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A multidisciplinary study of unusual red and blue lake pigments used in fifteenth-century Swedish wall paintings

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This study aimed to understand and characterise previously unidentified fibrous red and blue pigments used in fifteenth-century wall paintings by Albertus Pictor in Härnevi church (Sweden). The findings demonstrate the importance of the synergy of material science, technical art history and conservation. The investigations enabled us to recommend a combination of analytical techniques to determine a clear and robust outcome for future researchers. Both pigments were investigated with optical microscopy, UV fluorescence microscopy, scanning electron microscopy with energy-dispersive X-ray microanalysis (SEM-EDX), and Fourier transform infrared spectroscopy (ATR-FTIR). The red pigment was further analysed with high-performance liquid chromatography (HPLC-DAD). Raman micro-spectroscopy was employed to analyse the blue pigment. Binding media analysis with nano-LC-ESI-Q-TOF was used to identify the binder in samples taken from the red area. Both pigments were found to be prepared from wool shearings dyed with madder for the red pigment and indigo (likely from woad) for the blue pigment.

Albertus Pictor (~1440–1509) is the most well-known medieval mural painter in Sweden¹. He is believed to have been of German descent and a first-generation immigrant to Sweden². Pictor was the leader of an extraordinarily productive workshop to which 36 mural decorations in Swedish churches, mainly in the Lake Mälaren area, have been attributed. In some of the churches, there are readable signatures by Albertus Pictor, while in others the iconography, the technique and the outstanding workmanship justify an attribution to his workshop. His workshop also produced embroideries e.g., ecclesiastical textiles. This is supported by archival material where Albertus Pictor is mentioned alternately as a painter and as an embroiderer³.

One of the most well-preserved series of wall paintings by Albertus Pictor and his workshop is found in Härnevi church in Uppland (Sweden). They have been dated to around 1480^{1,4}. Härnevi church is one of only six churches with paintings attributed to Pictor and his workshop that has never been completely overpainted although the walls were covered with a lime wash in the eighteenth century (Fig. 1A, B)⁵. Research showed that these murals had only been subjected to one documented restoration and conservation intervention in 1956 during which the paintings on the walls were uncovered⁶.

The murals are painted primarily *al secco* which means that the paint was applied on dry plaster^{7,8}. It is the most common technique found in northern European mural painting. The plaster has been applied in one

levelling coat and covered with a lime slurry. After the initial sketch was carried out, the colour was applied, often in several layers and with semi-transparent shadows and white highlights. Previous binding media analyses from churches decorated by the same workshop have shown that collagen proteins (most likely animal glue) was the most common binder used by the Pictor workshop followed by casein. Egg proteins and drying oils have also been detected^{9–11}. Types of analysis used for these investigations included FTIR, GC-MS, HPLC and ion chromatography.

Lime and chalk were used as white pigments. Other pigments include red iron oxide, yellow ochre, carbon black, lead-tin yellow, red lead, massicot, malachite, atacamite, green earth, azurite and cinnabar¹². Of particular interest is the recent discovery of fibrous red and blue organic lake pigments used in different areas of the murals in Härnevi church (Fig. 2a, b). This discovery led to an in-depth study of these pigments using the methodology of technical art history in order to gain a comprehensive understanding of how they were used, their properties, appearance, preparation and chemical composition. The methodology developed, and the understanding of materials gained, can be used by other researchers going forward. To date this specific type of organic pigment has rarely been identified in wall paintings but there is some reason to believe that it has been overlooked more than we think due to the often poorly preserved areas where it has been used.

Dyestuffs for lake pigments are obtained from plants or other organic material such as insects. This article will focus on red and blue plant-based

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Fig. 1 | Views of Härnevi church. **A** Härnevi church (exterior) from the southeast. **B** Härnevi church (interior), view over the chancel. The vault as well as the walls is covered with wall painting.

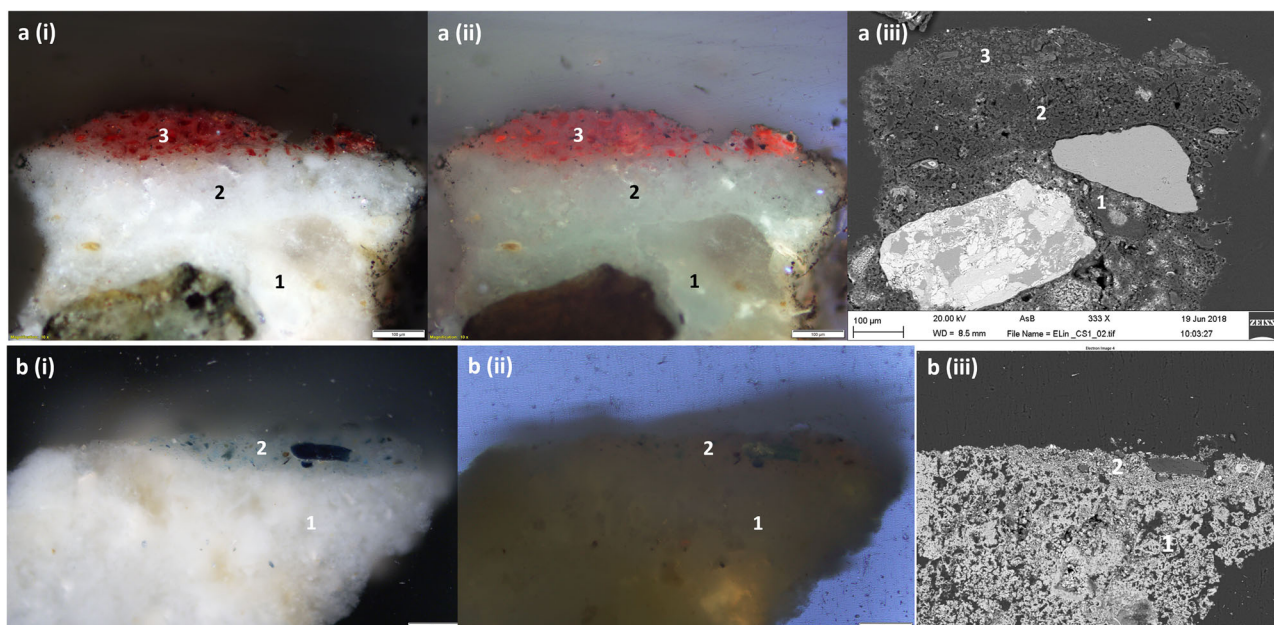


Fig. 2 | Results of optical microscopy and SEM on Sample Red 3 and Sample Blue 1. **a** Sample Red 3 embedded paint cross section. **a(i)** shows the mortar with aggregates (layer 1), thin slurry on the top (layer 2) followed by red paint layer pigmented with the fibrous red lake pigment (layer 3). **a(ii)** shows the same paint cross section under UV light, the top red layer (layer 3) exhibits a very noticeable orangey red fluorescence typical of madder lake pigments. **a(iii)** backscatter electron

image shows the mortar with aggregates (layer 1). **b** Sample Blue 1 embedded paint cross section. **b(i)** shows the slurry (layer 1) followed by blue paint layer pigmented with the fibrous blue lake pigment (layer 2). **b(ii)** shows the same paint cross section under UV light, the blue fibrous lake pigment shows a dull bluish fluorescence. **b(iii)** backscatter electron image shows the slurry (layer 1) and blue paint layer with fibrous blue lake pigment (layer 2).

lakes derived from madder and woad that could be obtained locally and were common in northern Europe during the medieval period.

Lake pigments are usually made by precipitating the liquid dyestuff onto an insoluble substrate in the form of hydrated alumina ($\text{Al}(\text{OH})_3$)¹³. However, lake pigments were not always prepared directly from insects or plants. A small number of findings also show that this type of red and blue lake pigment was prepared from either wool/ silk or textile shearings which had been dyed with madder and woad/indigo. This is supported very nicely by a contemporary early sixteenth-century coloured ink drawing from the Hausbuch der Landauerschen Zwölfbrüderhausstiftung (Nuremberg, Germany) which shows a man dyeing red and blue wool in a copper vat. The textiles used were proteinaceous, most commonly wool or silk¹⁴.

The textile material is boiled in an alkaline solution which creates a sticky protein-containing mass. The alkali used in the fifteenth century was commonly prepared from wood or plant ash extracted with water. Stale urine, wine lees and lime water could also be used¹⁴. The fibres dissolve to different degrees depending on the strength of the lye. The solution is dried, and the solid residue is ground with alum and the pigment is formed. The pigment is then boiled and rinsed to remove excess alum.

