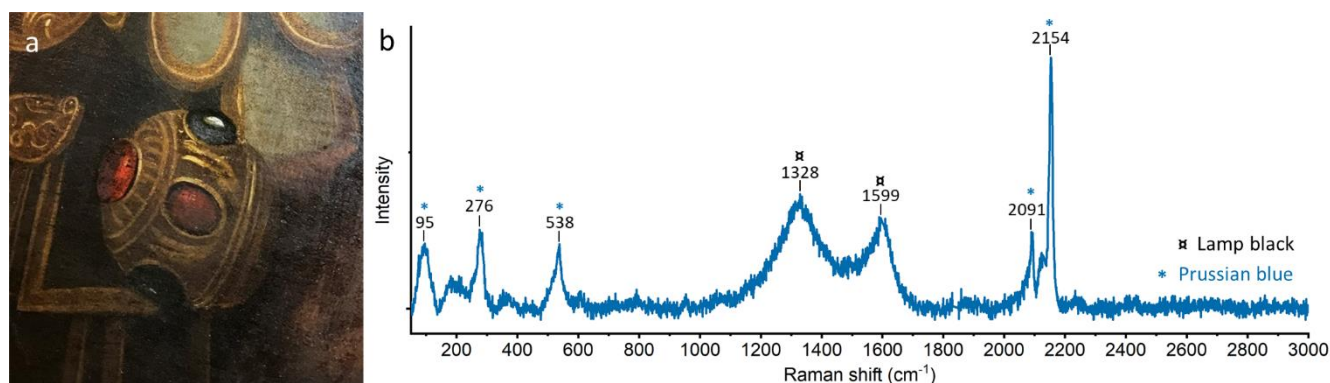


Figure 8. The sword's pommel with jewels (a) and spectra from the blue jewel identified as Prussian blue, with the main peak at 2154 cm^{-1} (b). The peaks at 1350 cm^{-1} and 1600 cm^{-1} come from carbon black. Spectrum acquired with a 785 nm laser.

From the similarity between these pigments, even though the peak positions do not match, the conclusion is that it is likely that the pigment is an earth pigment, but from a different origin than the ones listed in the data bases.

Jewel on sword pommel – location I

In this location it was the blue jewel on the pommel of the sword's hilt, shown in figure 8a, that was sampled. Also, here several types of pigments are used to make up the final colour. Lead white is found and its main peaks were matched against the UCL spectrum data base.^[17] This reference also mentions three very weak peaks between 600 and 850 cm^{-1} , but they are too weak to appear in the spectra in this analysis. The blue pigment in the jewel was identified as Prussian blue. Since the main peaks for Prussian blue are at a large Raman shift (2154 cm^{-1}) an extended range scan needed to be used. The spectrum is shown in figure 8b. In this spectrum the presence of carbon black is also seen.

The signature – location J

Figure 9a shows a photograph of the signature in location J below Domitian's elbow. The sampling was done on the vertical line of the capital L. Spectra showed that the black pigment used for the signature is carbon black, also known as lamp black or ivory black. The two very broad signature peaks of carbon are shown in figure 9b. No other pigments were found in the signature.

Domitian's letters – location K

Samples were taken from the letter N in the name Domitian. The samples gave a large fluorescence, but weak signals from lead tin yellow type 1 and chalk (calcium carbonate, CaCO_3) were seen. These are shown in figure S5 in the supporting information. As in the case of gypsum, chalk has been used both for the underworks of paintings and as a pigment.

Arm, illuminated – location L

In all samples of the illuminated part of the arm cinnabar and lead white, a mixture of red and white in different proportions, were found. One example of such spectra is shown in figure 9c. In some spectra taken from this sample, the double peak at 1050 cm^{-1} Raman shift, which is associated with lead white, is very minor and the cinnabar peaks are much stronger due to its inherently stronger Raman scattering ability.

