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Special Issue Reprint

Dyes in History and Archaeology 42

Edited by
Jo Kirby, Cecilie Brøns, Annemette Bruselius Scharff, Joanne Dyer,
Regina Hofmann-de Keijzer, Paula Nabais and Sara Norrehed

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Preface

This Special Issue of Heritage features contributions from the conference DHA42, held in the autumn of 2023. Dyes in History and Archaeology – DHA – is an annual international conference that focuses on the academic discussion of dyes and organic pigments used in the past. Every year since 1982, this meeting has united conservators, curators, art historians, scientists, academics, artists and craftspeople from museums, universities, research centres and other institutions. The aim is to bring these specialists together in order to investigate the history, production, application and properties of organic colourants, as well as their analytical characterisation and identification: the broad, interdisciplinary approach is of fundamental importance and the strength of these conferences. The focus is often on textiles, but it can also centre on other substrates, as well as on the use of dyes in pigment form on painted surfaces, or as inks.

The 42nd annual meeting was hosted in Copenhagen by the University of Copenhagen in collaboration with the National Museum of Denmark, the Centre for Textile Research (CTR), the Ny Carlsberg Glyptotek, and the Danish School of Conservation. Delegates, both in-person and online, were treated to a programme of papers and poster presentations over three days, together with a full day of guided visits to the National Museum of Denmark, the Glyptotek, Rosenborg Castle and David's Collection. Ten of the papers presented are included in this Reprint and the variety of subjects discussed gives a flavour of the very special ambience of DHA meetings. We are particularly grateful to the principal organisers of the meeting, Eva Andersson Strand, Annemette Bruselius Scharff, Cecilie Brøns and Ulla Mannering, together with all their colleagues, who made the delegates so welcome in a relaxed and friendly atmosphere.

Jo Kirby, Cecilie Brøns, Annemette Bruselius Scharff, Joanne Dyer, Regina Hofmann-de Keijzer, and Paula Nabais

Guest Editors

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Editorial

Dyes in History and Archaeology 42: Reflections on the Conference and Its Collection of Articles

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1. Introduction

This is the second of the Dyes in History and Archaeology series of conference papers to be published as a Special Issue of *Heritage*; as before, its focus is on the use of dyes extracted from naturally occurring sources or early synthetic dyes. While we tend to think of dyes primarily as textile colourants, they were also used to colour other substrates, including leather, wood, bone and paper; as inks; and, when converted into a solid form, as pigments. As the conferences attract participants from a wide range of subject fields—archaeologists, conservators, historians, museum curators, scientists, interested craftspeople and academics of all descriptions—the topics discussed are also broad in scope. However, the emphasis and heart of the discussions is always on the history of the dyes and not on their modern application.

2. The Conference in Copenhagen

The 42nd Dyes in History and Archaeology conference was held in Copenhagen, Denmark, the second to be held in Scandinavia, from 31 October to 2 November 2023, followed by a day of visits on 3 November. Our hosts were the Centre for Textile Research (CTR), University of Copenhagen, in collaboration with the National Museum of Denmark, the Ny Carlsberg Glyptotek and the Royal Danish Academy, Institute of Conservation. The conference itself took place across two centres, the Royal Danish Academy and the Centre for Textile Research, based in the University of Copenhagen. This, together with the reception at the Institute of Conservation (Figures 1 and 2), part of the Royal Danish Academy but a short distance away by foot or on one of the harbour buses, enabled delegates to see much of the city and the harbour area very easily. The sights they may have seen as they moved between different venues are reflected in the illustrations in this Editorial.

Figure 1. The Institute of Conservation, Royal Danish Academy, Copenhagen. Photograph: Mikkel Scharff.

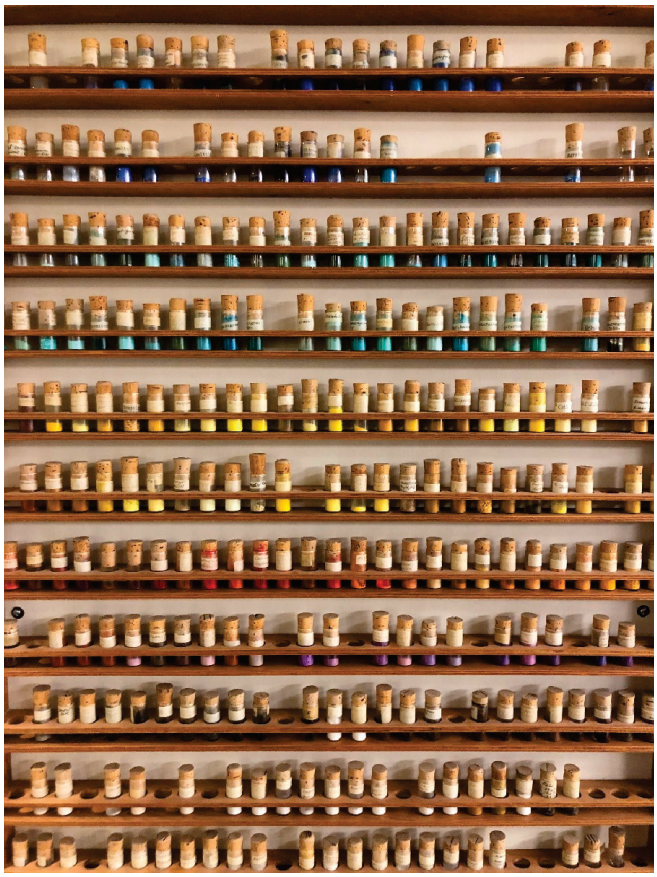

Figure 2. Collection of pigment samples, Institute of Conservation. Photograph: Cecilie Brøns.

Following the conference, delegates visiting the Ny Carlsberg Glyptotek had the luxury of being guided through the polychromy of Roman encaustic paintings, while those visiting the National Museum of Denmark looked even further into the past at an archaeological textile, now discoloured, but still showing the ancient, checked pattern. Visits to Rosenborg Castle (Figures 3 and 4), built in the seventeenth century by King Christian IV, and the David Collection, with its collections of Islamic art, porcelain, and Danish Golden Age paintings, represented more recent history, but all had some links with papers presented during the conference itself.

Figure 3. View of Rosenborg Castle, built by King Christian IV between 1608 and 1624, in Kongens Have ('the King's Garden'), Copenhagen. Photograph: Mikkel Scharff.

Figure 4. The Winter Room in Rosenborg Castle, used by Christian IV as an audience room, was linked by hidden audio channels to a room in the basement below where musicians played. The paintings incorporated in the panelling (completed in about 1620) were purchased in Antwerp. Photograph: Mikkel Scharff.

The subjects discussed during the conference included tapestries and waistcoats; blue dyes and red dyes; dyes on unusual substrates; medieval dyeing and eighteenth-century sources on dyeing (Figure 5); archaeological textiles; and early Modern fashion. The scope was broadened by the posters on display, which included topics such as textiles in a buried early medieval hoard in Scotland, late Iron Age children's clothing in Finland, and the logwood ink used by the painter Vincent van Gogh in France. Delegates had ample opportunity to study these during breaks and the dedicated poster sessions, so were able to discuss the contents with the authors. This broad range of subjects is typical of Dyes in History and Archaeology conferences, which foster questions, possible answers, and lively debate. (The book of abstracts is available at https://www.dyesinhistoryandarchaeology.com/past-meetings.php, accessed on 15 July 2025.)

Figure 5. Wool fabrics displayed during the conference dyed according to recipes in the workbook by Dominique Cardon and Iris Bremaud, *Les 157 couleurs de Paul Gout*, published in January 2023, which was itself based on Dominique Cardon's critical edition of Gout's manuscript *Mémoires de teinture* (Paris, CNRS Éditions, 2013). Photograph: Regina Hofmann-de Keijzer.

3. Survey of the Articles in This Special Issue

The ten papers included in this Special Issue are representative of this variety of topics. In addition, they reveal some interesting trends. One is the discussion of dyes used on substrates that are not textiles; another is the study of textiles that are not the most expensive or precious but were owned by middle-class people or peasants. A third is the surprising amount of information that can be gathered about dyes used on artefacts, even when valuable invasive techniques such as high-performance liquid chromatography linked to diode array or mass spectrometric detection (HPLC-PDA or HPLC-MS) are unavailable. However, perhaps the most significant of these trends is the ethical connection or conflict between modern investigation methods and traditional practices. This has been recognised and increasingly handled with tact and delicacy in the museum and conservation communities for some time, but is less well known to many research workers, including scientists, in other disciplines. An example is the desire to study dyes used by an indigenous people and with a long history that may still be in use today but are poorly understood or, indeed, unknown to researchers outside those communities. Tantalising for a research team—but how should they handle such a situation?

This was the state of affairs facing Thiago Sevilhano Puglieri and Laura Maccarelli in their study of the blue pigments used in the decoration of masks used by the Tikuna/Magüta people of the Amazon forest as part of female initiation rituals [1]. The use of a blue plant colourant had been mentioned by an ethnologist working with the Tikuna/Magüta people in the 1940s, but scientific examination of masks dating from this period, with the permission of this community, only identified inorganic blue pigments

and indigo, all widely available during this decade. The authors were very aware of the great cultural importance of colour and its use to the Tikuna/Magüta people, perhaps particularly blue, a colour which has an almost universal significance. They were also very sensitive to the fact that community engagement and participation in any research carried out were absolutely essential; the balance of the Tikuna/Magüta people with their surroundings must not be compromised, and their permission was obtained before any results were published. The authors decided to proceed with further study through community-based participatory research, whereby the community are fully involved with the project from the design of the research to the dissemination of the results, and their spiritual and cultural needs are given priority rather than the immediate research priorities of the scientists. Both parties benefit from such an approach.

At first sight, the investigation carried out by Elisa Palomino and co-authors might appear somewhat similar to the study of the aforementioned unknown blue pigment in that they were examining a practice that is poorly known in general: the dyeing of fish skins, or fish leather [2]. However, these materials have been used and dyed by local populations in Arctic regions of Alaska, Siberia, Northeast China, Northern Japan, Scandinavia and Iceland for centuries and are still used today. The skins are tanned using naturally occurring materials such as galls or barks, or industrially using chromium-containing agents or industrial vegetable tanning. A survey by the authors across these regions revealed the use of a great variety of plant and lichen dyes to give a range of colours, particularly browns, greens, golds and yellows, but also pinks and purplish colours. A wider range of colours was found in Northern Japan, where sources of indigo blue, sappanwood reds or pinks, and lac dye pinks and purples were available. The results suggest that traditional tanning and dyeing techniques (not only for fish leather) could provide environmentally friendly and sustainable alternatives to industrial production methods if suitably adapted.

Fish skin is one of the more unusual dyeing substrates discussed in Copenhagen; the other is perhaps a little better known: feathers. Renée Riedler, from the Weltmuseum Wien in Vienna, along with colleagues from Vienna and Mexico, discusses an unusual project in which the National Museum of Anthropology in Mexico City wished to commission a replica of a rare sixteenth-century featherwork insignia in the Weltmuseum Wien collection [3]. The replica, needed for didactic purposes, was to be as close to the original as possible, bearing in mind the fact that featherworking techniques used today are somewhat different to those used in sixteenth-century New Spain. Research into the account of the technique and the use of cochineal dye to give the intense red colour required, described in detail in the *Historia General de las cosas de Nueva España* by Bernardino de Sahagún (1575–7), as well as careful study of the feathers using Fibre Optic Reflectance Spectroscopy (FORS) and Multiband Imaging (MBI), enabled the team to commission an accurate reproduction of the insignia, made using appropriate, sustainably available feathers and easily reproducible dyeing methods.

The work carried out on the insignia is an example of what can be achieved with careful use of non-invasive methods together with historical documentary evidence. Another example is provided by the examination of Japanese folk textiles dating from the late nineteenth to the early twentieth centuries, discussed by Ludovico Geminiani and colleagues [4]. These were not the luxurious silk textiles usually examined; in this case, all the kimonos and other textiles were cotton, produced for a lower-class clientele. They were examined using Visible Reflectance Spectroscopy and External Reflection Fourier Transfer Infrared Spectroscopy (ER-FTIR), with the aid of a substantial purpose-made database of samples, including traditional Japanese colourants, synthetic materials and mixtures of materials, all in different concentrations and painted on Fabriano paper. Clearly, there are limitations to the identifications possible when a more diagnostic technique, but

one requiring sampling, is unavailable, but, as the authors explain, it is still possible for identifications to be made, either of the colourant itself or of its class. The identification of water-based animal skin glue or rice starch paste in areas decorated using resist printing techniques and hand colouring, as well as conventional dyeing with indigo and Prussian blue, means that the textiles will require careful cleaning and conservation treatment.

A very different and humbler example of peasant clothing is described by Anete Karlsone: orange-yellow aprons worn by Latvian women during the late eighteenth and early nineteenth centuries, documented by the writer and cultural historian Johan Christoph Brotze (1742–1823) [5]. According to this and other contemporary sources, the aprons were dyed with *Orlean*, or annatto, from the seeds of the shrub *Bixa orellana* L., then available as a medium-priced dye and imported into the region in quite large quantities in the early decades of the nineteenth century. From studying the use of other plant dyes, the author was able to obtain orange- and orange-yellow-coloured textiles, as illustrated by Brotze.