These insights are also supported by a group of fifteenth-century German recipes which describe the preparation of red and blue woolly lake pigments from textile shearings. The name *Parisrot* (Paris red) is often used for the red

pigment in the instructions, whereas *indich* or *endig* (indigo) is used for the blue lake. The recipes differ from each other in that sometimes it is recommended to extract the dyestuff from the textile and most likely discarding the residue after filtering (although this is not explicitly mentioned) as is described in the recipe found in the late fifteenth-century 'Colmarer Kunstbuch' (Bern, Bürgerbibliothek, Cod. Hist. Helv. XII 45), while the majority of the recipes recommend different levels of dissolving of the fibres and then utilising the residue itself as the pigment as can be found in different recipes including the mid fifteenth-century 'Nürnberg Kunstbuch' (see Table 1)¹⁵.

While our findings cannot completely eliminate other recipes, the texture and brittleness of the pigment produced with our own reconstructions indicates that both the red and the blue pigment found in Härnevi seem to be of the latter version on account of the undissolved fibres used directly as pigments (see Supplementary Figs. 2, 3 and 4).

The colour and the hue of the resultant pigment can differ depending on the recipe. Lake pigments prepared from wool shearings are primarily opaque but varying somewhat in translucency depending on the binder. They are sensitive to the caustic action of uncarbonated lime which renders them dark in colour so for the use on wall paintings they can only be used in *secco* techniques¹⁶.

There are a number of reasons given for why shearings are used to produce a lake pigment. One reason for using textile shearings as a basis for

Table 1 | Selection of fifteenth-century German recipes for red and blue lake pigments prepared from wool shearings

Document	Source and date of original text	Colour of pigment described	Historical terminology used for pigment in recipes with English translation	Materials described in recipe to make pigment	Preparation process described in recipe	Literature
Nuremberg, Nürnberger Stadtbibliothek, MS cent. VI. 89, (<i>Nürnberger Kunstbuch</i>), ff. 20v–21v [23, pp. 113–114]	S. Germany, mid-fifteenth century	Two recipes = red and blue	RED: <i>parisrot</i> (Paris red), <i>roter scherwollen</i> (red wool) BLUE: <i>indich</i> (indigo or woad), <i>plöbe scher wollen</i> (blue wool)	Materials: red and blue dyed wool, ashes, alum	Process to prepare a red and blue woolly pigment: dissolve a pound of red or blue wool in a lye made from ashes and water that has been boiled; heat mixture over a fire and bring to a boil; filter red or blue product twice through a cloth in this process; grind dissolved red or blue wool product together with alum on a stone slab; put final product in fresh water and bring to a boil again. Filter and lay out final dissolved product made into a red or blue lump to dry in the sun. Then you will have good <i>parisrot</i> (Paris red) or indigo/woad pigment.	Oltrögge D. Datenbank mittelalterlicher und frühneuzeitlicher kunsttechnologischer Rezepte in handschriftlicher Überlieferung. TH Köln – University of Applied Sciences Cologne, Institut für Restaurierungs- und Konservierungswissenschaften. https://www.th-koeln.de/kulturwissenschaften/kunsttechnologische-rezeptsammlung_25065.php . Accessed 23 January 2023. Ploss E.E. <i>Ein Buch von alten Farben. Technologie der Textilfarben im Mittelalter mit einem Ausblick auf die festen Farben</i> . Munich: Moos & Partner München; 1989: 140–141.
Bamberg, Staatliche Bibliothek, Msc. Med. 12, f. 181 v	S. Germany (Bavaria), fifteenth century	Blue	BLUE: <i>bloen indich</i> (blue indigo/woad), <i>wulle</i> (undyed wool)	Materials: undyed wool, lye, alum, indigo/woad dye	Process to prepare a blue woolly pigment: Undyed wool is dissolved (left to rot); the degraded wool is then poured onto some felt to dry; once product has dried then take woollen lump and grind well with alum on stone slab; then mix degraded wool with the blue indigo/woad dye to obtain blue pigment.	Oltrögge D. Datenbank mittelalterlicher und frühneuzeitlicher kunsttechnologischer Rezepte in handschriftlicher Überlieferung. TH Köln – University of Applied Sciences Cologne, Institut für Restaurierungs- und Konservierungswissenschaften. https://www.th-koeln.de/kulturwissenschaften/kunsttechnologische-rezeptsammlung_25065.php . Accessed 23 January 2023.
Bern, Bürgerbibliothek, Cod. Hist. Helv. XII 45 (<i>Colmarer Kunstbuch</i>), page 170, Chapter 110	S. Germany, 1478	Blue	BLUE: <i>Ein nützlich saff blow</i> (blue from clothlet), <i>lampersse blo wolle</i> (blue Lombardy wool coloured with indigo/woad)	Materials: blue wool shearings, strong ash lye, alum	Process to prepare a blue woolly pigment: Take blue wool shearings and put them in strong lye overnight before heating the mixture over a fire and bringing to a boil for a short period of time. Then add pulverised alum and mix. Then take wool and squeeze water out. The aqueous clothlet blue in the vessel is the final product to paint and embellish with. In this recipe it is not explicitly mentioned if the dissolved blue wool residue was discarded after the blue dye solution was squeezed out of it. The dissolved blue wool residue may still have been used as a lake pigment. This possibility cannot be ruled out.	Oltrögge D. Datenbank mittelalterlicher und frühneuzeitlicher kunsttechnologischer Rezepte in handschriftlicher Überlieferung. TH Köln – University of Applied Sciences Cologne, Institut für Restaurierungs- und Konservierungswissenschaften. https://www.th-koeln.de/kulturwissenschaften/kunsttechnologische-rezeptsammlung_25065.php . Accessed 23 January 2023.
Munich, Bayerische Staatsbibliothek, Cgm. 720 (<i>Bairisches Färbbüchlein</i>), Folio 226v–227r	Bavaria (Aldersbach), last quarter of fifteenth century	Two recipes = red and blue	RED: <i>parisrot</i> (Paris red), <i>rote scherwoll von mech/ischem tuch</i> (Red wool from Mechenen cloth) BLUE: <i>tunkel plaben endig</i> (dark blue indigo/woad), <i>tunkelplabe schwerwol vnd perait sey als di parisrot</i> (dark	Materials: ashes, lime, vinegar, rose water and fresh water, red wool, dark blue wool	Process to prepare a red woolly <i>parisrot</i> (Paris red): Boil ashes, lime, vinegar, rose water and fresh water together. Then take from the fire and add red wool before putting the mixture back on the fire and cooking it until the wool dissolves and becomes a thick mass. Then add pulverised alum and filter	Oltrögge D. Datenbank mittelalterlicher und frühneuzeitlicher kunsttechnologischer Rezepte in handschriftlicher Überlieferung. TH Köln – University of Applied Sciences Cologne, Institut für Restaurierungs- und Konservierungswissenschaften. https://www.th-koeln.de/kulturwissenschaften/kunsttechnologische-rezeptsammlung_25065.php . Accessed 23 January 2023.

Table 1 (continued) | Selection of fifteenth-century German recipes for red and blue lake pigments prepared from wool shearings

Document	Source and date of original text	Colour of pigment described	Historical terminology used for pigment in recipes with English translation	Materials described in recipe to make pigment	Preparation process described in recipe	Literature
Amberg, Staatliche Provinzialbibliothek, Ms. 77 (<i>Amberger Malerbüchlein</i>), folio 226 v	S. Germany (Bavaria), late fifteenth century (c. 1492)	Red	RED: <i>decoque abrasuram de scarlet</i> (red wool), <i>Parzrot</i> (Paris red)	blue wool and prepare it like Paris red [pigment])	everything through a cloth and let it drip until a red [fluid] comes out. Properly rid this mixture of impurities. Then pour the dissolved wool mass on a luke warm brick and then later grind it properly on a stone slab. Pour this colour in a [leather] skin and hang it up for 3 to 4 days. Then the colour becomes good. Process to prepare a blue woolly pigment dyed with woad/indigo: Prepare this pigment in the same way as the Paris red pigment. Then you have a good indigo colour.	Oltrogge D. Datenbank mittelalterlicher und frühneuzeitlicher kunsttechnologischer Rezepte in handschriftlicher Überlieferung, TH Köln – University of Applied Sciences Cologne, Institut für Restaurierungs- und Konservierungswissenschaften. https://www.th-koeln.de/kulturwissenschaften/kunsttechnologische-rezeptsammlung_25065.php. Accessed 23 January 2023.

red lake pigment is because it is easier to obtain a desired colour than from the raw material itself. The range of anthraquinones present in the root and the extraction method gives different hues; thus, by using already dyed textile material the most difficult step in the process has already been undertaken by the dyer¹⁷. A secondary reason is that this method could be considered more economical. It has been reported that various textile scraps could be combined, perhaps dyed with different dyestuffs^{18,19}. Mixed dyestuffs in a single pigment layer have therefore been used as confirmation of the connection between textiles and pigment manufacturing¹⁸. As indigotin is insoluble the use of the blue textile shearings was an easy option to obtain the pigment, therefore indigo dyed textiles were probably reused as pigment sources to reduce cost.