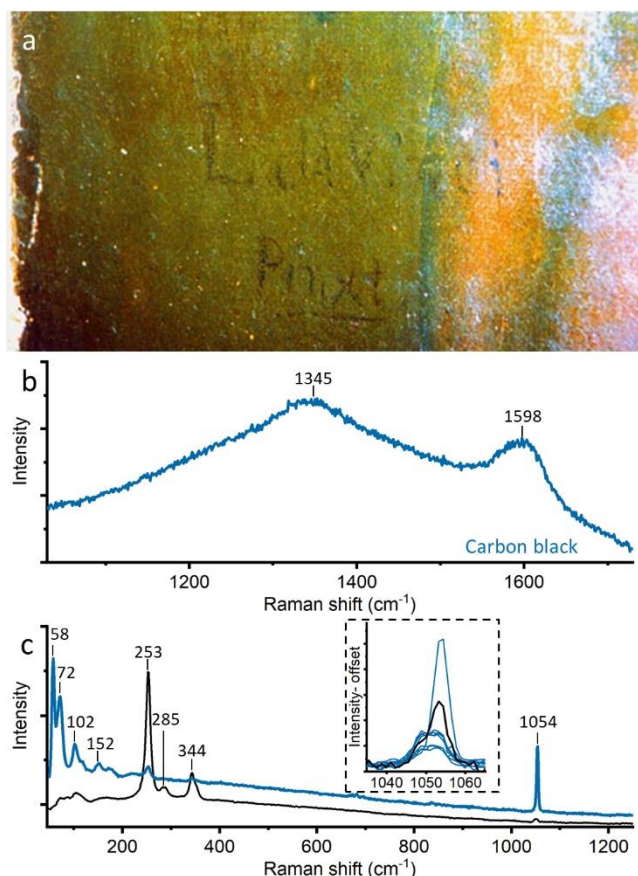


Figure 9. (a) The signature "L da Vinci" followed by "Pnixt" or more likely "Pinxt", Latin for "painted". (b) Spectrum from the signature in location J acquired with a 532 nm laser. The two broad peaks at approximately 1350 cm^{-1} and 1600 cm^{-1} are typical for amorphous carbon which was used as a pigment under the names carbon black, lamp black and ivory black. (c) Spectrum from location L, showing peaks from cinnabar and lead white acquired with 785 nm laser.

For the peak around 1050 cm^{-1} eight spectra were acquired from location L and studying it more closely, it is apparent that in all spectra there are double peaks at 1049 and 1053.5 cm^{-1} Raman shift and that the ratio of these peaks varied greatly, between 0.96 and 19.9 in our case. A graph showing this double peak can be seen as an insert in figure 9c, where one spectrum with a clear double

peak behaviour has been highlighted in black. The curve fitting parameter and the results of the curve fitting is included in the supporting information table S2 and table S3. The occurrence of the double peaks and its variations are expected, and are attributed to that lead white usually is a mixture of cerussite (PbCO_3) and hydroxy cerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$)^[34] and that the ratios between these are varying. There is a possibility that different lead white pigment mixtures were used in different places to create artistic effects but since a large variation is seen in samples from the same location it is more likely to be due to natural variations or non-ideal mixing in a single lead white pigment.

Summary

In total, fourteen pigments and their mixtures were identified in the investigation. Two of these compounds have historically served both as pigments and as materials for the ground layer of paintings. Table 4 contains a summary of pigments that were found in each sampling location.

Table 4. Pigments identified in each sample location

Sample location	Pigments identified (colour)	No of pigments
A	Red ochre, lead white, gypsum ^[a] (white), earth pigment ^[b] (brown)	4
B	Titanium white ^[c] , Terra verte ^[c] (green), ultramarine (blue), lead tin yellow type 1, Prussian blue	4
BA	Lead tin yellow type 1, chalk ^[a] (white)	2
C	Massicot (yellow), red ochre	3
D	-	0
E	Cinnabar (red),	1
F	Cinnabar (red), lead white, yellow ochre	3
G	Yellow ochre	1
H	Cinnabar (red), lead white, massicot (yellow), carbon black, azurite (blue), earth pigment ^[b] (brown)	6
I	Lead white, Prussian blue, carbon black	3
J	Carbon black	1
K	Lead tin yellow type 1, chalk ^[a]	2
L	Cinnabar (red), lead white,	2

[a] Could also originate from the backing layer. [b] Unspecified earth pigment. [c] Only one of these two pigments present, titanium white is most likely.

The vast majority of the pigments, twelve out of the fourteen, are traditional paint pigments that has been used since medieval or ancient times. However, one pigment, Prussian blue, is of considerably newer origin. It is a synthetic pigment that was first introduced in the year 1704, making it unavailable during medieval times when the painting is believed to have been created. This raises the possibility that either the painting was not