Dyeing aprons is a very typical example of the sort of work that could be carried out at home and is described in innumerable small manuals and other 'books of secrets' produced all over Europe from the medieval period onwards. On a larger scale, dyers' workshops and companies would have been busy dyeing goods for middle- and lower-class clients. A rare example of a book of recipes and accounts from a late eighteenth-century Antwerp dyer is described by Emile Lupatini and Natalia Ortega Saez [6]. Although the identity of the dyer is unknown, the authors have been able to suggest a site for the premises in the city and, from the dyes used—for example, cochineal for more expensive wool fabrics and soluble redwood dyes on cheaper, coarser cloths—they suggest the status of the clientele. The work of the establishment is set against the economic context of late eighteenth-century Antwerp, during a period described by the authors as one of economic stagnation, contextualisation which is particularly valuable for the reader.

The more expensive and precious side of the dyeing trade is elucidated by Irina Petroviciu and co-authors in their account of liturgical embroideries dating from the late fourteenth to the nineteenth centuries in the National Museum of Art of Romania, Bucharest [7]. The textiles, described as Byzantine, Moldavian, Wallachian, Greek, Russian, of Viennese origin, or from Constantinople (present-day Istanbul), were studied as part of a programme to document them within the museum collection: in effect, part of the museum cataloguing programme. The sample sites available were thus limited to damaged areas of the supporting silk fabric and, to some extent, embroidery threads visible on the back of the textiles. However, it was possible to show developments in the use of different dyes over time, including the consistent use of indigotin-containing blue dyes, weld and dyer's broom as yellow dyes, and, importantly, a carminic acid-containing red dye in the red satin supports of embroideries dating from the later decades of the sixteenth century onwards. This is typical of a very common European pattern of dye usage. Earlier liturgical textiles examined in other projects had been found to contain a more varied range of red dyes, but the invariable use of carminic acid-containing dye from about 1570 confirms the quite rapid spread of American cochineal usage right across Europe following its introduction.

Another precious, and indeed royal association is linked to an example of a rarely examined group of textiles: knitted silk waistcoats. One of the two examined by Jane Malcolm-Davies and co-authors is said to have been worn by King Charles I of England at the time of his execution, although it has not been possible to confirm this [8]. The other, from Drummond Castle, Crieff, Scotland, is said to have been worn by one of the Earls of Perth. Both are pale greenish-blue in colour and damask-knitted. Although analysis by high-performance liquid chromatography coupled with mass spectrometry (HPLC–MS) was used, the waistcoats were also examined by the non-invasive methods of confocal micro-Raman spectroscopy and molecular fluorescence in the visible region of the

spectrum, crucially aiming to build up a bank of reference data to help in the examination of other items, particularly knitted items, where sampling is impossible. This combination of methods enabled the identification of indigotin in both waistcoats and a yellow dye constituent, daphnetin, in the Scottish waistcoat, which would thus have originally been pale green in colour.

The colour purple also has some regal associations, particularly in the period before the time of Charles I and his waistcoat, although in medieval Europe the use of the exotic and expensive shellfish purple was no longer current: overdyeing a blue-dyed textile with a red dye or the lichen purple dye orchil was the method commonly used. This method was described by Pauline Claisse and co-authors in their study of a late fifteenth- or early sixteenth-century tapestry in the Musée de Cluny, Paris [9]. *La vue*—Sight, one of six *Lady and the Unicorn* millefleurs tapestries—was examined using the non-invasive methods of Hyperspectral Imaging Spectroscopy and LED µ-Spectrofluorimetry (LEDµSF) after conservation treatment had shown that, on the back of the tapestry, the Lady's skirt, now light blue, retained some purple coloration. A complete set of dyed wool samples was prepared for a comparison of the various possible dyes present and for light ageing using indigo extracted from woad; red anthraquinone dyes extracted from madder, kermes and cochineal; and orchil dye from the lichen *Lasallia pustulata* (L.) Mérat (1821). Comparison of the different dyed samples, before and after ageing, with the tapestry itself indicated that the purple colour had been obtained using indigo and orchil, not one of the anthraquinone red dyes. HPLC-PDA examination of a sample of purple wool taken from the back of the tapestry during conservation treatment identified the indigo, but not the purple dye constituent, presumably because the dye in the region sampled was too degraded.

Not all lichen colours are purple. Orchil lichens, in which the dye is extracted using alkali, give the characteristic purple dye, but another group of lichens, in which the dye is extracted using boiling water, gives yellows and browns. These lichens have been widely used, but in more recent centuries; until now, their use in the medieval period has not been identified. During their study of one of the *Heroes* tapestries, *Julius Caesar*, in The Cloisters Collection of the Metropolitan Museum, New York, Rachel Lackner and co-authors examined a sample of brown wool using high-performance liquid chromatography coupled to electrospray ionisation–quadrupole time-of-flight mass spectrometry (HPLC-ESI-qToF-MS) [10]. They identified chlorinated xanthone derivatives, including thiophanic acid, which are metabolites of lichens such as the Mediterranean species *Lecanora sulphurea* (Hoffm.) Ach. (1810). This species was used as a comparative sample for the analysis as its population is sufficiently large and stable. The results provide evidence for the use of boiling-water extraction of a non-orchil type (or crottle-type) of lichen dye in fifteenth-century France or the Southern Netherlands, although it is not possible to say which lichen was actually used.

4. Conclusions

The range of subjects covered in this Special Issue is interesting in several ways. The decision to proceed with community-based participatory research in a proper partnership with the Tikuna/Magüta people to investigate the unknown blue plant colourant they used in the past, and perhaps still use, should not be anything out of the ordinary; in fact, in heritage conservation in general, it is not unusual. This is not the case in every area of research, but its importance will gradually be recognised more widely.

It is particularly encouraging to see results of the study of textiles not owned by the nobility, or the rich and famous in general. It is true that higher-class textiles are more likely to have survived, but this is where documentary research can be so helpful, such as that represented in this collection by the recipe and accounts book of the eighteenth-century

dyer in Antwerp. An understanding of the historical and economic context during which a particular range of dyes were used serves to increase our understanding of an earlier time, but one that is still informing and contributing to our world today.

Today, non-invasive examination methods are certainly more powerful and versatile than used to be the case. Their use, backed up by a well-designed database of carefully constructed standard samples, has been amply demonstrated by several of the papers in this collection: on Japanese textiles, on feathers and on tapestry dyes, for example. It is interesting that, in each case, the range of dyes likely to be present was to some extent limited by traditional practice or by availability. Of course, other possible dyes should not be ruled out, but if there is no evidence whatsoever for their availability in that area of the world at that time, then the range selected as standard samples is at least a reasonable starting point. The non-invasive examination can also provide information towards the selection of an appropriate sampling area if a future opportunity to analyse a sample by a chromatographic separation technique arises.

It is also worth noting that the majority of investigations of historical and archaeological artefacts, like those described in this Special Issue, begin within the walls of a museum, gallery, or private collection. Without collaborations between disciplines and institutions to bring in a wider range of expertise, valuable, intriguing and perhaps unexpected information about our recent or long distant past would remain unrecognised and perhaps lost. The value of such collaborations is perhaps particularly significant in the fields exemplified by this collection of papers and it was given visible form by the conference participants themselves, from so many different countries and disciplines, talking and moving from venue to venue (Figure 6).

Figure 6. Evening view of Nyhavn, Copenhagen, looking towards the Inderhavnsbroen (Inner Harbour Bridge) for cyclists and pedestrians between Nyhavn and Christianshavn, with a harbour bus in the foreground. Photograph: Mikkel Scharff.

Conflicts of Interest: The authors declare no conflict of interest.

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Article

Blues from Tikuna/Magüta Masks and a Still Unknown Blue Colorant in Technical Art History and Conservation Science

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Abstract: Blue is one of the most challenging colors for humans to produce and one of the most important colors in art history. Literature from the Tikuna/Magüta culture, from the Amazon Forest, suggests the use of chemical reactions between the juice of the naïcü fruit and iron to produce a blue colorant still unknown among technical art historians and conservation scientists. Additionally, the coloring materials from the Tikuna/Magüta people were never chemically investigated. Therefore, this manuscript presents the investigation of blue colorants from twenty-two Tikuna/Magüta masks and one stamp used to decorate similar items. Collections from four museums, from the USA and Brazil, were examined, and Raman spectra indicated the presence of Prussian blue, phthalocyanine blue, indigo, ultramarine, crystal violet, amorphous carbon, anatase, and barium sulfate (or lithopone). Although the unknown blue colorant was not detected in this campaign, the authors hypothesize the chemical composition and reactions involved in its production by considering the chemistry of naïcü and anthocyanins. The continuation of this work with community-based participatory research (CBPR) approaches is also discussed, justifying why reproduction was not considered in this work and supporting a more socially responsible and inclusive practice in technical art history and conservation science.

Keywords: indigenous art history; technical art history; naïcü; community-engaged research; plant-based dyes; anthocyanin dyes; Raman spectroscopy

1. Introduction

The Amazon Forest is renowned for its human, cultural, and biological diversities. The artistic and cultural creations of the Amazonian people are deeply rooted in the region's natural surroundings, which serve as conduits for transmitting cultural narratives, spiritual beliefs, and ecological wisdom. The materials used by the Indigenous people hold invaluable insights into the cultural connections with the environment and the intricate ecological knowledge that has sustained their communities for centuries. However, to date, the paint and coloring materials created and used in this region remain under-studied [1]. Delving into the study of these colorants offers a unique opportunity to understand, appreciate, value, and respect their creative processes and heritage.

Specifically, the Tikuna/Magüta people have been using many colors in their cultural items, such as blues, greens, yellows, and reds, in creating their material culture. Inhabiting near the borders of Brazil, Peru, and Colombia, the variety of their materials becomes evident through the account of a Tikuna/Magüta artisan, who describes the use of 65 "colors" (or colorants, as interpreted by the authors of this manuscript) from several natural sources, such as seeds, flowers, leaves, roots, barks, and mud [2]. An example of their abundance of coloring materials is those present in masks used as part of the Tikuna/Magüta female

initiation rituals [3,4]. Additionally, studies have reported that it is the paints that give meaning to the masks, highlighting their importance: "when they do not have paint, it [the mask] is of no use" (p. 163, authors translation) [5].

Blue is one of the most challenging colors for humans to produce and has a profound importance in art history. Before ancient civilizations learned how to produce colorants, the use of blue was limited by the availability of natural resources like plants and minerals. Examples of plant-based materials are indigotin (from *Indigofera tinctoria*), genipocyanin (from *Gardenia jasminoids* and *Genipa americana*), and ventilein (from *Ventilago goughii*) [6]. Examples of natural inorganic materials are azurite and lapis lazuli. However, over time, humans learned how to mimic nature by synthesizing naturally occurring molecules or creating new compounds like Maya and Egyptian blues. Maya blue, for example, was produced by the ancient Maya civilization and is known for its exceptional durability and vivid color, which has survived centuries in artifacts and mural paintings [7]. The pigment is a complex formed by combining indigo dye with zeolitic clay minerals such as palygorskite or sepiolite. Objects painted with Maya blue were often of great significance, as the pigment was associated with important rituals and deities, highlighting the cultural relevance of the objects adorned with this vibrant material. Investigating ancient pigments is crucial for understanding the cultural practices of past civilizations and gaining insights into technological advancements, trades, rituals, and artistic achievements. Additionally, the investigation of pigments from different civilizations helps connect the broader narrative of human innovation in artistic and cultural practices.

In South America, plants like *Licania macrocarpa* Cuatrecasas [8], Cartelhana [9], *Cybistax antisyphilitica*, *Llangua*, *Sami*, and *Twi kshanate* [10], among others, including *Indigofera suffruticosa* Mill., have been used to produce blue colorants. Specifically, the Tikuna/Magüta people have prepared blue colorants using plant-based sources like bure or buré (*Calathea loeseneri* Macbride) [2], anil (*Indigofera suffruticosa* Mill.) [11], and "native strawberry" (without supplementary details in the referenced source) [2] for centuries. Dark blue or bluish-black hues have been prepared by using *Genipa americana* L. [12], which is also known as jenipapo, and the fruits from pacová [13]. Pacová is also known by the Indigenous name na'i^{n}ku. The term na'i^{n}ku appears to be interchangeable with naikú, naiku, naīku, nai'ku, naike, naicu, naīcü, naico, and na ico, and all these terms have been used to describe plants whose fruits are utilized for extracting dyes with purple, blue, black, and "chocolate" colors. Additionally, some of these terms seem to refer to specific plants. For example, naiku, naike, or nai'ku have been used to refer to the specie *Renealmia alpinia* [14–20], naiku also to *Renealmia alpinia* (Rottb.) Maas [21], and naico to *Renealmia* sp. (p. 30) [12]. Pacová has been linked to *Renealmia alpinia* [22], *Renealmia cernua*, *Renealmia exaltata*, *Renealmia petasites* [15], and *Renealmia petasites* Gagnep. [23]. These plants are from the family *Zingiberaceae*, genus *Renealmia* L.f., and many of their species could have been available to and used by the Tikuna/Magüta people.

The fruit of naīcü (the term chosen for use in this manuscript) is of particular interest due to references in the literature that point towards the use of chemical reactions to produce a blue colorant still unknown among technical art historians and conservation scientists. Curt Nimuendajú (p. 42), a German ethnologist and anthropologist (see more below), describes that "the juice of one fleshy fruit (T., na'i^{n}ku) furnishes a dark violet which, upon contact with iron, changes into a clear blue" [24]. This indicates the likelihood of a chemical reaction to create a still unknown organometallic blue colorant. Creutzberg (p. 69) [18], when writing about nai'ku, notes that by boiling or incorporating salts, a more durable paint can be produced, and when combined with soap, it takes on a blue hue. Gruber [13], albeit without detailing the resultant color, depicts the mixture of pacová with iron in the paint production practices of the Tikuna/Magüta people.