Although red lake pigments were infrequently used on large surfaces such as wall paintings, madder lakes were considerably cheaper than other types of red lakes (e.g., insect dye derived pigments) because it was native to Europe²⁰. Late fifteenth and early sixteenth-century pharmacy price lists from Munich (Germany) suggest that madder lakes were almost 40 times cheaper than lakes prepared from scale insects²¹.

Indigo is generally not recommended for mural painting on account of its inadequate light fastness²². Even so, Cennini recommends indigo for use on walls. He also suggests that the colour of azurite can be improved by the addition of woad²³. Indigo was commonly used in pigment mixtures, as it is naturally almost black in colour therefore other pigments were used in order to modify it. Recipes for mixed purples and blues containing indigo can be found on pages 100, 105, and 121 in the fourteenth-century *Liber diversarum artium*²⁴. Theophilus also mentions indigo for the use on walls in his treatise²⁵. It has been identified in wall paintings in Asia and India dating from the sixth to tenth century. In Europe, it has been identified in the Moritz Chapel in Freiberg Cathedral dating to 1560 and it was commonly used in English medieval wall painting from the thirteenth century onward¹⁸. The use of woad in wall paintings was rarely recorded but there is an entry in the fourteenth-century accounts of Countess Artois in France that could be interpreted as woad used for murals. The accounts mention both indigo from Bagdad and “inde” for use in interior decoration. The indigo is listed as seven times the price for “inde” and therefore “inde” has been interpreted as based on native species such as woad¹⁸.

The most common dyestuff for red lake pigments as well as for textiles in northern Europe during the late fifteenth century was the madder root, both cultivated and wild (*Rubia tinctorum* L. and *Rubia peregrina* L.)^{14,26}. In Sweden, wild plants of the same family (*Rubiaceae*) were also used for example, Northern bedstraw (*Galium boreale*) and Dyer's woodruff (*Asperula tinctoria* L.)²⁷. Madder root is believed to have been imported to Sweden from as early as the thirteenth century and during the fifteenth and sixteenth centuries the most frequently imported goods were luxurious textiles made of materials such as silk and wool²⁸. However, it should also be noted that customs documents show that dyestuffs were imported at this time as well²⁹.

Madder root contains 15 anthraquinone molecules capable of dyeing. These include alizarin, pseudopurpurin and purpurin³⁰. The anthraquinone compounds have different hues that vary between reds with an orangey tone to reds with a more pinkish hue which enables an extensive range of colours to be obtained from the root by variations in the dyeing process¹⁷. The root is cut or grinded into small pieces that are put into a water bath and the dye is extracted by soaking or boiling the mixture. After extraction, the remaining plant material is filtered off. The extracted dye can then be used for dyeing or for pigment making.

Blue dyes can be obtained from a number of plants but for medieval Europe woad (*Isatis tinctoria* L.) was the main source. It was cultivated on a large scale particularly in France, Germany and Italy where it was of considerable economic importance¹⁴. In fourteenth and fifteenth-century Germany, the growing and trading of woad for textile purposes was a flourishing business in around Erfurt and Cologne^{31,32}. Woad was not replaced until the sixteenth and seventeenth century by indigo (*Indigofera tinctoria* L.) imported from India and the far east. However, the indigo plant was probably the source for the solid indigotin used as a pigment in Europe

(due to its higher pigment content compared to woad) during and before the medieval times but its use as a dye was prohibited in much of Europe in order to protect the local woad trade. Chemically, there is little difference between the blue made from woad and the blue made from indigo and it has been reported that separating the two by analytical means is not possible. However, recent work by Laursen and Mouri has suggested that there are markers to differentiate these molecules (‘pseudoindirubin’)³³.

The colouring matter for these blue lakes is found in the leaves of *Isatis tinctoria* L. and *Indigofera tinctoria* L. in the form of soluble, colourless precursor glycosides. Woad contains three of these precursor glycosides, indican, isatan A and isatan B, which are converted by enzymatic hydrolysis to indoxyl. The indoxyl molecules are combined by air oxidation and forms indigotin¹⁴. Indigoids need to be converted into water-soluble form by fermentation before dyeing. After fermentation the paste of the leaves turns into a yellowish green. The textile can then be added. When it is removed from the bath and exposed to the air the reduced indigotin is reformed to its blue colour through oxidation. Blue indigotin is also formed on the surface of the dye bath and can be skimmed off and used as a pigment¹⁴.

Methods

The surface and stratigraphy of the wall paintings were examined with a set of complementary scientific examination techniques. The focus of this paper is on the characterisation of the unusual red and blue lake pigments present in the murals.

Macroscopic and microscopic observations

The investigation started with non-invasive scientific examination methods: technical photography with visible light, UV fluorescence photography and macro-photography. A Canon EOS 60D was used for both VIS and UVF images but with an addition of a Kodak Wratten 2E filter for UVF. The UV light has been provided by UVA Spot 400/T Blacklight Large area UV lamp (315–400 nm). All UVF images are unprocessed.

Macro-photographic documentation in situ of both the red and blue pigments was performed with a portable DINO Lite microscope model AM4013MT with 1,3 megapixels and up to 200x magnification. All macro images are unprocessed.

Light microscopic studies of the unmounted samples and the paint cross-sections of the red and blue lake were performed on an Olympus BX41 analytical microscope. A 100 W Halogen projection lamp provided normal reflected light in bright field and in dark field illumination. An Osram HBO 50 high-pressure mercury lamp and Olympus filters U-M11011v2 (excitation 355–425 nm, emission 470 nm) and U-MWB2 (excitation 460–490 nm, emission 520 nm) were used for UV fluorescence microscopy. Normal reflected light in bright field and in dark field illumination using an Olympus LED fluorescence excitation light source (range 365–635 nm) was used on the samples (labelled Blue1 and Blue2) where the blue fibrous pigment was present. The same Olympus UV filters were also used with this light source.

Sample description and preparation

Micro-samples were taken for analysis from the mural (see Table 2). Three of these samples (labelled Red1, Red2, and Red3) were prepared as paint cross-sections by mounting them in a 1-component methacrylate (Technovit 2000 LC, Heraeus Kulzer, Germany) that polymerizes under UVA light (315–400 nm). Two further samples were collected for analysis (labelled Blue1 and Blue2). Both samples were mounted in the light curing resin (CEM4000 Lightfix). After preliminary grinding with silicone-carbide (SiC) paper, the surfaces of all five paint cross-sections were dry polished with sheets (Micro-Mesh®) using grades 1800 through to 12,000.

Scanning electron microscopy coupled with energy dispersive X-ray microanalysis (SEM-EDX)

Cross-sections of the red and blue lake pigments were analysed with scanning electron microscopy coupled with energy dispersive X-ray microanalysis (SEM-EDX) in order to obtain elemental analysis of substrate and

Table 2 | Sampling areas of wall paintings in Härnevi church (Sweden)