executed in medieval times or that it has been altered at a later date. Such alterations, often made in attempts to repair or enhance an aging artwork, are relatively common but can sometimes be challenging to prove. In this case, however, X-ray analysis and the assessment of a conservator indicate that the two areas where Prussian blue was found, the laurel wreath and the swords pommel, has been altered. Furthermore, the presence of most pigments that were available in medieval times does not necessarily imply that they were used in the painting during that period. Many traditional art pigments continue to be in common use today. While some have been replaced by synthetic alternatives that can be produced in large quantities at a lower cost, but from a spectroscopic point of view it is the same compound. It is only when the commonly used contemporary pigment differs from the traditional one, we can make a distinction, like with the Prussian blue which is a very widely used pigment. Another such modern pigment is titanium white (TiO_2 , anatase) that due to its non-toxicity, hiding power, low cost, availability and stability now by far is the dominating white pigment in use. The situation becomes yet more complex in suspected cases of intentional forgery. A forger with technical expertise can deliberately use historically appropriate pigments and substrates, and even incorporate older canvases or ground layers, to mimic an original and to confound provenance and dating techniques (e.g., radiocarbon dating of the support). Such practice has been thoroughly described both in scientific and popular literature.^[35,36] Therefore, establishing authenticity typically requires a combination of stratigraphic, material and contextual analyses (cross - sections, binding - media characterization, documentary evidence and provenance research) rather than reliance on a single test. Raman spectroscopy for painting studies is inherently limited by its spatial sampling: typical laser spots cover only a few square micrometres, so each measurement characterizes only a microscopic fraction of the object. Many measurement attempts are at risk of produce no interpretable Raman spectrum because of insufficient signal-to-noise or strong fluorescence that mask Raman bands. The situation is further complicated by varnish layers and centuries of soot, where a clear Raman signature is best obtained from the back side of microsamples or cross - sections, as in this study. Returning to the question posed in the Introduction. Could this still be an original work by Leonardo da Vinci? The vast majority of the identified pigments, including those used in the signature, are consistent with medieval or earlier materials. In contrast, the localized presence of Prussian blue provides evidence of a post-medieval addition. The two locations where Prussian blue was found were analysed by X-ray imaging and by a conservator/art historian, respectively; both analyses point to a later intervention (restoration, overpainting, or retouching) rather than a post-medieval execution.

Conclusion

An old painting depicting the roman Emperor Domitian has been investigated by Raman spectroscopy to identify pigments used when painted. The series of emperor paintings is historically connected to Titian where Emperor Domitian is supposed to be painted by another artist and is signed "L daVinci" which makes it interesting from an art historical point of view and opens up the possibility that this emperor was already painted at the time Titian

painted the remaining emperors. A total of 14 pigments were identified. Thirteen are traditional pigments used since the medieval period and throughout the Renaissance. Two locations contained Prussian blue, a synthetic pigment first produced in the early 18th century, which therefore post-dates the painting's purported medieval origin. This finding is most plausibly explained by later intervention (retouching, overpainting, or restoration) rather than by reattribution to a post-medieval execution. X-ray imaging of one such area, the laurel wreath, revealed structural evidence of added leaves, consistent with later additions. In the laurel wreath there was also a likely match for titanium white, which is considered a predominantly modern pigment. The black pigment in the signature was a carbon-based soot pigment which would have been readily available to da Vinci. Raman spectroscopy with low cut off Raman filters is here shown to be a powerful tool for identifying pigments in artwork. Although Raman spectroscopy is a powerful tool, reliable results require either careful cleaning of the paint surface or the collection of microsamples. Analysing pigment grains from the back or cross-sections minimizes interference from varnish layers and centuries of soot, which otherwise can obscure spectral features. Sampling large paintings poses a challenge for detailed Raman spectroscopy because only a fraction of the work can be analysed practically. We therefore concentrated sampling on areas showing the painting's characteristic colours and on regions suspected to contain both historically appropriate and more recent pigments. In addition to Raman signatures of ancient pigments, the study also reports resonant and non-resonant Raman response of Prussian green and blue, expressing different ratios of Fe^{2+} and Fe^{3+} states, valuable for both pigment identification and discrimination of the compounds in battery research and neighbouring fields where these compounds are also commonly used.

Acknowledgements

The authors would like to thank the owners of the Domitian painting, for giving us the unique opportunity to work with such a delicate object. They have also been very helpful during sampling and the transportation of the painting. Much appreciated is also the discussions we have had, and their commitment to sort out the provenance and background of the painting. We also thank conservator Inger Nyström Godfrey, Studio Västsvensk Konservering (SVK) in Gothenburg, who prepared the X-ray images, photographer Helena Christerdotter for the photos taken of the painting and William Brant at the Department of Chemistry -Ångström; Structural chemistry, Uppsala University for providing the Prussian green reference compound and knowledge on Prussian blue analogues. We acknowledge the Swedish Research Council (Grant Id 2023-05244) providing resources for the maintenance of the Raman spectrometers used.