Except for anil and jenipapo [1], a survey of the literature reveals a dearth of scientific investigations into the aforementioned blue colorants used by the Tikuna/Magüta people, including the still unknown blue derived from naīcü. This gap in knowledge impacts the art historical understanding of Indigenous material choices, the appreciation

of Tikuna/Magüta cultural items, which are present in museums worldwide, and the conservation steps needed to preserve these items. Therefore, this work aims to chemically investigate blue colorants present in Tikuna/Magüta masks, expecting to find chemical fingerprints of such an unknown blue. Masks selected from the collections of the Magüta Museum located in Benjamin Constant (Brazil), the Museum of Archaeology and Ethnology (MAE) from the University of São Paulo (Brazil), the Peabody Museum of Archaeology and Ethnology from Harvard University (USA), and the Fowler Museum from the University of California, Los Angeles (USA) were investigated.

2. Materials and Methods

2.1. The Investigated Items

Curt Nimuendajú (1883–1945) was a German researcher who arrived in Brazil in 1903. Nimuendajú conducted ethnographic trips in 1929, 1941, 1942, and 1945 in order to study the Tikuna/Magüta people and their material culture [25]. As most of the Nimuendajú's trips were conducted in the 1940s, it was decided that the items considered for this research (Figures 1–4) would be contemporary with this and were all collected (albeit by other researchers) from the 1940s onward, meaning that at least some were produced in that decade or earlier. Additionally, another criterion for object selection was having visibly well-preserved blue colors. Naïcü is rich in anthocyanins [26], which are well-known to be unstable molecules. However, as naïcü was described as being mixed with iron to produce a new compound with still unknown chemical stability, it was supposed, in this first phase of the project, that the naïcü-derived blue might be stable, leading to the choice to investigate well-preserved blue colors.

Figure 1. Tikuna/Magüta items from the MAE. Reference numbers: RG 8649, RG 10034, RG 8716, RG 9984, RG 8753 (2), RG 8753, RG 8889, RG 8892, RG 8894, RG 8898, RG 8902, RG 8710, RG 8764, RG 9454, and RG 10098 (by Ader Gotardo); credits: Museu de Arqueologia e Etnologia da Universidade de São Paulo.

Figure 2. Tikuna/Magüta item 996-24-30/11694 from the Peabody Museum; credits: Gift of Richard E. Schultes, 1996. Courtesy of the Peabody Museum of Archaeology and Ethnology, Harvard University, 996-24-30/11694. No photo is available from item 47-8-30/5627.

Figure 3. Tikuna/Magüta item X64.965 (by Thiago Sevilhano Puglieri and Christian De Brer) from the Fowler Museum; credits: ©Photo courtesy of the Fowler Museum at UCLA; Tikuna/Magüta.

MM374 **MM383** **MM384** **MM385** **MM387**

Figure 4. Tikuna/Magüta items from the Magüta Museum. Reference numbers: MM374, MM383, MM384, MM385, and MM387 (by Thiago Sevilhano Puglieri); credits: Thiago Sevilhano Puglieri.

It is worth noting that for the Tikuna/Magüta people, the term mask is related to the part that covers the head and the body (p. 105) [27], so all the items investigated here were considered masks or part of them. Only one item from the MAE collection, RG 10896, is a stamp used to decorate masks.

From the MAE (Figure 1), the considered items were collected by Harald Schultz (1909–1965) in 1958 (RG 8649, RG 8710, RG 8716, RG 8753, RG 8753 (2), RG 8764, and RG 10896) or 1956 (RG 8889, RG 8892, RG 8894, RG 8898, RG 8902, RG 9454, and RG 9984). It is important to note that the collection dates do not necessarily reflect the actual production dates of the items; the same is true for the items from the Peabody and Fowler Museums. For mask RG 10034, no date information was found. Other details from these items can be found in the Supplementary Materials.

From the Peabody Museum (Figure 2), two items were investigated, and both were collected by Richard E. Schultes (1915–2001), a Harvard professor, ethnobotanist, and conservationist [28]. One of the items was collected in 1946 (47-8-30.5627) in Leticia, Colombia, and the other in 1958 (996-24-30.11694) in Rio Loretoyacu, Amazonas, Colombia. They were received by the museum in 1947 and 1996, respectively [29]. Other details from these items can be found in the Supplementary Materials.

From the Fowler Museum (Figure 3), mask X64.965 was selected. This item was collected by Peter T. Furst (1922–2015), a cultural anthropologist from Germany who worked at UCLA, the State University of New York, the University of Pennsylvania, and the Museum of Indian Arts and Culture [30]. This item entered the Fowler Museum collection in the 1960s.

From the Magüta Museum (Figure 4), items MM374, MM383, MM384, MM385, and MM387 were selected. This collection was created with the participation of the Tikuna/Magüta people, and the museum is located in Benjamin Constant, Amazonas State, Brazil, close to the area where Nimuendajú conducted his research [31]. This collection was created between 1988 and 1991 (p. 100), and the masks are from the end of the 1980s (p. 105) [27]. However, the overpainting of some of the Magüta Museum's items (p. 163) has been reported [27]. Therefore, items with potential overpainting, as determined by visual examination using visible light and UV radiation, were not considered for this research.

2.2. Chemical Investigation

All the samples were investigated using Raman micro-spectroscopy. Raman spectra were collected with Renishaw inVia Microscopes (Wotton-under-Edge, UK) (with nominal spectral resolutions of about 4 cm^{-1}), employing a Leica DM2500 M or a Leica DMLM microscope (Leica Geosystems AG, Heerbrugg, Switzerland) equipped with a CCD camera using a 785 nm (diode laser, 1200 L/mm grating) laser line. The laser line was focused onto the samples by a $\times$50 Leica objective (NA 0.50, 8 mm working distance), and the laser power was kept below values that could degrade the sample. The microscopes

were coupled to a Renishaw Peltier-cooled CCD array detector. The Raman spectra were analyzed and manipulated using the Renishaw WiRE® 3.1 software and OriginPro® 2022b software.

3. Results and Discussion

This section is divided into three parts. The first concerns the investigation of blue colorants found in the Tikuna/Magüta masks. The second is devoted to discussing the continuation of this research through community-based participatory research (CBPR) and the justification of why reproduction was not considered in this work. The third is related to the hypotheses behind the unknown blue.

3.1. Blue Colorants from the Tikuna/Magüta Masks

The masks considered in this manuscript are ceremonial items, and it is of the utmost importance to remember that, as per their wishes, specific knowledge about the Tikuna/Magüta people must not be disclosed to ensure their balance with the surroundings and protect their well-being (p. 127) [2]. For example, scientific investigations can reveal Indigenous knowledge, which can be disclosed by publishing the results. In this work, consent for sampling and analytical investigation was requested from Tikuna/Magüta representatives and the institutions holding the collections. Regarding the publication of the results, consent was obtained from a Tikuna/Magüta representative leadership before publishing them. Additionally, this manuscript solely discusses coloring materials previously made public. The authors are grateful to the Tikuna/Magüta people for all the support given to this project.

Raman micro-spectroscopy results show the presence of Prussian blue, phthalocyanine blue, indigo, and ultramarine as blue colorants in the investigated samples. In some instances, the synthetic dye crystal violet or amorphous carbon was also found. Anatase and barium sulfate (or lithopone) were found in low concentrations in a few items. All the results are summarized in Table 1, and Figure 5 shows representative Raman spectra of the main colorants with their main bands highlighted.

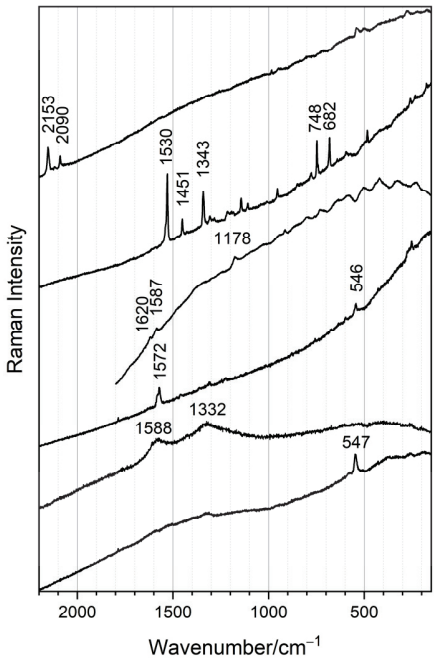

Figure 5. Representative Raman spectra (785 nm) of each colorant identified in this research. From the top to the bottom: Prussian blue, phthalocyanine blue, crystal violet, indigo, amorphous carbon, and ultramarine.

Table 1. Summary of results.

Museum	Item's Identification	Main Raman Bands/cm^{-1} and Attributed Colorants
Fowler Museum	X64.965	547, 584 (ultramarine)
Peabody Museum	47-8-30/5627	253, 546, 598, 1226, 1310, 1572, 1582 (indigo, sample 1) 1332, 1588 (amorphous carbon, sample 2)
	996-24-30/11694	1572, 1582 (indigo)
Museum of Archaeology and Ethnology (MAE)	RG 10034	176, 235, 259, 485, 594, 641, 681, 748, 780, 833, 848, 953, 1008, 1108, 1143, 1160, 1185, 1194, 1214, 1307, 1341, 1430, 1451, 1528 (phthalocyanine blue)
	RG 10896	915, 1178, 1587, 1620 (crystal violet)
	RG 8649	275, 504, 531, 2090, 2153 (Prussian blue) 542 (ultramarine) 142 (anatase)
	RG 8716	1572, 1582 (indigo)
	RG 8753	2092, 2154 (Prussian blue)
	RG 8753-2	277, 533, 2091, 2153 (Prussian blue)
	RG 8764	1573, 1583 (indigo)
	RG 8889	2092, 2155 (Prussian blue) 544 (ultramarine) 987 (barium sulfate and/or lithopone) 143 (anatase)
	RG 8892	280, 2091, 2154 (Prussian blue) 144 (anatase)
	RG 8894	2089, 2149 (Prussian blue) 144 (anatase)
	RG 8898	2093, 2154 (Prussian blue) 143 (anatase)
	RG 8902	544 (ultramarine)
	RG 9454	2090, 2152 (Prussian blue) 252, 544, 1225, 1248, 1310, 1572, 1582 (indigo) 1325, 1597 (amorphous carbon) 144 (anatase)
	RG 9984	278, 2091, 2152 (Prussian blue) 543 (ultramarine) 145 (anatase)
	RG 8710	282, 505, 533, 2092, 2154 (Prussian blue) 1325, 1599 (amorphous carbon)
Magüta Museum	MM374	175, 258, 484, 594, 642, 681, 748, 782, 833, 848, 954, 1008, 1109, 1144, 1185, 1195, 1217, 1308, 1343, 1451, 1530 (phthalocyanine blue)
	MM383	484, 682, 748, 954, 1109, 1144, 1308, 1343, 1451, 1530, 1539 (phthalocyanine blue)
	MM384	175, 259, 484, 594, 682, 748, 780, 954, 1109, 1144, 1185, 1195, 1217, 1308, 1343, 1451, 1530 (phthalocyanine blue)
	MM385	176, 235, 259, 484, 495, 596, 642, 681, 748, 783, 833, 848, 954, 1008, 1109, 1132, 1144, 1158, 1186, 1196, 1217, 1308, 1343, 1429, 1451, 1530 (phthalocyanine blue)
	MM387	175, 259, 484, 594, 682, 748, 780, 954, 1109, 1144, 1185, 1195, 1217, 1308, 1343, 1451, 1530, 1539 (phthalocyanine blue)

The presence of Prussian blue was identified mainly by the bands at ca. 2153 and 2090 cm^{-1}, attributed to $1A_g$ and E_g ν(CN) stretching vibrations, respectively [32]. The presence of indigo was indicated mainly by the bands at ca. 1582 and 1572 cm^{-1}, attributed to symmetric A_g stretching vibrations of ν(C=O), ν(C=C), and ν(C-C) modes [33]. Indigo spectra acquired were also compared to the ROD00176 Raman spectrum from the Infrared and Raman Users Group (IRUG) database. Ultramarine was indicated by its most intense band due to lazurite at ca. 545 cm^{-1}, attributed to the symmetric stretching vibration of radicals S^{3-} [34]. Phthalocyanine blue was identified mainly by the presence of bands at ca. 1530, 1451, 1343, 748, and 682 cm^{-1} [35], and the presence of crystal violet was verified by the bands at ca. 1620, 1587, 1178, and 915 cm^{-1} [36,37]. Amorphous carbon was identified by its two characteristic broad features at ca. 1575 and 1320 cm^{-1}, assigned to the G and D bands, respectively [38]. The presence of anatase was suggested by the observation of its most intense band at ca. 143 cm^{-1}. Anatase presents a high scattering cross-section, and because only low-intensity bands were observed, the results suggest that it is from a natural mineralogical impurity [39]. The presence of barium sulfate or lithopone was indicated by their most intense band at ca. 987 cm^{-1}. Lithopone could be differentiated from barium sulfate by the observation of a medium-intensity band at ca. 342 cm^{-1} [40]. However, the low concentration and the luminescence background present in the spectra did not allow their differentiation.

Naturally derived ultramarine, or its source, lapis lazuli, contains minerals like calcite, diopside, pyrite, sodalite, and wollastonite, in addition to the main chromophore, lazurite. Even after purification to remove these associate minerals, calcite usually remains present. Additionally, natural ultramarine usually produces fluorescence bands in the Raman spectra when employing 785 nm laser wavelength [41]. Because neither calcite nor fluorescence bands were observed in the Raman spectra in this investigation, the results indicate the use of synthetic ultramarine. Differentiating synthetic from natural indigo is not trivial with Raman spectroscopy [42], and the results obtained here did not allow their distinction.