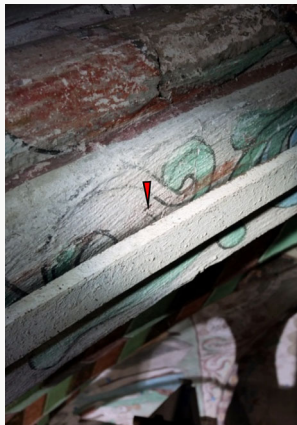
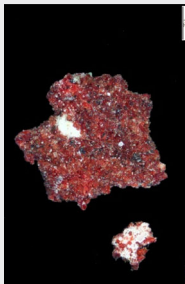
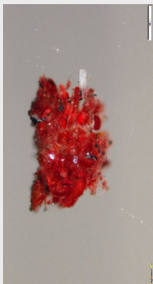
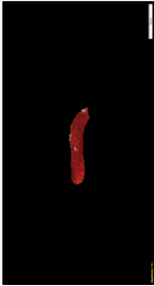
Table 2 Sampling areas of wall paintings in Härnevi church (Sweden)					
SAMPLE RED 1		Description, location	Analytical methods		
Sampling area, view of overall area	Sampling area, detail				
		Pigment sample Red 1. Dark red paint. Southern part of the triumphal arch. Decorative pattern with leaves.	Optical microscopy, FTIR, SEM-EDX, HPLC-DAD		
Sample 1 divided into					
				Type	Analysis performed
Loose pigment sample. Unmounted, 50x magnification (stacked)				Optical microscopy, HPLC-DAD	
		Isolated fibre sample Washed in H ₂ O, 100x magnification (stacked)	Optical microscopy, FTIR		
		Cross section, paint layer only Mounted, 100x magnification (stacked)	Optical microscopy, SEM-EDX		
SAMPLE RED 2		Description, location	Analytical methods		
Sampling area, view of overall area	Sampling area, detail				
		Pigment sample Red 2. Pink paint. Eastern part of the western vault. The crowning of Mary, drapery of blue garment with red lining.	Optical microscopy, FTIR, HPLC-DAD		

Table 2 (continued) | Sampling areas of wall paintings in Härnevi church (Sweden)

Sampling area, detail		Description, location	Analytical methods	
SAMPLE RED 2 Sampling area, view of overall area			Analytical methods	
Sample 2 divided into		Type	Analysis performed	
		Loose pigment sample Unmounted, 200x magnification (stacked)	Optical microscopy, HPLC-DAD	
		Isolated fibre sample. Washed in H ₂ O, 100x magnification (stacked)	Optical microscopy, FTIR	
Sampling area, detail		Description, location	Analytical methods	
SAMPLE RED 3 Sampling area, view of overall area			Analysis performed	
		Pigment sample Red 3. Pink paint. Eastern part of the western vault. The crowning of Mary, drapery of blue garment with red lining.	Optical microscopy, SEM-EDX, nano-LC-ESI-Q-TOF	
				
Sample 3		Type	Analysis performed	
		Cross section, paint layer, ground and plaster. Mounted, 100x magnification (stacked)	Optical microscopy, SEM-EDX, protein analysis by nano-LC-ESI-Q-TOF.	

SAMPLE BLUE 1 Sampling area, view of overall area		Sampling area, detail	Description, location	Analytical methods
			Pigment sample Blue 1. Pale blue paint. Southern part of the western vault. Image of God the Father and Christ, drapery on blue garment.	Optical microscopy, SEM-EDX, FTIR, Raman micro-spectroscopy
Sample 4 divided into			Type	Analysis performed
		Isolated blue fibre sample. Washed in H ₂ O, 200x magnification (stacked)		Optical microscopy, FTIR, Raman micro-spectroscopy
		Cross section, blue paint layer and ground. Mounted, 100x magnification (stacked)		Optical microscopy, SEM-EDX

mordant as well as possible presence of inorganic pigments within the layer build-up. Sample imaging and analysis with chemical mapping and spot analysis was conducted on polished paint cross sections with a ~20 nm carbon coating using a Carl Zeiss Sigma variable pressure field-emission-gun scanning electron microscope (VP-FEGSEM) equipped with an Oxford Instruments X-Max 80 mm² Silicon Drift Energy-dispersive Detector. Backscattered electron (BSE) imaging and Energy-dispersive X-ray Spectroscopy (EDX) were conducted in high vacuum using high current mode and accelerating voltage of 20 keV, working distance of 8.0 mm and aperture of 60 µm. EDX mapping data were acquired and processed using the Oxford Instrument Aztec software. All EDX maps shown have had the Aztec TruMap function applied, which removes background and artifacts, and resolves element peak overlap issues.

Fourier-transform infrared spectroscopy with attenuated total reflection (ATR-FTIR)

Fourier Transform Infrared Spectroscopy with attenuated total reflection (ATR-FTIR) was carried out using a Perkin Elmer Spectrum One FTIR Spectrometer with Spectrum software version 5.0.1 and fitted with a Universal ATR Sampling Accessory. The ATR crystal used was a diamond /thallium-bromide (C/KRS-5) with a penetration depth up to 2 µm. 32 accumulations were used at a resolution of 4 cm⁻¹. Individual red fibres were isolated from the loose pigment samples under stereomicroscope and washed on a glass depression slide. The fibres were initially washed in water (a small amount of alcohol was added to reduce water tension) to remove excess material. The water was allowed to evaporate, and the fibre transferred to a clean depression slide. Then it was washed in a solution of MeOH and 1 M HCl to remove the coating of lime and possibly traces of aluminium potassium sulphate. The washed and dried fibre was placed directly onto the ATR crystal. The recorded spectra from the Härnevi samples were compared with reference spectra from the database of aged silk and wool fibres. Individual fibres were also isolated from reconstructed madder lake pigment on a wool substrate as well as a cochineal lake on a silk substrate. These fibres were also analysed with ATR-FTIR.

Fourier transform infrared spectroscopy (FTIR) using Perkin Elmer Frontier FTIR spectrometer with Perkin Elmer Spectrum Spotlight 200 FTIR microscope and Specac diamond compression cell was used to identify the blue fibre substrate and the colourant. 16 accumulations at transmission mode were used. The aperture window ranged between 20 × 20 µm and 100 × 100 µm. Scan range between 4000 cm⁻¹ and 600 cm⁻¹. Individual blue fibres were isolated from the pigment samples and washed in water with a small amount of alcohol according to the method described for the red pigment fibres. The washed fibre was placed in the glass depression slide. The recorded spectra were compared with reference spectra of aged blue wool fibres and indigo.

Raman micro-spectroscopy

Raman micro-spectroscopy was used for the verification of the indigo component in the blue fibre sample. Measurements were carried out with a BWTek i Raman Plus coupled with a with BWTek optical microscope. The spectra were recorded at 40× magnification using a 785 nm (λ₀) near-infrared diode laser. Acquisition time was an average of 6 s with the laser operating at 100% of its maximum power (495 mW) and an integration time of 2000 ms. The scan range was between 0 cm⁻¹ to 4000 cm⁻¹. Raman shift and baseline correction were employed.

A reference spectrum of natural indigo from L. Cornelissen & Son (London) was used for comparison. Raman spectra of the reference sample were obtained using an inVia™ Confocal Raman Microscope (Renishaw, Wotton-under-Edge, Gloucestershire, UK). The spectra were recorded at 50× magnification with a 785 nm (λ₀) near-infrared diode laser. Raman spectra were obtained with a 15 s exposure on the sample with a scan range between 0 cm⁻¹ and 4000 cm⁻¹. A 1200 L/mm (633/780) diffraction grating was used to measure the Stokes Raman scattering. The laser was operated at 0.05% of its maximum power, ensuring that the sample was not overexposed

and damaged by the laser source during scanning. Raman shift and baseline correction were employed.

High-performance liquid chromatography with diode array detection (HPLC-DAD)

The dyestuff in the loose pigment samples was analysed using a gradient high pressure chromatography (HPLC) system with a UV diode array detector. The Merck-Hitachi HPLC system comprised: L-7200 auto-sampler, L-7100 gradient pump, Jones Chromatography Genesis C18 4 µm 250 by 4.6 mm column, L-7350 column oven, L-4500 diode array detector and L-7000 HPLC system manager software. A multi-step extraction approach was employed. The first extraction of the dyestuff was made with 200 microliters MeOH 50% + 0.1 M HCl. The samples were then placed into a water bath of 80 °C for 30 min. After the dye had been extracted the sample solution was filtered and the filtered extract analysed in the HPLC. The second extraction was made from the residue from the first extraction. This time 200 microliter extraction fluid of MHCl + 50% MeOH was used. The sample was placed in a water bat of 90 °C for 30 min and then filtered and analysed with HPLC.