Keywords: Raman spectroscopy, pigments, medieval artwork, da Vinci, Emperor Domitian, Prussian green

- [1] M. Aubert, A. Brumm, M. Ramli, T. Sutikna, E. W. Saptomo, B. Hakim, M. J. Morwood, G. D. Van Den Bergh, L. Kinsley, A. Dosseto, "Pleistocene cave art from Sulawesi, Indonesia" *Nature* **2014**, *514*, 223–227.
- [2] A. Quiles, H. Valladas, H. Bocherens, E. Delqué-Kolich, E. Kaltnecker, J. van der Plicht, J.-J. Delannoy, V. Feruglio, C. Fritz, J. Monney, M. Philippe, G. Tosello, J. Clottes, J.-M. Geneste, "A high-precision chronological model for the decorated Upper Paleolithic cave of Chauvet-Pont d'Arc, Ardèche, France" *Proceedings of the National Academy of Sciences* **2016**, *113*, 4670–4675.
- [3] N. Carroll, "Art and Human Nature" *The Journal of Aesthetics and Art Criticism* **2004**, *62*, 95–107.
- [4] L. Rogers, G. Kaplan **2007**, pp. 137–150.
- [5] C. McAndrew, *The survey of global collecting 2023*, Art Basel & UBS, Basel, Switzerland, **2023**.
- [6] J. Padfield, D. Saunders, J. Cupitt, R. Atkinson, "Improvements in the acquisition and processing of X-ray images of paintings" *National Gallery Technical Bulletin* **2002**, *23*, 62–75.
- [7] D. L. Howard, M. D. de Jonge, D. Lau, D. Hay, M. Varcoc-Cocks, C. G. Ryan, R. Kirkham, G. Moorhead, D. Paterson, D. Thurrowgood, "High-Definition X-ray Fluorescence Elemental Mapping of Paintings" *Anal. Chem.* **2012**, *84*, 3278–3286.
- [8] S. A. Centeno, "Identification of artistic materials in paintings and drawings by Raman spectroscopy: some challenges and future outlook" *J Raman Spectroscopy* **2016**, *47*, 9–15.
- [9] R. J. Meilunas, J. G. Bentsen, A. Steinberg, "Analysis of aged paint binders by FTIR spectroscopy" *Studies in Conservation* **1990**, *35*, 33–51.
- [10] L. Hendriks, I. Hajdas, E. S. B. Ferreira, N. C. Scherrer, S. Zumbühl, G. D. Smith, C. Welte, L. Wacker, H.-A. Synal, D. Günther, "Uncovering modern paint forgeries by radiocarbon dating" *Proceedings of the National Academy of Sciences* **2019**, *116*, 13210–13214.
- [11] E. Albertini, L. Raggi, M. Vagnini, A. Sassolini, A. Achilli, G. Marconi, L. Cartechini, F. Veronesi, M. Falcinelli, B. G. Brunetti, C. Miliani, "Tracing the biological origin of animal glues used in paintings through mitochondrial DNA analysis" *Anal Bioanal Chem* **2011**, *399*, 2987–2995.
- [12] K. Janssens, M. Alfeld, G. Van der Snickt, W. De Nolf, F. Vanmeert, M. Radepon, L. Monico, J. Dik, M. Cotte, G. Falkenberg, C. Miliani, B. G. Brunetti, "The Use of Synchrotron Radiation for the Characterization of Artists' Pigments and Paintings" *Annual Review of Analytical Chemistry* **2013**, *6*, 399–425.
- [13] M. Dalivalle, M. Kemp, R. B. Simon, *Leonardo's Salvator Mundi & the collecting of Leonardo in the Stuart Courts*, Oxford University Press, Oxford, **2019**.
- [14] V.-M. Margarita-Ana, "Twelve Caesars' Representations from Titian to the End of 17th Century: Military Triumph Images of the Spanish monarchy" *PTHA* **2015**, *5*, 655–663.
- [15] V. Bernasconi, E. Cetinić, L. Impett, "A Computational Approach to Hand Pose Recognition in Early Modern Paintings" *J. Imaging* **2023**, *9*, 120.
- [16] V. Bernasconi, L. Impett, "Decoding early modern gestural patterns through hand networks" *Digital Scholarship in the Humanities* **2025**, *40*, 461–476.
- [17] I. M. Bell, R. J. H. Clark, P. J. Gibbs, "Raman spectroscopic library of natural and synthetic pigments (pre- $\approx$ 1850 AD)" *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **1997**, *53*, 2159–2179.
- [18] G. Marucci, A. Beeby, A. W. Parker, C. E. Nicholson, "Raman spectroscopic library of medieval pigments collected with five different wavelengths for investigation of illuminated manuscripts" *Analytical Methods* **2018**, *10*, 1219–1236.
- [19] M. C. Caggiani, A. Cosentino, A. Mangone, "Pigments Checker version 3.0, a handy set for conservation scientists: A free online Raman spectra database" *Microchemical Journal* **2016**, *129*, 123–132.
- [20] C. R. Vynhal, "A Free and Fun Chemistry Resource for Use in Multidisciplinary 'Chemistry of Archaeology and Art' Courses: The Cultural Heritage Science Open-Source (CHSOS) Database of Analytical Spectra from Historical and Modern Pigments" *J. Chem. Educ.* **2023**, *100*, 4653–4662.
- [21] H. G. M. Edwards, N. F. Nik Hassan, P. S. Middleton, "Anatase—a pigment in ancient artwork or a modern usurper?" *Anal Bioanal Chem* **2006**, *384*, 1356–1365.
- [22] H. G. M. Edwards, "Analytical Raman spectroscopic discrimination between yellow pigments of the Renaissance" *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2011**, *80*, 14–20.
- [23] S. Barros, A. J. C. Santos, "Green pigments: tradition and modernity in painting according to Portuguese 19th century technical literature" **2011**.
- [24] W. H. Watercolors, "A Vibrant Surface: Investigating Color, Texture and Transparency in" *Science and Art: The Painted Surface* **2020**, 404.
- [25] Y. G. Wang, M. Wang, Y. Q. Wang, Q. Zhang, H. N. Zhou, H. L. Zhao, "Electrochromic properties of three-colour prussian green ECDs and the evolution of Fe ions during the discoloration process" *Materials Letters* **2022**, *311*, 131627.
- [26] I. Costantini, P. P. Lottici, K. Castro, J. Madariaga, "Use of Temperature Controlled Stage Confocal Raman Microscopy to Study Phase Transition of Lead Dioxide (Plattnerite)" *Minerals* **2020**, *10*, DOI 10.3390/min10050468.
- [27] E. Brenner, *Nomenclatura et Species Colorum Miniatae Picturae — thet är: förteckning och proff på MINIATUR färgår*, **1680**.
- [28] C. Rönnerstam, L. Hålldahl, "Nomenclatura Et Species Colorum Miniatae Picturae: Researching Seventeenth-Century Pigments in Sweden" *Studies in Conservation* **2006**, *51*, 254–259.
- [29] J. Thyrt, T. Edvinsson, "Evading the Illusions: Identification of False Peaks in Micro- Raman Spectroscopy and Guidelines for Scientific Best Practice" *Angew Chem Int Ed* **2023**, e202219047.
- [30] B. Lafuente, R. T. Downs, H. Yang, N. Stone in *Highlights in Mineralogical Crystallography* (Eds.: T. Armbruster, R.M. Danisi), De Gruyter (O), **2015**, pp. 1–30.