Prussian blue, a Fe^{3+} ferrocyanide, is the only compound identified here that could potentially be the chemical product from the reaction between naïcü and iron. However, as discussed in Section 3.3, there is no evidence of naïcü being a source of cyanides to form Prussian blue. Prussian blue was first synthesized in 1704 (p. 302), and ultramarine in the early 19th century (p. 302) [43]. Copper phthalocyanine blue, although discovered at the beginning of the 20th century, was introduced and described as an artists' material at the end of the 1930s (p. 284) [43]. Indigo was first synthesized and commercially produced at the end of the 19th century [42], and crystal violet is an early synthetic organic dye used since the 19th century [44].

Although it is reported that some Tikuna/Magüta communities insist on using natural colorants in the masks (p. 164) [5], most of the colorants identified here are likely synthetic. This is not a surprise, given that in the 1940s, Nimuendajú reported the loss of the Tikuna/Magüta's traditional material culture to more or less one-third [31]. Furthermore, the replacement of natural colorants with synthetic ones by the Tikuna/Magüta people was also documented elsewhere [45]. These results reinforce the expected transformations in the Tikuna/Magüta artistic practices and serve as a warning of the potential loss of their former traditional material knowledge, emphasizing the need to increase scientific investigations in this area.

In some instances (items RG8649, RG8889, RG9454, and RG9984), more than one blue colorant was found in the same sample. In others (items RG9454 and RG8710), blue colorant(s) were mixed with amorphous carbon. Assuming that all these materials are original to the items, the use of a wide range of blue colorants alone or mixed with other materials suggests that the artists had the intention of achieving specific blue hues. Additionally, since materials in Indigenous ceremonial items are usually intertwined with spiritual meanings, the use of specific colorants could also be related to spiritual reasons, which still needs to be investigated in collaboration with the community.

The Tikuna/Magüta masks are made of bark trees called tururi and obtained from several types of trees. Specifically, about the myths and meanings, in Tikuna/Magüta mythology some masks, for instance, come ready-made from the tururi trees, as in the myth of the "man who killed his wives" (p. 384, authors translation). In this myth, the character who will avenge his sisters' death brings masks to the enemy brother-in-law's party, which were obtained simply by arrowing the tururi tree. This specific tree, known as tüerumaũ, is believed to also give rise to jaguars and hawks (p. 384–385). In addition to the paints in the masks, the human bodies underneath them are also colored, and this superposition of painted bodies and masks is critical in their culture (p. 386) [3]. For example, in the myth about the jaguar Torama rü ai, a young man decided to wear a jaguar mask for one of the young girl's parties. He painted his body with watery clay before wearing it. However, because he was supposed to paint it also with açafroa (which is likely curcuma), he metamorphosed into a jaguar (p. 94–97) [46]. The Tikuna/Magüta people also use other materials to paint their bodies when wearing the masks, like jenipapo and urucum, and the paintings have the power of reversibility (p. 97) [46]. As already mentioned, the paints are also what give meaning to the masks (p. 163) [5]. Still, these material choices and meanings have yet to be systematically explored in the context of technical art history.

For example, it is reported that replacing natural colorants with synthetic ones changes the masks' value at the moment of exchange with food and drink (p. 171) [5]. However, the role and significance of coloring materials are unclear when considering a broader understanding of the values and meanings of colors, natural resources, and coloring techniques in terms of social, environmental, spiritual, and cultural interconnectedness. About blue, for instance, a follow-up of this research is to understand what are the meanings associated with such a color, with the different natural materials used to produce different blues, and with the nature's transformations the Tikuna/Magüta people perform by chemically reacting, for example, naïcü's juice with iron.

Concerning the blue colorant prepared from naïcü with iron, unfortunately, it was not found in this work. Its reproduction in the laboratory, its acquisition from the Tikuna/Magüta community, or the investigation of degraded items would be the most natural ways to proceed in conventional technical art history or conservation science approaches. However, in this work, none of them were chosen, and this choice, together with the hypothesis behind the naïcü blue, is discussed in the next two sections.

3.2. Community-Based Participatory Research (CBPR) as a Continuation of This Research

A few reasons could explain why the naïcü blue was not detected in this research. Firstly, it may not have been used to decorate the investigated items. Secondly, it could have been used, but because it may be chemically unstable, it is now degraded, and Raman micro-spectroscopy did not detect potential degradation products. Additionally, if present, its concentration could be below the detection limit of the technique employed here.

In conventional technical art history and conservation science approaches, three main pathways would be considered to proceed with this investigation: (1) The researcher obtains a sample of the blue from the Tikuna/Magüta community and investigates it in the laboratory using different analytical techniques; (2) The researcher procures the raw materials and attempts to reproduce the blue in the laboratory for analytical investigation; (3) The researcher investigates degraded masks from museum collections to search for traces of degradation products that could be related to the unknown blue; all the options would consider the publication of results in scientific journals. More than one option could be considered simultaneously, but all are usually investigator-driven and academically-centered approaches that generate benefits mainly to the researchers and their scholarly fields. Some of those options consider community engagement, but Indigenous members usually participate as subjects or sources of materials, and their needs are often not considered in the formulation of research questions or the use and dissemination of the results. To help explore more socially responsible and inclusive practices in technical art history and

conservation science, the authors of this manuscript decided to investigate alternatives, such as community-based participatory research, CBPR, to proceed with this investigation.

Only a few examples of community-engaged research (CER) involving the scientific investigation of Indigenous sacred and ceremonial items are available in the literature; for instance, see [47–49]. However, fields like conservation, archaeology, health, and education have been exploring CER for a long time, and they are valuable sources of case studies and methodological frameworks. CER can be seen as a continuum from community-driven to investigator-driven research (p. 3, chapter 1) [50], from more to less collaborative. Many approaches exist within such a continuum, and the authors of this manuscript have chosen to proceed with CBPR. CBPR aims to "create an effective translational process that will increase bidirectional connections between academics and the communities that they study" (p. 3, chapter 1) [50], having social justice and empowerment at its foundation. The community has a broad participation, from the formulation of research questions and hypotheses to data collection, interpretation, use, and dissemination. It considers power-sharing with the community members, promotes mutual learning and reciprocity, is based on the community's resources and strengths, considers the sustainability of the outcomes, and disseminates results for all partners and interested parties. Details are outside this manuscript's scope, but the readers can learn more about CBPR in texts like those by Hacker and Atalay [50,51]. Additionally, our CBPR experience should result in a specific publication about the method in the context of technical art history.

The Tikuna/Magüta people are a living culture, producing colorants from natural sources, and there is no reason not to consider their participation in this research. In 2023, in collaboration with community members, we mapped some of their needs related to their cultural heritage and started exploring how technical art history and conservation science can engage with them for mutual benefits. Within a CBPR project, it is possible to consider research actions with more or less community engagement. For example, the results of this manuscript are part of an action closer to researcher-driven research but connected to other actions (still in their initial phases) with more extensive community participation. Thus, when considering the reciprocity principle of CBPR, it would not be reasonable to reproduce or request the Tikuna/Magüta people to prepare the naïcü blue for this manuscript, and therefore, for the researchers' benefit, without having a well-developed action that can also directly benefit the community. Additionally, naïcü is not readily available, and it is impossible to access the Amazon Forest and collect native plants for research without proper authorization.

Therefore, to continue this research, a fourth option is proposed and considered: that the researchers and community work together to prepare and chemically investigate the naïcü blue. However, to guarantee mutual benefits, the results should be shared only after the research group has at least one well-developed action plan that will directly address at least one of the community's needs by using the scientific results. This option is proposed as an alternative to increase the social impacts of research in technical art history and conservation science, and it is not expected to replace the others. For example, the Tikuna/Magüta people are living and producing their colorants, but this may not be the reality for other cultures. Therefore, the methodological approaches need to be defined case by case. The challenges, risks, and benefits of CBPR also need to be considered, and they will be addressed in a future publication.

3.3. Hypothesis behind the Still Unknown Blue Colorant

Concerning the chemical nature of the unknown blue, it can at least be hypothesized in this manuscript. Naïcü refers to plants from the family *Zingiberaceae*, genus *Renealmia* L.f. One of the plants attributed to the term naïku is *Renealmia alpinia* (Rottb.) Maas [21], and the peel of its fruit is rich in anthocyanins, with lower amounts of flavonoids and phenolic compounds and minor amounts of carotenoids [26]. Anthocyanins are derivatives of flavylium compounds, and although there are eighteen basic structures, the most common are pelargonidin, cyanidin, delphinidin, peonidin, petunidin, and malvidin (p. 252) [52].

For the pericarp of *Renealmia alpinia* (Rottb.) Maas, cyanidin-3-O-glucoside and delphinidin-3-O-glucoside are reported (Figure 6) [53].

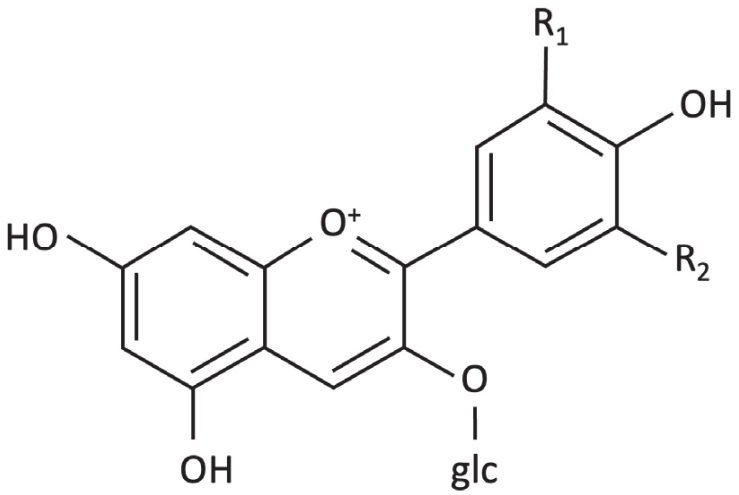

Figure 6. Chemical structures of cyanidin-3-O-glucoside (R_1 = OH, R_2 = H) and delphinidin-3-O-glucoside (R_1 = OH, R_2 = OH); glc = glycoside.

Anthocyanins were employed in cultural heritage items for millennia to produce watercolors and paints and to dye textiles, with hues ranging from red to blue [54–56]. Humans have been reacting anthocyanins with metal ions, such as aluminum ions, achieving mostly violet and purplish hues. Regarding blue hues, the use of anthocyanins in arts and cultural heritage is described mainly by their extraction from nature, not by human-made chemical processes with iron ions, as in the case of the Tikuna/Magüta people. There are only a few instances where similar blue systems with iron are described, and their chemical composition and analytical identification were also not explored. One work reports the use of hollyhock (*Althaea rosea* (L.) Cav.) flowers (p. 251) [55] to dye, and another the use of piñon (*Pinus edulis*) pitch and sumac (*Rhus trilobata*) withes with leaves (p. 66) [57].

Supposing that the blue prepared from naïcü is indeed the result of the chemical reaction between iron ions and anthocyanins, the Tikuna/Magüta people have been mimicking one of the strategies that nature uses to fix the blue color, which is complexation with metallic ions. The blue in hydrangea, for instance, is attributed to a complex of Al^{3+} with delphinidin-3-O-glucoside and the copigment 5-O-caffeoylquinic [6]. For petals of *Commelina communis*, the blue hue is attributed to a structure composed of the anthocyanin malonylawobanin, the flavone flavocommelin, and ions Mg^{2+} in a ratio of 6:6:2 [6]. Similar supramolecular structures were proposed for *Salvia patens* and *Salvia uliginosa* (with anthocyanins, flavones, and ions Mg^{2+}), and *Centaurea cyanus* and *Nemophila menziezii* (with anthocyanins, flavones, and ions Fe^{3+} and Mg^{2+}). Other plants for which blue was related to the presence of anthocyanins and Fe^{3+} are *Corydalis ambigua* and *Meconopsis grandis* [6]. The effect of iron ions has also been investigated in similar systems [58], and a study evidenced that the chemical reactions between ferric chloride and cyanidin-3-glucoside and delphinidin-3-glucoside result in the formation of blue chelate complexes [59]. Therefore, it is reasonable to expect the formation of anthocyanin–Fe^{3+} chelates of cyanidin-3-O-glucoside and delphinidin-3-O-glucoside for the blue produced by the Tikuna/Magüta people, resulting in structures similar to those proposed in Figure 7. This reasoning will form the basis for future investigations including the community, as detailed above.

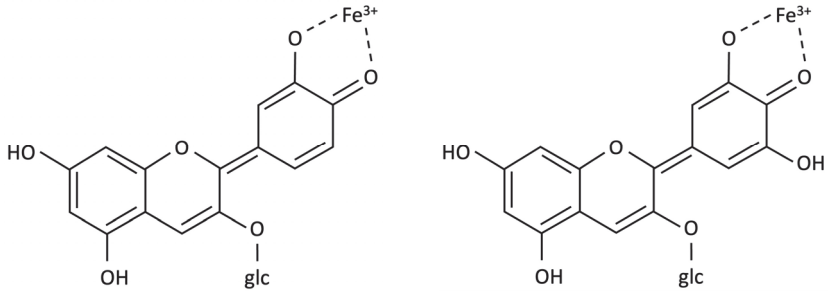

Figure 7. Representation of the potential chelates in the blue pigment prepared by the Tikuna/Magüta people by mixing fruits from naïcü with iron. (**a**) is from cyanidin-3-O-glucoside and (**b**) from delphinidin-3-O-glucoside; glc = glycoside. Not all the Fe^{3+}–ligand chemical bonds are represented in this figure.