Nano-liquid chromatography coupled to electrospray quadrupole time-of-flight mass spectrometer (nano-LC-ESI-Q-TOF)

The binding media analysis of the cross sections and a loose sample was carried out using nano-liquid chromatography coupled to electrospray quadrupole time-of-flight mass spectrometer (nano-LC-ESI-Q-TOF). 40 µL of 50 mM NH₄HCO₃ containing approximately 10 µg/mL of trypsin was applied to the samples and let to react at room temperature for 2 h. After the trypsin digestion, the solutions were taken from the surfaces and purified on reverse phase C18 (ZipTip). After equilibrating, binding and washing steps, target compounds were desorbed from the stationary phase. The solutions were consequently used for analysis. Measurement was carried out using Dionex UHPLC Dionex Ultimate3000 RSLC nano connected with mass spectrometer Bruker ESI-Q-TOF Maxis Impact. 10 µL of peptide solution were previously dried and then dissolved in 97:3:0.1% mixture of water:acetonitrile:formic acid. Consequently, they were loaded on trap column Acclaim PepMap 100 C18 (100 µm × 2 cm, size of reverse phase particles 5 µm, Dionex with flow rate of mobile phase A 5 µL/min for 5 min. The peptides were eluted from trap column to analytical column Acclaim PepMap RSLC C18 (75 µm × 250 mm, size of reverse phase particles 2 µm) using following gradient: 0 min 3% B, 5 min 3% B, 85 min 50% B, 86 min 90% B, 95 min 90% B, 96 min 3% B, 110 min 3% B. Mobile phase A was 0.1% formic acid in water and mobile phase B was 0.1% formic acid in acetonitrile. The flow rate during gradient separation was set to 0.3 µL/min. Peptides were eluted directly to the ESI source – Captive spray (Bruker Daltonics). Measurement was carried out in positive ion mode with precursor selection in the range of 400–2200 Da; from each MS spectrum up to ten precursors were selected for fragmentation. Peak lists were extracted from raw data by Data Analysis (Bruker Daltonics). Proteins were identified using Mascot version 2.2.04 (Matrix Science) by searching protein database Uniprot version 20110-12. Parameters for database search were set as follows: oxidation of methionine and hydroxylation of proline as variable modifications, tolerance 50 ppm in MS mode and 0.05 Da in MS/MS mode.

Results and discussion

Two types of fragmentarily preserved pigments with characteristic elongated fibres have been observed in the wall paintings, one red and one blue pigment. The red pigment is usually painted in two layers on garments, one pink followed by a deep red layer. In floral decorations it has been painted in only one thick layer. The blue pigment is even more fragmentarily preserved but seems to have been painted in one layer and has been mixed with another blue pigment and the same red lake pigment to obtain a purple hue. Both lake pigments were investigated with optical microscopy, UV fluorescence microscopy, scanning electron microscopy coupled with energy-dispersive X-ray microanalysis (SEM-EDX), Fourier transform infrared spectroscopy with attenuated total reflection (ATR-FTIR) and high-

performance liquid chromatography coupled with diode array detection (HPLC-DAD). In addition, Raman micro-spectroscopy was employed to analyse the fibrous blue lake pigment (see Table 3, summary of analytical findings).

Red lake

Scientific analysis with optical microscopy, SEM-EDX, and ATR-FTIR resulted in a better understanding of the layer stratigraphy and the composition of each layer as well as the specific particle morphology of the red lake pigments (Fig. 2a (i-iii)). The results for the mortar show a high lime content in relation to the aggregate which is quite small in particle size. On top of the mortar is a layer of lime slurry that has been applied generously. The ATR-FTIR results also show the presence of dolomite ($\text{CaMg}(\text{CO}_3)_2$), which was also confirmed with element mapping. All techniques show that the pink layer is a mixture of the fibrous red lake and a calcium-rich substance. The calcium-rich substance is probably chalk and not gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) because of the low sulphur content (see also discussion of blue pigment below). Red lake pigments are sensitive to the alkalinity of lime, therefore the admixture of chalk that has a lower pH is more likely. The red layer on top of the pink layer has not been mixed with any other pigment according to the SEM-EDX analysis. Figure 3a, b demonstrate this clearly through the microscopic investigations where a darker red layer from the drapery is shown.

Investigations on mounted and unmounted samples with optical microscopy and scanning electron microscopy (SE and BSE images) resulted in a better understanding of the morphology of the fibrous pigment as well as aspects such as the diameter of the red and blue pigment which can indicate the type of fibre used. The lake pigment fibres (particles) appear often large and irregular in shape with ragged edges, something that is consistent with previous studies of this kind of pigment¹³. Due to the heavy degradation of the fibres it was not possible to use the traditional microscopic techniques to visualise scales which are characteristic of wools. The approximate diameter of the different fibres (particles) varied between 15–27 μm (some fibres as thick as 40 μm) which corresponds to wool and not silk which is thinner³⁴. Under ultraviolet (UV) light the red particles in both mounted and unmounted samples exhibit a very noticeable orangey red fluorescence typical of madder lake pigments (Fig. 2a(ii)).

Elemental analysis with SEM-EDX (spot analysis and element mapping) of the pigment layer shows that aluminium, sulphur, magnesium, silicon, copper, chlorine and potassium are present in the fibrous particles (layers 3 and 4). The single element maps for aluminium and sulphur show very similar and clear results for the fibrous pigment. Therefore, it is difficult to deduce that the sulphur detected here can be solely associated with the molecular structure of wool as has been suggested in other research on woolly lake pigments^{14,35}. In the woolly lake pigment analysed here the presence of both aluminium and sulphur is more likely to be associated with potash alum [$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] (Fig. 4a, b). This finding is not unusual given the use of alum for the dyeing of wool fibres and the grinding of the jelly-like product (dissolved fibres) with alum on a stone slab which is described in some fifteenth and sixteenth-century German recipes, forming the red and blue pigment (see Table 1). However, it is also acknowledged that the sulphur detected could also include that from the wool keratin (the sulphur content of wool varies between 2 and 5%). Calcium and oxygen associated with the presence of lime or chalk was found in layer 3, whereas in layer 2 (slurry) magnesium was found in addition to these. Interesting is also the marked proportion of magnesium in all analysed particles but this is likely due to the presence of dolomite in the final slurry layer (see Supplementary Fig. 5). Noteworthy are also the small amounts of copper in all particles which could have its origin in the raw madder root, where trace amounts are present, but a more likely explanation is that the presence comes from the preparation of the wool where a copper or brass vat (vats often referred to as ‘coppers’) or utensil was used in the dyeing process³⁶. This is supported by an early sixteenth-century coloured ink drawing from the Hausbuch der Landauerschen Zwölfbrüderhausstiftung (Nuremberg, Germany) which shows a man dyeing blue and red wool in what seems to be

Table 3 | Summary of analytical findings

SAMPLES	SEM-EDX	ATR-FTIR	Raman micro-spectroscopy	High Pressure Liquid Chromatography (HPLC-DAD)	Nano-LC-ESI-Q-TOF
CS1 (Red1) mortar/slurry	Lime, feldspar (aggregate) The presence of Si, Al and Na indicates the use of feldspar as an aggregate	Dolomite	-	-	-
CS1 (Red1) fibrous pigment	-	Wool	-	Alizarin, purpurin, small amount munjistin	-
CS2 (Red2) fibrous pigment	Alum	Wool	-	Alizarin, purpurin, small amount munjistin	-
CS3 (Red3) fibrous pigment	Alum	-	-	-	Animal glue, egg protein, keratin most likely from wool *Analysis by Stepanka Kuckova, University of Chemistry and Technology, Prague, Czech Republic
CS26 (Blue 1)	Alum (blue fibre), blue copper pigment	Wool, woad/indigo *Analysis by Swedish National Heritage Board, Visby, Sweden	Woad/indigo *Analysis by Swedish National Heritage Board, Visby, Sweden).	-	-
CS27 (Blue2) mortar	Mixture (lime and dolomite)	Dolomite	-	-	-
CS27 (Blue 2) fibrous pigment	Alum (blue fibre), blue copper pigment	Wool	-	-	-

*Unless otherwise specified all the analysis was carried out at the University of Glasgow (Centre for Textile Conservation and Technical Art History / Kelvin Centre for Conservation and Cultural Heritage Research / Geoscientific Electron Microscopy and Spectroscopy GEMS facility).

Fig. 3 | Results of optical microscopy and SEM on Sample Red 1. a Sample Red 1 embedded paint cross section, optical microscopy. **a** shows the light microscopic image (layer 4) of the top darker red paint layer (red glaze) with the fibrous red lake pigment. **b** Sample Red 1 embedded paint cross section, SEM-EDX. **b** shows the backscatter electron image (layer 4) of the same area of the top darker red paint layer (red glaze) with the fibrous red lake pigment.