- [31] E. Chen, B. Zhang, F. Zhao, C. Wang, "Pigments and binding media of polychrome relics from the central hall of Longju temple in Sichuan, China" *Herit Sci* **2019**, 7, 45.
- [32] R. Ashok, Ed. , *Artists' pigments: a handbook of their history and characteristics*. 2, Oxford Univ. Press, New York, **1997**.
- [33] L. Burgio, R. J. H. Clark, S. Firth, "Raman spectroscopy as a means for the identification of plattnerite (PbO₂), of lead pigments and of their degradation products" *Analyst* **2001**, 126, 222–227.
- [34] M. Vagnini, R. Vivani, A. Sgamellotti, C. Miliani, "Blackening of lead white: Study of model paintings" *Journal of Raman Spectroscopy* **2020**, 51, 1118–1126.
- [35] A. Moxley, "The art of forgery" *The Undergraduate Scholar* **2010**, 1–10.
- [36] C.-J. Vallgren, Kunzelmann & Kunzelmann, A. Bonnier, Stockholm, **2009**.

Entry for the Table of Contents



An old painting, of the Roman emperor Domitian has been investigated by Raman Spectroscopy. The painting contains the signature L da Vinci which make it a very interesting object to study. The pigments in the painting were identified in order to evaluate if they correspond to pigments contemporary with the mentioned artist.