4. Conclusions

The use of a single blue colorant (ultramarine, indigo, phthalocyanine blue, crystal violet, or Prussian blue) or a mixture of blue colorants (Prussian blue and ultramarine or Prussian blue and indigo—in addition to black) by the Tikuna/Magüta people in their female initiation ritual masks evidences their artistic knowledge and intention to achieve specific shades of blue, which could also be attributed to spiritual reasons. The results also evidence the replacement of natural colorants with synthetic ones and the potential loss of former Tikuna/Magüta traditional material knowledge, a warning for the urgent need to investigate their past and present painting practices. The urgency is also due to the fact that many of the natural Tikuna/Magüta colorants present in museums are already degraded, and the documentation of their materials and techniques is scarce and sometimes ambiguous. The replacement of materials, the loss of former traditional knowledge, and the possible low chemical stability of former colorants may be related to the non-identification of the unknown blue in this research.

Although a few traditional approaches from technical art history and conservation science could be considered to continue this research, the authors propose an alternative with a paradigm shift to prioritize the people culturally and spiritually connected to the items instead of prioritizing the material understanding and the researchers. The proposed approach involves community engagement through CBPR and aims to help promote more socially responsible and inclusive practices in technical art history and conservation science based on examples from fields like conservation, health, and archaeology. Because there are no systematic CBPR studies in technical art history and conservation science, much work needs to be performed regarding case studies and the development of methodologies and ethical considerations.

In addition to investigating the materiality related to the Tikuna/Magüta coloring practices, it is also important to understand, for example, the meanings of the colors, of the materials used in their coloring practices, of the chemical reactions they performed when transforming nature, and of the replacement of natural colorants by modern ones. These kinds of inquiries are relevant both in art history and conservation, and the engagement of the Tikuna/Magüta community as collaborators is fundamental in answering them.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/heritage7090222/s1, **Table S1.** Additional information from the Tikuna/Magüta items from the Museum of Archaeology and Ethnology from the University of São Paulo (MAE, Brazil). Photos: RG 8649, RG 8710, RG 8716, RG 8753, RG 8753 (2), RG 8764, RG 8889, RG 8892, RG 8894, RG 8898, RG 8902, RG 9454, RG 9984, RG 10034, and RG 10896 (by Ader Gotardo); credits: Museu de Arqueologia e Etnologia da Universidade de São Paulo. The items' descriptions were obtained from the MAE's collection website (http://sophia.mae.usp.br) accessed on 2 March 2024; the English descriptions are the authors' translation. **Table S2.** Additional

information from the Tikuna/Magüta items 996-24-30/11694 and 47-8-30/5627 from the Peabody Museum of Archaeology and Ethnology from the Harvard University (U.S.A.). Photo: credits: Gift of Richard E. Schultes, 1996. Courtesy of the Peabody Museum of Archaeology and Ethnology, Harvard University, 996-24-30/11694. The items' descriptions were obtained from the Peabody Museum's collection website (https://collections.peabody.harvard.edu/collections) accessed on 2 March 2024.

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Traditional Fish Leather Dyeing Methods with Indigenous Arctic Plants

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Abstract: Along the Arctic and sub-Arctic coasts of Alaska, Siberia, north-eastern China, Hokkaido, Scandinavia and Iceland, people have dressed in clothes or worn shoes made of fish skin for millennia. (Within this article, the terms fish skin and fish leather are used to indicate different processes of the same material. Fish skin: Skin indicates the superficial dermis of an animal. Fish skin is referred to as the historical raw material that is tanned following traditional methods such as mechanical, oiling and smoking tanning, using materials such as bark, brain, urine, fish eggs and corn flour. Fish leather is used to refer that the fish skin has passed one or more stages of industrial vegetable or chrome tanning production and is ready to be used to produce leather goods). These items are often decorated with a rich colour palette of natural dyes provided by nature. In this study, minerals and raw materials of plant origin were collected from riverbanks and processed by Arctic seamstresses who operated as designers, biochemists, zoologists, and climatologists simultaneously. During our research, an international team of fashion, tanning and education specialists used local Arctic and sub-Arctic flora from Sweden, Iceland, and Japan to dye fish leather. Several plants were gathered and sampled on a small scale to test the process and determine the colours they generated based on the historical literature and verbal advice from local experts. This paper describes the process and illustrates the historical use of natural dyes by the Arctic groups originally involved in this craft, building on the traditional cultural heritage that has enabled us to develop sustainable dyeing processes. The results are promising and confirm the applicability of these local plants for dyeing fish skins, providing a basis for a range of natural dye colours from local Arctic flora. The aim is to develop a moderate-sized industrial production of fish leather in this colour palette to replace current unsustainable chemical dyeing processes. This project represents an innovation in material design driven by traditional technologies, addressing changes in interactions between humans and with our environment. The results indicate that new materials, processes, and techniques are often the fruitful marriage of fashion and historical research of traditional methods, helping the industry move towards a more sustainable future.

Keywords: historical fish skin; traditional natural dyes; indigenous arctic and sub-arctic flora; local cultural heritage; sustainable fashion

1. Introduction

The historical significance of fish skin has often been overlooked within material culture studies, with archaeologists typically emphasizing their role as a food source rather than as a raw material [1]. The scarcity of surviving material culture from both plant and animal sources, creates gaps in the archaeological record [2]. However, traditional Indigenous practices reveal the versatility of fish skins, particularly salmon skin, which has been used widely for both sustenance and clothing [3].

The Indigenous Inuit, Yup'ik, Alutiiq, and Athabascan of Alaska; Siberian Peoples like the Ulchi, Nivkh, and Nanai; the Ainu from Hokkaido Island in Japan and Sakhalin Island in Russia; the Hezhe from northeast China; the Saami of northern Scandinavia, and Native Icelanders all have historical evidence of fish skin production.

These Peoples developed specialised techniques for harvesting and processing fish skin to craft suitable clothing, essential for survival in one of the harshest climates in the world. Fish skins were used for wind protection and insulation. Distinct costumes with stylistic variations in design, decoration and dyeing techniques throughout the Circumpolar North reflect resilience, cultural diversity, and the work of highly skilled individuals [4]. Arctic societies have constantly adapted to environmental change through material innovation and technological advances, often facilitated by interactions with both nearby and distant communities [5].

Historically, the natural hues of animal skins provided humans with their earliest access to colour, inspiring artists to create lavish artwork by blending the earth-toned colours found in different fish species. The Ainu People, for example, skilfully manipulated the subtle shades of fish skins to create intricate patterns on their garments (Figure 1A) [3]. Accounts of travels around Iceland in the mid-to-late 18th century describe Icelanders wearing traditional shoes made from the skin of the spotted wolfish (*Anarhichas minor*) [6]. The beautiful natural pattern of the skin, resembling that of a leopard, made dyeing unnecessary (Figure 1B).

(**A**) (**B**) (**C**)

Figure 1. Historical fish skin artefacts. (**A**) Ainu salmon skin robe. Botanic Garden & Museum (HUNHM), Field Science Center for Northern Biosphere, Hokkaido University, Sapporo, Japan. (**B**) Spotted wolfish skin shoes. National Museum of Iceland. Reykjavik, Iceland. (**C**) Nanai fish skin boot with indigo dyed panel. Amur River, Siberia. Penn Museum. Philadelphia, USA.

Plant-based dyestuffs have long been used for leather dyeing, with tannins extracted from bark serving as one of the earliest known technologies [2,7]. Natural dyes extracted from flowers, fruits, wood, and bark [8], often supplemented with wood ash and metallic salts, have been used to achieve a range of muted hues [9]. These ancient dyeing techniques have contributed to the development of diverse artistic craftsmanship [10].

In Arctic societies, access to natural raw materials limited colour options to the subtle beauty of earth shades and tonal contrasts [2]. Traditional sources of natural dyes vary depending on climate and geography [11]. These dyestuffs, derived from plants and insects, can be categorised into direct dyes, insoluble vat dyes, and mordant dyes, each offering unique properties for colouring [12].

Yellow dyes, for instance, can be derived from a range of sources, including weld and dyer's greenweed, while browns, greys, and blacks are achieved using tannin-bearing substances such as tree barks, nuts, and galls [12].

Indigo, sourced from various plants, introduced a deep blue hue to societies, diverging from the earth tones prevalent in traditional palettes [2] and has been widely used to dye panels decorating Nivkh and Nanai fish skin coats and boots (Figure 1C).

The use of natural dyestuffs from plant sources, often termed "green dyeing," offers biodegradable and environmentally friendly alternatives to contemporary synthetic dyes [13,14].

Despite the rich history of fish skin use, studies on fish skin dyes remain limited, with conservators often focusing more on preservation techniques rather than the pigments or tannins used to produce the artefacts [2]. This paper aims to address this gap by assessing different fish skin dyeing processes using Indigenous Arctic and sub-Arctic plants, thereby contributing to a deeper understanding of traditional dyeing techniques and their cultural significance.

2. The Project

The FishSkin project, funded by the EU under H2020-MSCA-RISE-2018, brings together experts to explore the potential of fish skin as a sustainable raw material. Through practice-based research and interdisciplinary collaboration, fostering international partnerships we aim to develop natural dyeing techniques for fish leather while supporting local dyestuffs and traditional processes. Drawing on our experiences as tanners, dyers, designers, and educators, we aim to address sustainability challenges in the fashion industry by integrating design practices with environmental and social considerations. Four case studies conducted in locations such as Sigtuna in Sweden, Kyoto and Fujino in Japan, and Reykjavik in Iceland provide valuable insights into natural dyeing techniques for fish leather, laying the groundwork for future research and development efforts.

This project was supported by the Nordic Fish Leather tannery in Iceland which supplied the industrially tanned fish leather used in some of the samples. Empirical tests were carried out at Ars Tinctoria laboratory. In collaboration with Nordic Fish Leather and Ars Tinctoria laboratory we plan to experiment further to replace modern chrome-tanned fish leather with vegetable tanning methods, taking advantage of their very low environmental impact. Both institutions are partners of the EU-funded FishSkin project https://www.fishskinhorizon.org/ (accessed on 11 January 2024).

2.1. Project Aims

This paper aims to uncover the historical use of Indigenous Arctic plants for fish skin dyeing, gathering and recording geographical and historical information about them to identify various specimens and documenting their qualities within natural dyeing history. By consulting literary sources, as well as local experts, we aimed to explore the potential of these natural dyes. The focus was on reviving old traditions and local cultural heritage to discover sustainable processes for the future, contributing to collective knowledge [15]. Natural dyeing, using raw plant materials, offers an ideal approach to colouring while connecting products to specific places, people, and experiences. By adopting a restorative method of making, we aim to shift the focus from scarcity and extraction to abundance and regeneration [10].

2.2. Materials and Methods

2.2.1. Fish Leather a Food Waste by-Product

Fish leather is a by-product of the waste stream of the seafood industry [16] where fish are not killed solely for their skin, which represents only a minor part of the value of the animal. Using fish skin for leather production prevents the waste of this renewable resource. Industrially produced fish leather is exclusively sourced as a by-product of the fish farming industry.

When using fish skin from fish farms, it should be noted that some practices are highly controversial and that, in order to ensure quality, sustainability, and animal welfare, land-based fish farms are the best option. Moreover, the fish leather market risks increasing fishing pressure on certain species, and must rely on waste skins from active fisheries.

Fish leather is known for its high tensile, tear, and stitch strength due to its intersecting fibre pattern, making it durable over time. Despite its high performance and lower price

compared to exotic skins, fish leather remains a niche product, unlikely to penetrate the mass market due to capacity constraints and its manual production process.

Nordic Fish Leather, the largest fish leather tannery globally, has been processing this material since 1994, drawing on Iceland's ancient tradition of making wolfish skin shoes (Figure 1B) [17]. NFL tannery, using only Icelandic renewable energy, must ensure eco-friendly tanning processes despite being less polluting than other leathers production processes. They supply fish leather to fashion brands like Nike, Jimmy Choo, John Galliano, Christian Dior, Prada, and Salvatore Ferragamo. The tannery has revitalised this historic eco-luxury material, reviving ancestral tanning techniques and providing employment for the local coastal community [4].

The fish leather samples used for this project were a by-product of the seafood industry. Lotta Rahme's tests were performed with farmed salmon from Norway and salmon skins were traditionally tanned by herself. The rest of the tests were executed with Icelandic-farmed salmon industrially tanned by Nordic Fish Leather.

2.2.2. Traditional Tanning Methods

Indigenous Arctic Peoples developed traditional tanning methods with considerable local differences. They could opt to soften the skins without any tanning solution, or they could alternatively choose to use three groups of tanning materials: fats, vegetable and mineral. To prepare the tanning bath, the early tanners used materials of animal origin such as urine, brains, liver, kidneys, bone marrow, fish oil, fish roe, butter, eggs, or materials of vegetable origin such as cornmeal, tree bark, leaves, gallnuts or a combination of the above [18]. Alum tanning, or "tawing", a process that emerged from accidental immersion in alum-bearing waters, was also used in this project [19].

Lotta Rahme's samples were fully tanned by herself from scratch using some of the traditional tanning methods mentioned using materials such as gallnut or sallow bark.