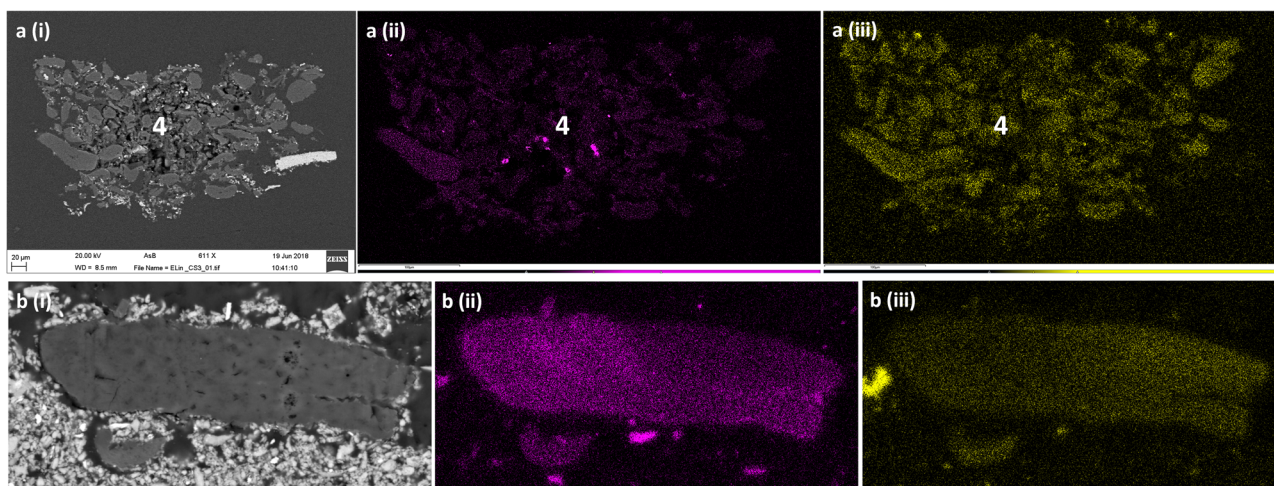
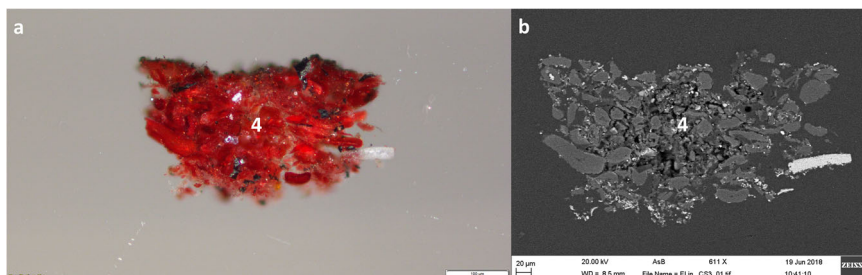


Fig. 4 | Results of SEM-EDX on Sample Red 1. a SEM-EDX of Sample Red 1. **a**(i) shows the backscatter electron image with the fibrous red lake pigment. **a**(ii) and **a**(iii) shows the element maps for aluminium and sulphur. **b** SEM-EDX of Sample

Blue 1. **b**(i) shows the backscatter electron image with the fibrous blue lake pigment. **b**(ii), (iii) show the element maps for aluminium and sulphur.

a copper vat (see Supplementary Fig. 1). A similar amount of copper was also determined in a fibrous pigment produced from textile shearings (colourant most likely madder) used to tint the original red glaze on Christ's lips of the Holy Blood Altarpiece (dated 1499–1505) by Tilman Riemenschneider and his workshop in Rothenburg o. d. Tauber, Germany (see Supplementary Table 1).

The pigment substrate has been identified as wool. The FTIR spectra shows organic sulphur at 1040 cm^{-1} . The amide I band for wool is at 1635 cm^{-1} while for degraded silk it is closer to 1600 cm^{-1} (Fig. 5a, b)³⁷. This molecular information was used to determine that the pigment substrate is wool and not silk.

From the HPLC analysis, chromatograms show peaks of alizarin, purpurin and a small amount of munjistin (Fig. 6a, b). Extraction with 0.1 M HCl in 50% methanol produced 3 peaks which were identified on the basis of their retention time (Fig. 6a) and confirmed from their UV-visible spectra by comparison with library spectra. The UV spectra of extracted dyestuff confirm the molecules of each of these components (see Supplementary Fig. 6). The small peak at 9.5 min produced a weak and noisy spectrum with a 66.7% match to munjistin. Peak 2 at 12.4 min gave a 99.3% match to alizarin and peak 3 at 14.4 min a 99.7% match to purpurin. The second extraction (Fig. 6b) with 1 M HCl in 50% methanol produced 2 smaller peaks for alizarin and purpurin. This shows that the pigment has a natural plant-based source.

Madder (*Rubia tinctorum* L.), wild madder (*Rubia peregrina* L.), Indian madder (*Rubia cordifolia* L.), dyer's woodruff (*Asperula tinctoria* L.) and northern bedstraw (*Galium boreale* L.) all contain these anthraquinones^{30,38}. Previous research on these types of pigments made by Kirby et al.¹⁷ has concluded that extraction of the dye with stronger alkali

results in greater amounts of alizarin and purpurin¹⁷. The pigment found in Härnevi has a high degree of undissolved fibres and the alkali must therefore have been relatively weak, and this might be the reason for the low alizarin content that was detected. However, it has been reported that the high level of percentage variations can also be an explanation. The same study on madder lakes of the fifteenth to seventeenth centuries revealed that most samples fell within the range 30–65% alizarin and 35–70% purpurin¹⁷. Based on the analysis and findings reported in the literature, the result has been interpreted as being most likely madder (*Rubia tinctorum* L.). This is also supported by the strong orange-red fluorescence of the fibrous red lake pigment under ultraviolet (UV) light visible in the paint cross sections which is characteristic of madder lakes³⁹.

Red lake pigments prepared from textile shearings have previously been identified on early fifteenth to early sixteenth-century panel paintings and polychromed wooden sculptures from Sweden, Germany, Austria, The Netherlands and Belgium [refs. 17,32,40–42; see Supplementary Table 1]. To the authors' knowledge this type of fibrous pigment has only been observed once before in early fourteenth-century wall paintings in Frankfurt Cathedral (Germany) although scientific analysis still needs to be carried out on the red pigment used in this specific mural⁴³. The workshop of Albertus Pictor seems to have been using this type of pigment frequently. Similar red pigments with a fibrous character have recently been found on other Swedish murals by the workshop such as in the churches of Kumla, Täby and Almunge among others although in these murals the pigments have been identified only by macro photography using a portable microscope (see Supplementary Table 1). It is interesting to note that in 1993 Nord and Tronner already analysed a fragmentarily preserved red organic pigment from the murals in Täby church⁴⁴. The result of the analysis was inconclusive

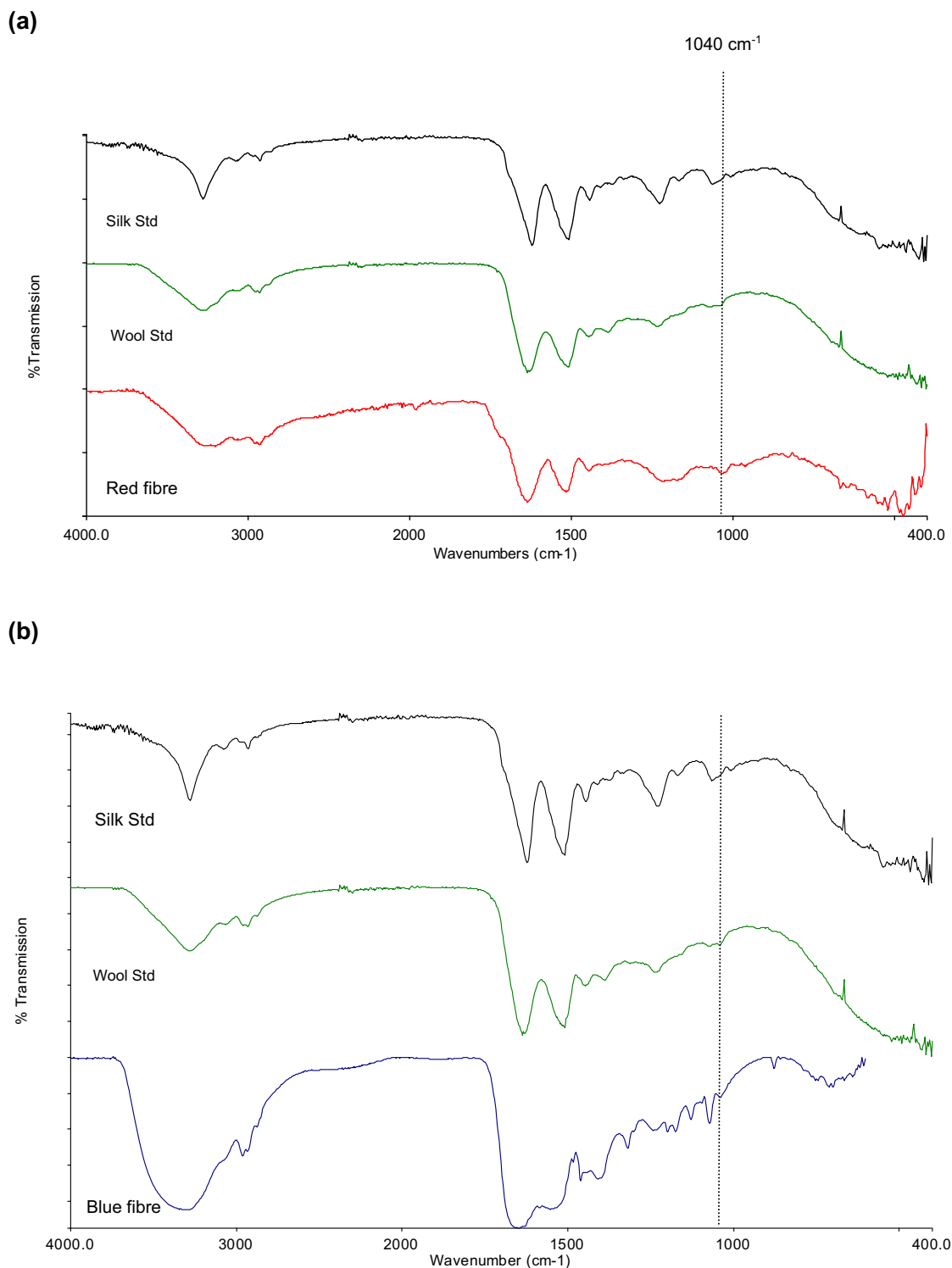


Fig. 5 | Results of analysis with ATR-FTIR. a FTIR spectrum of red fibrous pigment shows organic sulphur at 1040 cm^{-1} . **b** FTIR spectrum of blue fibrous pigment shows organic sulphur at 1040 cm^{-1} .

but the dyestuff was interpreted as more likely to be brazilwood than madder, kermes or cochineal¹².

Previous researchers have not been able to identify both the dyestuff and the substrate of this pigment on a wall painting. Helen Howard became the first to identify red lake dyestuffs in English medieval wall paintings in the late 1990's. Howard also identified kermes and brazilwood lakes in the same paint layer in fourteenth-century wall paintings in the Chapter house of Westminster Abbey. Due to the mixture of dyes in the same layer, the

pigment was interpreted as based on textile shearings from textiles coloured with different dyestuffs¹⁸.

The paint binders were identified as animal glue and egg using nano-LC-ESI-Q-TOF as described in the methods section. The analysed cross section showed both bovine collagen and ovalbumin. The protein analyses further supported the manufacturing from wool shearings as keratin from sheep was also found in the cross-section sample. The binder might have served as protection for the pigment from the caustic environment.

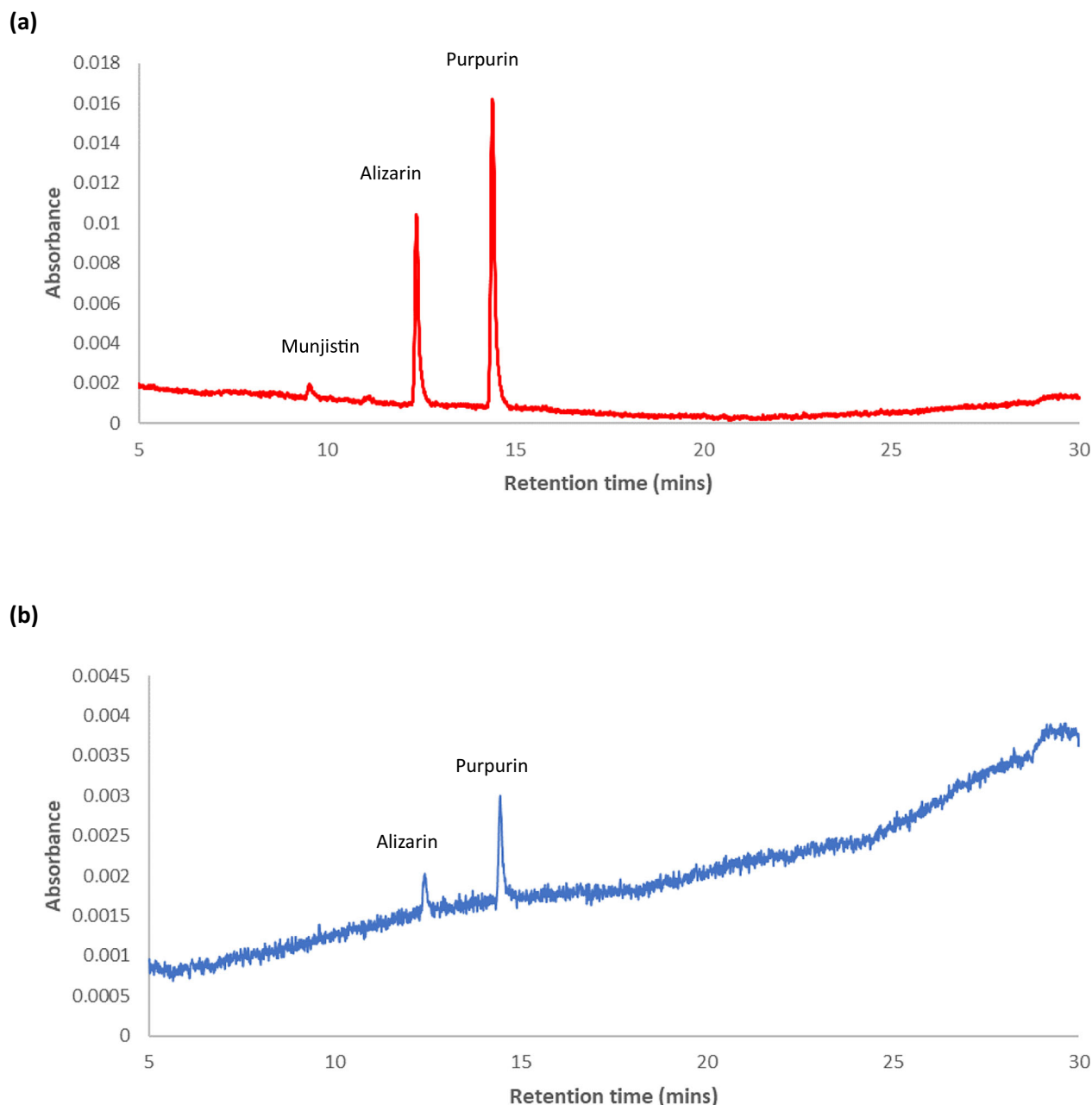


Fig. 6 | Results of analysis with HPLC-DAD. a, b HPLC chromatograms for samples Red1 and Red2 showing the presence of munjistin, alizarin and purpurin (see also UV-VIS spectra in Supplementary).

Contemporary historical documentary sources such as the fourteenth-century *Liber diversarum arcium* recommend that pigments sensitive to lime should be tempered with egg yolk to protect them²⁴.

Blue lake

Analysis of the cross sections by SEM-EDX shows that the blue fibrous lake pigment has been mixed with a finely ground blue copper-containing pigment (Fig. 2b (i-iii)) and a calcium-rich substance to create a pale blue paint. The calcium-rich substance is probably chalk of marine origin due to the presence of microfossils. The presence of copper in the light blue particles as well as the information gathered from optical microscopy suggests the use of azurite $[\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2]$.

The pigment substrate of the blue lake has been identified as wool. The FTIR spectrum for the fibres showed a typical spectrum for protein with amide A and N-H stretching at 3292 cm^{-1} , amide I (primarily C=O stretching of polypeptide chains) at 1646 cm^{-1} , amide II (N-H bending and

C-N stretching) at 1546 cm^{-1} , CH_2 vibrations (scissoring) at 1410 cm^{-1} and amide III (NH, CN and CC vibrations) around 1228 cm^{-1} , as well as peptide C-C stretching at 1065 cm^{-1} . The proteinaceous composition together with the fibre diameters observed in situ and with the aid of optical microscopy clearly indicate that the fibrous particles are wool³⁵.