Samples dyed with Icelandic and Japanese natural dyes used chrome-tanned fish leather from the Icelandic tannery Nordic Fish Leather. Chrome tanning, now the most widely used method globally, involves immersing fish skins in a solution containing chromium sulphate [20]. This method, which takes just one day, produces thinner and softer leather compared to traditional techniques. The main advantages of mineral tanning over traditional tanning are convenience and cost-effectiveness. Commercially, chrome-tanned leather is more affordable than vegetable-tanned leather. However, due to its chemical-intensive nature, chrome tanning is less environmentally friendly and has potential environmental impacts.

2.2.3. Traditional Dyeing Methods

We used natural materials such as bark, pinecones, roots, flowers, leaves, galls, mushrooms, lichens, and seaweed to achieve our desired colours. All dye materials were prepared by hand, involving chopping, drying, and grinding to extract the pigment fully. Every mordant and modifier used was environmentally safe when diluted and released into soil. In our dyeing process, we employed a range of natural resources, resulting in various chemical and physical transformations. Using principles of bush chemistry [2], we integrated plant and animal materials, such as wood ash, urine, and tree bark, to produce acidic and alkaline solutions and mordants like alum or iron. Tannins were also used in colour fixation.

Dyestuffs were locally sourced to avoid harming endangered species or insect biodiversity. By favouring natural materials, we ensured that fish leather could eventually biodegrade and enrich the soil contributing positively to the ecosystem. We advocate for a shift away from fossil-fuel derived manufacturing processes and non-compostable materials in textile systems, employing low-impact, energy-efficient methods to minimise environmental footprint.

2.3. Collection and Processing of Plant Material: Extraction of Tannins and Dyes

Materials were chosen based on criteria such as abundance and availability. The bark of trees was collected for tannin extraction, dried under shade, and oven-dried for two days before being ground into a coarse powder using a mill [21]. The extraction of tannins from plant parts typically involves using water as a solvent, but the method can vary depending on whether solid/powder or liquid tannins are desired.

Plant collection and dyeing are best performed earlier in the growing season to obtain better colouring from younger plants and a more diverse colour palette [22]. The resulting colour depends not only on the plant selected but also on factors like location, weather conditions (dry or wet), and time of year.

2.4. Dyeing Process

For dyeing fibres, washing the material beforehand is usually recommended, but since fish leather comes ready for dyeing from tanning, this step was skipped. The prepared skin was treated with alum and soaked in cold water for over an hour. It was important to adjust the alum amount carefully, as fish skins are sensitive to pH levels. Using a deep stainless-steel pot is preferable to avoid affecting the dyeing process with other metals.

The soaked fish leather is heated in the pot, maintaining the water temperature, according to the tanning method used, from 25 °C to just below 70 °C. After cooling overnight, the leather is rinsed and ready for dyeing. Preparing the dye vat involves filling a large stainless-steel pot three-quarters full of water and adding the prepared plant material. The plants were typically cut into smaller pieces and crushed before being placed in the pot. After heating with the lid on for 20 min, the water began boiling, and then the heat was reduced to simmer for an hour. The resulting dye water is sieved, and the dyeing process was begun by immersing the material to be dyed in the vat, simmering for over an hour at a temperature adapted to the tanning method. After cooling, the skins were left to stand for one to two days, until the colour became stronger.

Fish skins are more delicate than other materials and cannot withstand high temperatures, which can result in less intense colours. Additionally, fish skins are sensitive to significant changes in acidity, or pH levels. It is crucial not to leave fish skins in baths with iron for extended periods, as this can make the skins more brittle. For the brightest and longest-lasting colours, tanning fish skins with gallnuts before dyeing is recommended.

3. Traditional Swedish Natural Dyes by Lotta Rahme

The roots of dyed textiles in Sweden trace back to archaeological findings in Birka (800 BC), revealing fragments of dyed fabric. Wild plants, including roots, berries, bark, leaves, lichen, and later fungi, served as the primary sources of dye fibre. These plants were typically gathered in late spring and summer, with some peasants selling dye plants to local dyers. Written evidence of plant dyeing can be found in Olaus Magnus's "A Description of the Northern Peoples" [23]. Carl Linnaeus played a significant role in documenting locally used dye plants during his travels across Sweden. Numerous dye formula books from the 18th century, based on Linnaeus's observations and other contemporary studies, have been preserved to this day. Brown dye, for instance, was commonly derived from bark, according to Linnaeus's findings [24].

With 40 years of experience as a traditional tanner, Lotta Rahme (Figure 2) has learned techniques from women of various cultures who still uphold ancestral knowledge. Recognising the urgency in safeguarding and passing on these vanishing traditional skills, she has devoted herself to their conservation and transmission. Through teaching courses, authoring books, and producing films, Lotta has played a crucial role in regaining the title of Master Tanner and elevating traditional tanning to the status of Intangible Cultural Heritage in Sweden.

Figure 2. Swedish tanner Lotta Rahme. ©Freja Zeidlitz.

In the summer of 2021, Lotta Rahme spent time in Dalarna, west of Mora, choosing to use locally available plants for dyeing. Lotta adapted wool dyeing recipes for use with fish skins (Figure 3). Typically, wool yarn is pre-treated with a mordant such as alum and cream of tartar to ensure durable and long-lasting colours. Lotta opted to tan her skins with gallnuts or sallow bark. Additionally, she sometimes added alum, salt, or cream of tartar directly to the dye bath as needed.

Figure 3. Experiments by Lotta Rahme on dyeing fish leather with lichens, mushrooms, roots, gallnuts, and bark. © Lotta Rahme.

3.1. Gallnut Tanning

Gallnuts are pathological excrescences formed on oak leaves in response to certain insect bites, creating a protective tissue around the eggs [21]. These galls contain a high concentration of tannins, making them valuable for tanning purposes. Oak and sumac gallnuts (*Rhus*) are particularly prized for their 40% to 70% gall tannin content [25]. This traditional tanning method has ancient roots, with practices dating back to Mesopotamia [26], where gallnuts were ground and boiled to produce colours ranging from dirty yellow to brown. To achieve black dye, the fibre is often mordanted with ferric alum or iron mud [27]. The Greek philosopher Theophrastos of Eresos also documented the use of gallnuts for tanning and dyeing materials [28,29].

Lotta Rahme finds that skins tanned with gallnuts yield the brightest and longest lasting colours. For this project Lotta tanned eleven salmon skins with gallnuts, a vegetable tanning method that produces white leather (Figure 4).

Figure 4. Eleven salmon skins were tanned with gallnut.

3.2. Sallow Bark Tanning

Tan, primarily found in tree bark, varies in quantity depending on the season, age, and size of the trees. The inner bark contains the highest proportion of tan, while the epidermis usually contains none [21]. Vegetable tanning was discovered when hides and skins thrown into pools of rainwater or bog water absorbed the tannin from tree bark [19].

Alder (*Alnus*) bark is widely used by Arctic Peoples for skin colouring, particularly among the Saami. The bark is boiled in water or chewed, spit on the skin, or rubbed in to produce a red-brown colour. Sometimes ash is used in the alder bark extract to enhance the colour [30]. In northern Europe, local tree barks like birch (*Betula*), willow (*Salix)*, larch (*Larix*), and spruce (*Picea*) are the main vegetable tanning materials [25].

Salmon skins can be tanned with sallow bark (*Salix caprea*) (Figure 5), which produces soft, smooth, light brown leather. The bark is best peeled from branches in spring when it contains the most tannin. After boiling the bark in water for an hour, the skins are placed in the solution once it cools to 20 degrees Celsius. The bark bath is stirred and strengthened over a period of up to 10 days. To obtain a black skin, the skins are soaked for 2 h in a solution containing sallow bark and iron.

Figure 5. Two salmon skins were tanned with sallow bark *(Salix caprea*).

3.3. Dyeing with Lichen

Lichens have long been used as dye plants in Nordic countries, producing a hue known as "moss brown." Linnaeus documented their use as early as 1732, particularly noting their collection after rain when they are easier to scrape off stones [24]. In Sweden, the collection of lichens was once an important source of income, with *Umbilicaria pustulata* and *Parmelia saxatilis* being commonly collected species [31]. Byttelet, a red dye made from crabseye lichen (*Ochrolechia tartarea*), was also widely used, with significant quantities being exported from western and southern Sweden in the late 18th and early 19th centuries [32].

Lotta Rahme discovered dyeing recipes with lichen in J.P. Westrings' book '*Svenska Lafvarnas Färghistoria*' [33] (Figure 6). Given the endangered status of the tiny beard lichen *Usnea glabrata* in Sweden, she opted to use herringbone beard lichen (*Usnea dasopoga*) instead.

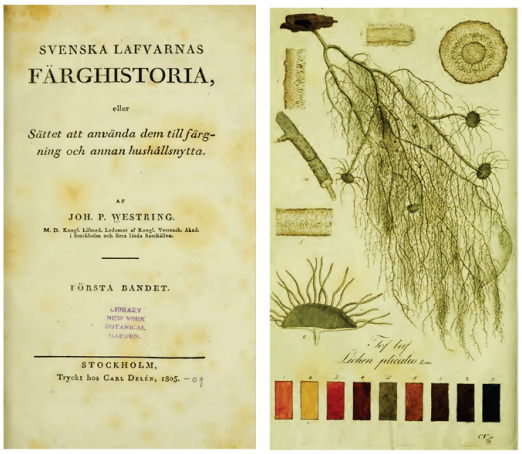


Figure 6. Tiny beard lichen *Usnea glabrata*. Westring, J.P (1805) Svenska Lafvarnas Färghistoria.

For the herringbone beard lichen (Figure 7), 50 g of the beard lichen was boiled in 3.5 litres of water for 3 h, resulting in a 1-litre solution to which 30 g of alum was added. The skins were soaked in a bath for 24 h.

Figure 7. Herringbone beard lichen *(Usnea dasopogo)*, 50 g, collected in July. Boiled for 3 h in 3.5 litres of water, giving 1 litre of solution, with 30 g of alum added. The skin was in the bath for 24 h.

Similarly, 54 g of horsehair lichen (Figure 8) (*Bryoria capillaris*), was boiled for 4 h in 3.5 litres of water to give a 1-litre solution, to which 30 g of alum was added. The tanning baths were allowed to cool to 25 °C before the skins were placed in them. The skins were left to soak for 24 h in the bath.

Figure 8. Horsehair lichen *(Bryoria capillaris)*, 54 g collected in July. Boiled for 4 h in 3.5 litres of water, giving 1 litre of solution with 30 g of alum added. The skin was in the bath for 24 h.

3.4. Dyeing with Roots

Roots have historically been important in traditional dyeing practices, with various cultures sourcing them to achieve desired colours. The technique of tanning the skin with tormentil rhizomes dates to the late sixteenth century and is a known practice among the Saami and settlers in northern Scandinavia and along the Baltic coast [24]. Tormentil, renowned for its medicinal properties, has been used as a dye plant due to its availability when other tanning plants were limited. The Saami in northern Sweden combined the rhizomes of tormentil (*Potentilla erecta*) with grey elder bark to produce a red dye substance [24].

Lotta Rahme used roots from tormentil (Figure 9) (*Potentilla erecta*), totalling 157grams, which were collected in July and dried. These roots were simmered in 2 litres of water for 1 h, resulting in 7 decilitres of solution. The skins were then soaked in the bath for 36 h.

Figure 9. Roots from Tormentil *(Potentilla erecta),* 157 g, collected in July, dried, and simmered in 2 litres of water for 1 h, giving 7 decilitres of solution. The skin was in a bath for 36 h.

3.5. Dyeing with Mushrooms

Sweden's diverse flora and climatic conditions have endowed it with a rich variety of mushrooms, which have been used in various applications. Mushrooms contain essential minerals such as calcium, iron, phosphorus, potassium, and copper, which play a crucial role in natural dyeing by acting as fixatives that help the dye adhere to fibres, particularly iron and copper [27]. While the use of mushrooms for dyeing is a relatively recent practice in Sweden compared to the historical use of lichens in the eighteenth and nineteenth centuries, recently there has been a resurgence of interest in using mushrooms for dyeing wool and other natural fibres, owing to the relatively straightforward dyeing process [24].

Lotta Rahme used surprise webcap mushrooms (Figure 10) (*Cortinarius semisanguineus*), totalling 40 g, which were dried. These mushrooms were boiled for 40 min in 2.5 litres of water, resulting in 1.2 litres of solution. Additionally, 25 g of alum and 12 g of tartaric acid were added to the solution. The skins were immersed in a bath for 22 h.

Figure 10. Surprise webcap mushroom *(Cortinarius semisanguineus),* 40 g, dried. Boiled for 40 min in 2.5 litres of water, giving 1.2 litres of solution to which 25 g of alum and 12 g of tartaric acid were added. The skin was left in a bath for 22 h.