The Raman analysis (Fig. 7) showed the peaks associated with indigotin, the colour component of both woad (*Isatis tinctoria* L.) and indigo (*Indigofera tinctoria* L.). Baran et al.⁴⁵ reported that the most intense signal of the ring stretching mode is observed near 1571 cm^{-1} with a pronounced shoulder at 1581 cm^{-1} due to the stretching vibrations of the conjugated system of C=C, C=O and N-H groups⁴⁵. The vibration of this conjugated system gives rise also to bands near 1700 , 1622 , and 1363 cm^{-1} . The band attributed to rocking vibrations of N-H groups is observed at about 1224 cm^{-1} . Vibrations involving C-H rocking are recognized at 1481 , 1459 , and 1247 cm^{-1} whereas the vibrations of five- and six membered rings are identified at 1309 , 1014 , 756 , and 674 cm^{-1} . The differentiation between

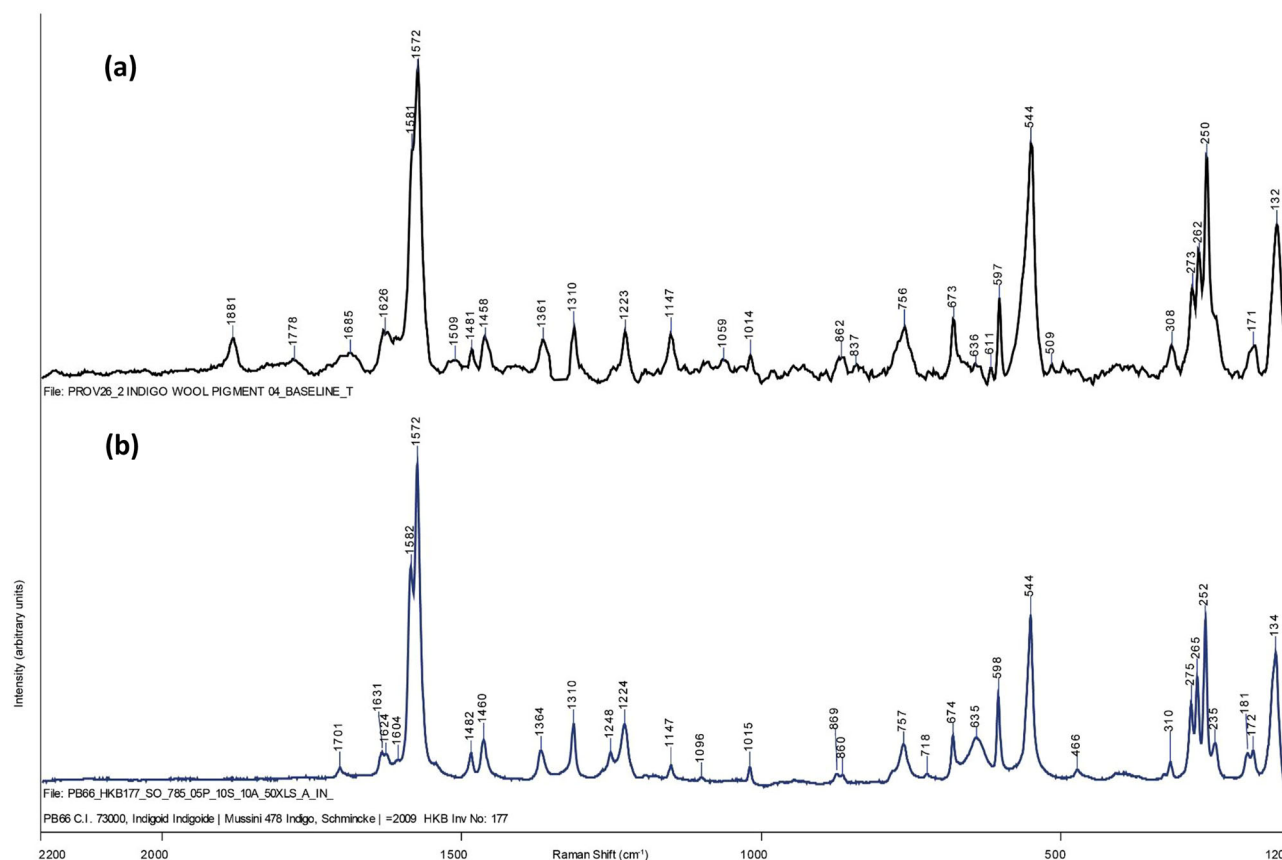


Fig. 7 | Results of analysis with Raman micro-spectroscopy. Raman analysis of blue fibrous pigment from Sample Blue 1 (Spectrum ‘a’) and a reference sample of genuine indigo from L. Cornelissen & Son, London (Spectrum ‘b’) for comparison.

indigo and woad was not attempted, however, the early date of the wall painting, c. 1480, means that the origin of the dye is most likely from woad.

It is possible that the woad/indigo lake was originally purple or blue with a violet cast judging from the mixture of colours, the fact that it has only been found on the garments of Christ who is commonly associated with blue and purple in medieval iconography further supports this interpretation⁴⁶. However, since the pigment and paint is so fragmentarily preserved it is not possible to say for sure what the original colour might have been.

Interdisciplinary collaboration using the methodology of technical art history and a combination of analytical techniques have enabled us to characterise unusual and complex red and blue fibrous lake pigments which were intentionally used to enhance and nuance the colour scheme of specific areas of the wall paintings by Albertus Pictor and his workshop in Härnevi church (Sweden). It was determined that the fibrous pigments found in the murals are made from degraded wool shearings which have been dyed with madder root and woad or indigo. The blue lake pigment has also been mixed with the some of the madder lake and finely ground azurite resulting in a mauve colour, which would be supported from an iconographic perspective as Christ’s robe was either purple or blue.

The chemistry of these pigments is very complex and required a powerful suite of analytical techniques to fully understand their properties and chemical composition. This included optical microscopy, UV fluorescence microscopy, scanning electron microscopy coupled with energy-dispersive X-ray analysis (SEM-EDX), Fourier transform infrared spectroscopy with attenuated total reflection (ATR-FTIR), high-performance liquid chromatography coupled with diode array detection (HPLC-DAD) and Raman micro-spectroscopy. Through the analysis, insights were also gained on the preparation of this pigment. For example, the presence of copper being due to the use of copper vessels for the dyeing process and not solely a possible pigment such as azurite. This is especially clear with the red lake pigment. Another feature is the importance of understanding why

certain elements have been detected in marked quantities. The presence of aluminium and sulphur combined with the art-technological primary sources allowed us to identify the presence of alum in the final pigment used.

Here the access to the samples from the murals in Härnevi church enabled us to develop a methodology to thoroughly investigate the materials used by this painter and his workshop. The pigment identifications were realised using a suite of elemental and molecular techniques in order to report robust findings of both the origin and use of the red and blue pigments. More specifically, the historical pigment preparation method used was identified through the use of material science analysis combined with insights gained from the study of contemporary art-technological recipes from appropriate primary sources. Previous studies reported the presence of sulphur to be associated with wool. The FTIR analysis proved conclusively that the fibrous material was wool and a small proportion of the sulphur in the fibres is likely to have contributed in a small way to the proportion determined in the elemental analysis.

However, the identification of both aluminium and sulphur in both the red and blue lake particles using SEM-EDX confirmed that the pigment making process used alum in the final stage after the semi-degradation of the fibres. We also report for the first time the conclusive identification of a blue woolly lake pigment, which is a completely new pigment to the palette not only for the workshop of Albertus Pictor but for the medieval painter in northern Europe in general.

In this study, we have established criteria for the identification of woolly lake pigments used in wall paintings. It is likely that these pigments have been used more extensively in painting and polychromy than has been currently reported. This comprehensive approach has led to new findings in this understudied area of sacred art in churches of northern Europe.

The technical details of the execution of wall paintings in Sweden and in northern Europe in general are still not fully understood. Detailed knowledge about the materials and techniques used in the making of an

artwork contributes to understanding about the processes of deterioration and it is essential when deciding upon compatible conservation interventions.

Data availability

Data available on request due to restrictions e.g., privacy or ethical. The data presented in this study are available on request from the corresponding author.

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Author contributions

Idea for project: E.L.; scientific analysis: M.S., M.R., and E.L.; Interpretation of results: M.S. and M.R.; Writing and review: M.R. and M.S. with comments from E.L.; preparation of manuscript and figures: M.R. and M.S.; funding, acquisition: E.L. and M.R.; All authors read and approved the final manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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