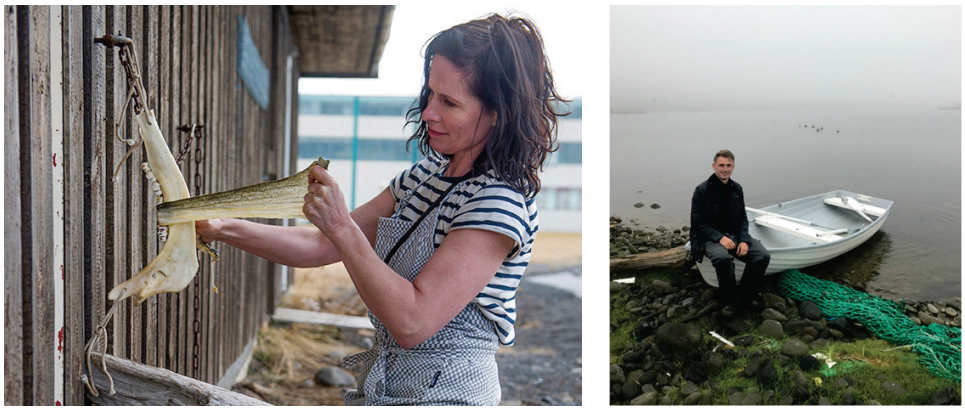
4. Icelandic Natural Dyes by Katrín María Káradóttir and Sigmundur Páll Freysteinsson

Natural dyeing is a longstanding tradition in Iceland dating back to the settlement period, with wool, cotton, and linen being the primary materials dyed. Due to its sub-Arctic

climate, Iceland has a relatively limited plant diversity compared to other regions. While Iceland boasts approximately 500 vascular plant species, Norway has around 1,300, and the UK has between 4,000 and 6,000. This reduced plant diversity in Iceland results in fewer options available for natural dyes compared to more biodiverse regions [34].

The decrease in plant diversity and the rise of invasive plant species could also affect the availability of natural dye sources [22]. While Icelandic plants have historically been used for dyeing, challenges exist in obtaining certain colours, such as red/pink, leading to the importation of materials like *Rubia tinctorum* for specific shades.

Traditional Icelandic plant dyeing has been developed by Katrín María Káradóttir (Figure 11A), a professor in fashion design and the principal investigator of the Horizon 2020 FishSkin project at the Icelandic University of the Arts, along with Sigmundur Páll Freysteinsson, a fashion designer who specialises in traditional natural dyeing techniques (Figure 11B). This project involved gathering a variety of plant specimens and conducting dyeing tests at the textile workshop of the Iceland University of the Arts in Reykjavík. The skins to be dyed were tanned at the Icelandic tannery Nordic Fish Leather in Sauðárkrókur, with an absolute minimum of chromium; therefore, the skins could tolerate much higher temperatures than the skins tanned only with vegetable tannins. The plants tested included flowers and leaves of lupine (*Lupinus*), wood cranesbill (*Geranium sylvaticum*), tansy (*Tanacetum vulgare*), bark of birch (*Betula*), dye lichens, northern dock (*Rumex longifolius*), heather (*Calluna vulgaris*), bearberry (*Arctostaphylus*) and cones of spruce (*Picea*). Additionally, experiments with alternative materials like the dulse (*Palmaria palmata*, red algae) and toothed wrack (*Fucus serratus*, brown algae), both seaweeds (algae) from the ocean were explored to enhance the variety of the dyed skins.



(**A**) (**B**)

Figure 11. (**A**) Katrín María Káradóttir from Iceland University of the Arts tanning fish skins and her student (**B**) Sigmundur Páll Freysteinsson picking up salted shield lichen (*Parmelia saxatilis)* in Langanes, Iceland.

4.1. Icelandic Lichens

In Iceland, various species of lichen, including salted shield lichen (*Parmelia saxatilis*), dye lichens, and rock lichens, have been historically used for dyeing purposes. These lichens contain acids that make them suitable for dyeing, and they can produce brownish colours ranging from dark to light tones, as well as red-brown hues. However, due to their rarity and slow growth, they are not suitable for large-scale industrial dyeing but can be used for limited-edition projects. The over-picking of lichens has led to their classification as an endangered species requiring protection.

For this project, 300grams of a dye lichen was collected from Langanes, with the permission of the landowner (Figure 12A). The lichens were dried before being transported back to Reykjavík. In the dyeing process, the lichens were placed in a deep dye pot overnight and then alum-mordanted fish leather was added to the pot. The mixture was heated to just below 70 °C for over an hour and the fish skin was left in the dye bath for two

days before being removed, rinsed, and stretched to dry. The resulting fish skin exhibited a brown colour with a soft texture and minimal clumping of the roe (Figure 12B).

(**A**) (**B**)

Figure 12. (**A**) Salted shield lichen collected from Langanes with the permission of the landowner. (**B**) Salmon skin dyed with Icelandic salted shield lichen (*Parmelia saxatilis)*.

4.2. Icelandic Seaweed

Seaweed, marine algae, encompasses a rich diversity, with over 1500 green species, 200 brown species, and more than 7000 red species. They offer a wide range of properties, making them versatile resources that can be used in numerous ways. Foraging for seaweed remains a fundamental practice, akin to traditional land-based farming. In Iceland, a country surrounded by lush coastal areas, seaweed is abundant.

For Katrín María Káradóttir, the process of exploring seaweed for natural dyeing began with foraging on the coast near her home where she collected various types of algae, including dulse (*Palmaria palmata*) and toothed wrack *(Fucus serratus*) (Figure 13A).

(**A**) (**B**)

Figure 13. (**A**) Dulse (*Palmaria palmata*) and toothed wrack *(Fucus serratus*). (**B**) Fish skin colour chart made with Icelandic indigenous flora.

These species provide a subtle palette of colours (Figure 13B), ranging from browns and greens to golds and subtle purples. Red/pink has been very difficult to obtain from

Icelandic plants, but the roots of both yellow bedstraw (*Galium verum*) and northern bedstraw (*Galium borale*) have been successfully used. However, the roots of these plants are very small, and the process is so time-consuming that it is believed that these plants have only been used to dye embroidery thread in small quantities [34]. Therefore, Icelanders have for centuries imported a relative, *Rubia tinctorum*, to easily obtain pink shades, even though it is possible to obtain it from Icelandic nature.

4.3. Lupine Flowers

Lupine (*Lupinus*), although not originally native to Iceland, has thrived since its introduction, with records dating back to 1885. It has spread across the country and is commonly used for large-scale land reclamation efforts. Due to its abundance, lupine is well-suited for industrial dyeing purposes.

Both the flowers and leaves of lupine offer potential for dyeing. When using lupine flowers (Figure 14A,B), which yield a green hue, a test was conducted by boiling 180 g of flowers to create a dyeing solution. Adding fish leather treated with alum to this solution resulted in a beautiful light green colour with darker shades interspersed.

(**A**) (**B**)

Figure 14. (**A**) Salmon skin dyed with lupine flowers (*Lupinus*). (**B**) Lupine flowers (*Lupinus*) dye bath.

Similarly, dyeing with lupine leaves (Figure 15A,B), involved dipping fish skin pre-treated with alum into a dye vat that had been created by boiling 136 g of lupine leaves. The result was a dark brown colour with subtle yellow undertones.

(**A**) (**B**)

Figure 15. (**A**) Salmon skin dyed with lupine leaves. (**B**) Lupine leaves.

4.4. Wood Crane's Bill

The wood cranesbill (*Geranium sylvaticum*) is a bushy herbaceous perennial plant that typically reaches heights of up to half a meter. This plant thrives in various habitats, including grove-like and moist heath forests, wet meadows, fens, and morasses across Iceland. The species name "*Geranium sylvaticum*," meaning "of woodland," reflects its natural habitat preference. In folklore, it is also known as "Odin's Grace" as it was historically used to dye war cloaks blue-grey, believed to offer protection to soldiers in battle. Legend has it that carrying wood cranesbill brings prosperity and wealth [35].

The plant is known for producing black and grey colours when boiled with bog iron from marshes. For dyeing purposes, 600 g of wood cranesbill (Figure 16A,B) was boiled to create a dye solution, and fish skin pre-treated with alum was immersed in the solution to create a sample. The resulting colour was a grey-green hue.

(**A**) (**B**)

Figure 16. (**A**) Salmon skin dyed with wood cranesbill (*Geranium sylvaticum)*. (**B**) Wood cranesbill (*Geranium sylvaticum)*.

5. Traditional Japanese Dyes: Matsuyama Issey and Mitsuhiro Kokita

Matsuyama Issey (Figure 17B) is a fifth-generation artisan specialising in the traditional Japanese dyeing of religious monk robes. Growing up watching his father and grandfather practice this ancient craft, Issey decided to continue his family's tradition.

(**A**) (**B**)

Figure 17. (**A**) Matsuyama Issey: Natural dye master. (**B**) Mitsuhiro Kokita educator at Kyoto Seika University with Lotta Rahme.

Mitsuhiro Kokita (Figure 17B), a fashion designer and associate professor, in the Fashion Department, Faculty of Popular Culture, Kyoto Seika University, and the Japanese principal investigator of the Horizon 2020 FishSkin initiative, sought collaboration with

Matsuyama-san to develop a new palette of fish skin colours using traditional Japanese vegetable dyes.

Matsuyama Issey specialises in a traditional dyeing technique known as shinzen (dip-dyeing). He draws inspiration from historical records like the "Nuidono-tsukasa-shiki" and "Kusagusa-noyoudo," which comprehensively detail various dyes and colouring techniques used during the mid-Heian period (10th century). These records mention dyeing materials such as sappanwood (Biancaea sappan), roots of gromwell (Lithospermum), safflower (Carthamus tinctorius), madder (Rubia argyi), and Gardenia, as well as mordants like Camellia ash, straw ash, wood ash, alum, and tessho (ferrous acetate), each contributing to a wealth of Japanese dyeing traditions [36].

For the traditional *shinzen* (dip-dyeing) process, skins were washed with water at a temperature of 40 °C for 5 min. Mordanting was performed at a water temperature of 40 °C for 40 min. Following this, they were washed in soapy water at a temperature of 50 °C for 10 min and then dried. The dyeing was performed at a water temperature of 40 °C for 50 min. After dyeing, the skins were washed in cold water, followed by hot water, and then washed once more in cold water before being left to dry. Rakkudai maintained a pH level of 4, sappanwood maintained a pH level of 6, and *Scutellaria* maintained a pH level of 6.

Skins were reoiled using a 6% fish oil-based medium, 2% phosphoric acid, and 1% emulsifier, maintaining a pH level of around 4 to 5. The wetting took 20 min and the reoiling process took 60 min. After reoiling, 0.5 g of formic acid was added three times at 15 min intervals. The pH after the reoiling process was around 3 to 4. The skins were softened in a drum with a drum temperature of 40 °C at 25.92 rpm with 4 golf balls for 180 min, maintaining a pH level of around 5. To improve colour fastness, different mediums were used: (1) five layers of spray, (2) one layer of Clear TS1125, (3) 0.5 layer of non-brushing thinner, and (4) two layers of lacquer thinner.

5.1. Koganebana/Scutellaria

The Baikal skullcap or Chinese skullcap (*Scutellaria baicalensis*) (Figure 18A), a perennial plant indigenous to the northern mountains of China, found its way to Japan during the Kyōhō era (1716–1736), when seeds were imported from Korea and cultivated in the botanical gardens of the shogunate. Initially grown for medicinal and aesthetic purposes in Japan, it later became valued as a natural dye. *Scutellaria* offers good lightfastness and can produce deep colours when used with alum or iron mordants. The main pigment composition found in the root of the large-flowered skullcap (*Scutellaria baicalensis*) is baicalin, offering not only vibrant hues employed for colouration in textiles but also the added benefit of its medicinal properties [37]. The resulting colour was a beautiful intense yellow (Figure 18B).

(**A**) (**B**)

Figure 18. (**A**) *Scutellaria baicalensis*. (**B**) Salmon skins dyed with *Scutellaria baicalensis*.

5.2. Rakkudai/Lac Dye

Rakkudai (Figure 19A), commonly known as lac dye, is derived from the scale insect *Kerria lacca*, which is predominantly found in Southeast Asia. These insects are either collected from the wild or cultivated for their resin. When the female lac insects invade trees, they secrete a resin that forms a protective covering around them, which is harvested by breaking it off the branches. The dye is then extracted from the stick lac before it is used for dyeing cloth.

(**A**) (**B**)

Figure 19. (**A**) Rakkudai/lac dye. (**B**) Fish skins dyed with Rakkudai/lac dye.

The history of lac dye in Japan dates to the Nara period (710–784), when it was introduced to the country. Over time, lac dye became widely used, particularly during the Edo period (1603–1867). It was commonly employed to dye cotton imported from China, used in Yuzen dyeing, and served as a pigment for painting. Aside from its role as a natural dye, lac has a longstanding history of medicinal use in Japan [38]. A beautiful, intense pink colour was obtained after the dyeing process (Figure 19B).

5.3. Suoh/Sappanwood

Sappanwood (*Biancaea sappan*) (Figure 20A), a small tree belonging to the legume family and native to India, thrives in tropical regions. Its use as a natural dye in Japan traces back to ancient times, with records of its importation during the Nara period (710–784). During the Heian period (794–1185), sappanwood was highly prized for its ability to produce exclusive shades of red and purple, primarily reserved for the emperor and court nobles. Commoners, on the other hand, predominantly used indigo and earthy browns for their dyeing needs [39].

(**A**) (**B**)

Figure 20. (**A**) Sappanwood. (**B**) Salmon skins dyed with Sappanwood.

In the dyeing process, finely chopped sappanwood chips are boiled in water with a small amount of rice vinegar to create a dye bath. The resulting liquid, once strained, is then used for dyeing. Depending on the mordant and dyeing method, sappanwood can produce various tones of pink, red and purple, offering a versatile palette [40]. The final colour obtained from this method was a light pink shade (Figure 20B).

6. Traditional indigo Dyeing: Takayuki Ishii, Elisa Palomino and Lotta Rahme

Historically, earth tones dominated traditional colour palettes until the widespread use of indigo, which introduced a deep blue hue to many societies [2]. Indigo, derived from various plants, has been known since ancient times, with evidence of its use dating back to ancient Egypt [41,42].

Dyer's knotweed (*Persicaria tinctoria*, syn. *Polygonum tinctorium*) was introduced to Japan from China [43]. During the Edo period (1603–1868), Awa indigo dye appeared in markets across Japan, enriching the economy and culture. Artisans in Tokushima continue the legacy of Awa indigo today. "Sukumo" refers to the natural dye derived from the indigo plant, a member of the Polygonaceae (knotweed family), whose leaves are dried and fermented [44]. However, the success of Sukumo indigo dyeing is subject to land quality, environmental conditions, water purity, humidity levels, and temperature fluctuations. Thus, achieving consistent results requires continual experimentation.

Awa indigo dyeing has been preserved and passed down through generations by indigo masters. Lotta Rahme (Figure 21), and Elisa Palomino (Figure 22A), a research associate at the Smithsonian Arctic Studies Center and principal investigator of the Horizon 2020 FishSkin project at Central Saint Martins, University of the Arts, London, have teamed up with Takayuki Ishii (Figure 22A), a master indigo dyer working in the Fujino mountains in Japan, to create a new range of fish skin shades using traditional Japanese indigo.

Figure 21. Lotta Rahme dyeing fish skins with indigo in Takayuki Ishii's workshop.

It takes almost a year to produce Awa indigo. Takayuki cultivates his own, beginning with planting the seedlings in spring. In summer, the matured plants are harvested, and their leaves (Figure 22B) are carefully ground to a fine consistency before being thoroughly dried and stacked in his "Nedoko" or bed. Sukumo, the resulting mixture, holds the indigo colour pigments. However, these pigments are not water-soluble in their natural state and require a transformation. Initially, the indigo leaves are combined with alkaline substances like lime and wood ash lye in a container. This process converts the pigments (indigotin) into water-soluble yellowish green components (leuco-indigotin). The mixture is left to ferment for a week under meticulous temperature control, maintaining a pH level of 11.5. At Takayuki's workshop, there are several vats that are nestled into the floor (Figure 22B), and thermally insulated, maintaining a stable temperature of around 20 °C, each is at varying stages of maturity, resulting in a range of colour strengths.

The process begins by immersing fish skins in the indigo vat for four minutes, followed by airing them for another four minutes. This allows the dye to penetrate and imbue the material with colour. As the fish skins are exposed to air, the water-soluble leuco-indigotin molecules react with oxygen, returning to their water-insoluble state, and the indigotin pigments, are now fixed to the fibres. After thorough washing in water, any excess or unfixed colour substances are rinsed away, revealing a vibrant indigo hue. The fish skins were dyed once, twice, and three times to achieve varying intensities of colour (Figure 23A,B).

(**A**) (**B**)

Figure 22. (**A**): Indigo dyeing process performed by Elisa Palomino, research associate at the Smithsonian Arctic Studies Center with indigo master Takayuki Ishii, at Fujino. (**B**) Indigo vats.

(**A**) (**B**)

Figure 23. (**A**) leaves of dyers knotweed. (**B**) Salmon skins dyed with Sukumo, a fermented dye made from the leaves of dyers knotweed.

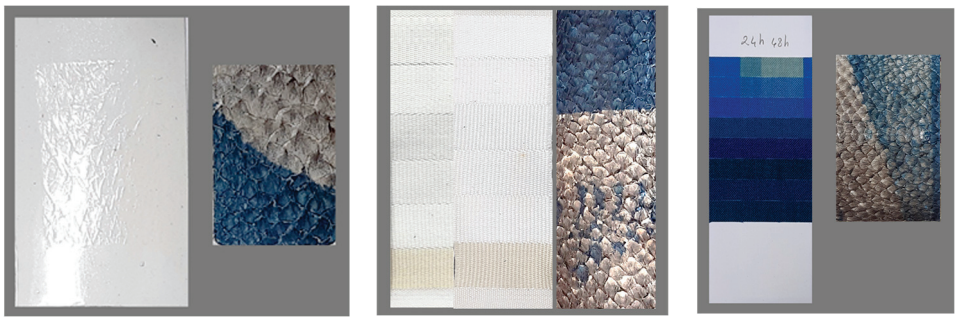
Takayuki's innovative approach to Sukumo production has been documented in his book "The Way of Indigo," which outlines a method using a small quantity of leaves. This approach challenges traditional notions of Sukumo production, previously believed to require large quantities of dried leaves [45]. The decline in Sukumo artisans and the increase in demand have disrupted the balance between supply and demand, making Sukumo

indigo dyeing less accessible. Takayuki's Sukumo recipe, developed over ten years of research and collaboration, offers a solution to this challenge.

7. Light Fastness Tests

Colour fastness tests were performed at the Italian analytical laboratory Ars Tinctoria. Fastness properties were analysed following updated ISO standards. The key properties to be tested were resistance to direct sunlight, which is an important factor, and the intensity of natural light and UV content, which fades colours and intensifies the hue of natural dyes, thus altering the colour.

ISO 15701:2022 (IULTCS/IUF 442) Leather—Colour fastness to migration into polymeric material [46]: For this test, migration was tested on standard PVC layers. This test helps to understand if there will be potential colour migration into plastic materials, and eventual stain of polymeric finishing applied, by contact with neighbouring materials. The results of this test on the indigo-dyed fish skins can be observed in Figure 24A (rate 5/5 for greyscale, where the value 5 represents the highest standard). Fish skins tanned with gallnut and dyed with either herringbone beard lichen (*Usnea dasopoga*), horsehair lichen (*Bryoria capillaris*) or roots of tormentil *(Potentilla erecta*) also scored 5/5 for greyscale. Fish skins dyed with rakkudai scored 5, those dyed with sapanwood scored 4/5, and those dyed with *Scutellaria* scored 4. Fish skins dyed with toothed wrack *(Fucus serratus*) scored 5. Such excellent results together allow for combining the dyed fish skin obtained with any other neighbouring material without the risk of colour transfer.



(**A**) (**B**) (**C**)

Figure 24. (**A**) Colour fastness to migration into polymeric material (PVC). (**B**) Colour fastness to artificial perspiration. (**C**) Colour fastness to artificial light. Xenon arc fading lamp test.

ISO 11641:2012 (IULTCS/IUF 426) Leather—Colour fastness to perspiration (on multifibre) [47]: This test was developed to understand eventual colour fading or migration into different textile fibres with artificial acidic perspiration. A compendium of different fibres, from acetate, cotton, nylon, polyester, acrylic and wool was used in this test. The results for the indigo-dyed fish skins in Figure 24B show a light stain on nylon (rated 4/5), while other types of fibres showed excellent performance (5). Fish skins tanned with gallnut and dyed with herringbone beard lichen (*Usnea dasopoga*) showed a light stain on nylon, cotton, acetate (rated 4/5), and wool (4). Those dyed with horsehair lichen (*Bryoria capillaris*) scored 5 for acetate, cotton, polyester, and acrylic; 3 for nylon and 2 for wool. Fish skins tanned with gallnut and dyed with roots from tormentil *(Potentilla erecta*) showed a stain on wool (3/4) polyester, acrylic (4) acetate, cotton, and nylon (4/5). Fish skin dyed with sappanwood scored a low value of 3 for nylon, 4 for acetate and 4/5 for cotton, polyester, acrylic, and wool. Fish skins dyed with *Scutellaria* show a light stain on nylon and wool (rated 4/5), while other types of fibres showed excellent performance (5). Fish skins dyed with rakkudai showed a light stain on all fibres 4/5. Fish skins dyed with toothed wrack *(Fucus serratus*) showed a light stain on acetate, cotton, and nylon (4), while they showed excellent performance for polyester, acrylic, and wool (5). Also, in this case staining was rated against greyscale where perfect values were represented by a rating of 5.

ISO 105-B02:2014 Textiles—Tests for colour fastness—Part B02: Colour fastness to artificial light: Xenon arc fading lamp test [48]: This test emulates the weathering of a colour sample by exposition to natural solar light. In this case, samples' colour fading is rated against a blue scale on fabrics representing values 1 to 8, where 8 is the highest standard. The lightfastness obtained for the indigo-dyed fish skins (Figure 24C) was 2, which was a very weak result. Fish skins dyed with toothed wrack *(Fucus serratus*) scored 3. Fish skins dyed with rakkudai scored 3/4, those dyed with *Scutellaria* scored 3, and those dyed with sapanwood scored an even lower value (1). When using these dyes, it is recommended to avoid direct sunlight. However, fish skins tanned with gallnut and dyed with beard lichen (*Usnea dasopoga*) scored a remarkable 8 and those dyed with horsehair lichen (*Bryoria capillaris*.) scored 7. Fish skins tanned with gallnut and dyed with roots from tormentil *(Potentilla erecta*) scored 7.

The colour fastness tests showed sufficient light fastness, considering the fact that all samples tested were dyed with natural dyestuffs. The best results of the three different tests were from the fish skin samples tanned with gallnut and dyed with herringbone beard lichen (*Usnea dasopoga*), horsehair lichen (*Bryoria capillaris*), or with roots from tormentil *(Potentilla erecta*), on all portions of the sample tested for 24 h.

8. Conclusions

The dyeing techniques explored in this paper demonstrate the intricate relationship between geographical location, available natural resources, and local tradition and culture. Throughout history, the diverse arrays of colourants used serve as a testament to human ingenuity and creativity in discovering and refining dyestuffs from nature.

While synthetic dyes gained prominence in the mid-19th century, the resurgence of interest in natural dyes today aligns with the emerging sustainable movement. Natural dyeing not only offers beautiful colours but also promotes ecological consciousness by using renewable resources while supporting local livelihoods.

Fashion design, deeply intertwined with material culture, has the potential to foster deeper relational connections between people and their environment. By engaging with natural raw materials and dyes, fashion designers can create products that not only adorn the body but also contribute positively to ecosystem health.

However, challenges remain in integrating natural dyes into industrial production due to factors such as low yield and labour costs. Nonetheless, local small-scale initiatives are viable for meeting the current demand for natural dyes while providing economic opportunities for local communities.

Traditional tanning and dyeing techniques, offer environmentally friendly alternatives with unique properties. These techniques, although time-consuming and requiring specific skills, provide insights into sustainable material processing methods that can be adapted for modern use.

This research highlights the importance of understanding and preserving traditional practices and their biochemical logic to reconnect with our environment offering new perspectives on the interactions between people and nature.

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Article

Practical Dyeing and Technical Imaging: Replicating a Colonial Feather Insignia from Mexico

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Abstract: A colonial feather insignia from New Spain dating to the late 16th century is one of a group of seven unique feather objects kept in museums in Austria, Germany, and Mexico. The insignia represents a highly skilled example of a featherworking tradition documented in historical sources such as the Florentine Codex. In order to make a replica for the National Museum of Anthropology in Mexico City (MNA), an interdisciplinary team carried out technical and material studies before preparing the necessary raw material. At the centre of this work are bird feathers dyed with organic dye and naturally coloured feathers that cover most of the insignia's surface. By working with historical documents, artisans, reference collections of bird skin, and the application of multiband imaging (MBI) and fibre optic reflectance spectroscopy (FORS), it was possible to identify both the bird species and the organic dye used or naturally presented in the feathers. Dyeing experiments to colour-match the different shades of red were conducted by applying traditional recipes and materials. The true value of this research is not necessarily in the finished product or outcome but in the journey itself—specifically in the methods developed and the practical experience gained along the way.

Keywords: Mesoamerican featherwork; replica; cochineal; bird feathers; feather dyeing; multiband imaging (MBI); fibre optics reflectance spectroscopy (FORS)

1. Introduction

The object of this interdisciplinary research is a 16th century colonial feather insignia (Figure 1) from Mexico (Weltmuseum Wien, inv. no. 43.381), which represents a highly skilled example of a featherworking tradition called *amantecayotl* in classical Nahuatl, the language that was spoken in various regions of Mesoamerica around the 15th and the 16th centuries.

The insignia belongs to a unique group of seven pre-colonial and early colonial feather objects preserved in Europe and Mexico: a feather headdress, known as *penacho* (Weltmuseum Wien, inv. no. 10.402, Austria), four feather shields (Weltmuseum Wien, inv. no. 43.381, Vienna; Württemberg State Museum, inv. no. KK_orange_6 and E1402, Germany; Chapultepec Castle, inv. no. 10-92265, Mexico), and a disc or chalice (National Museum of Anthropology, inv. no. 11.3213, Mexico). These objects are testimonies to a colonial history and witnesses of the encounter between the Old and New Worlds.

Thousands of similar objects were destroyed by the *conquistadors*, and hundreds were shipped to Europe where they were distributed amongst the nobility and royalty [1].

Figure 1. Feather insignia (side **a**,**b**), New Spain (E.16.c.), inv. no. 43.381. @ KHM-Museumsverband.

Due to their fragility and susceptibility to insect infestation, only a few have survived in museums. To compensate for the absence of such featherwork in historical collections and for conservation reasons, the National Museum of Anthropology in Mexico City (MNA) has in the past commissioned replicas of the above-mentioned *penacho*, one shield, and the disk from contemporary *amantecas*. Such featherworks are important to museum visitors because of their iconic status and their role in the exhibition narrative and are therefore on permanent display. By using replicas, it is possible to expand the lifespan of the original objects (e.g., preventing light damage) while ensuring public accessibility.

The replicas at the MNA differ from the original in terms of design, size, and material for three major reasons: contemporary craft practices are different from the ancient techniques; feathers from culturally important bird species of the Aztec period are endangered today; and all replicas were made from reference images, without sight of the originals, with the exception of the disc.

Unlike most feather replicas at the MNA, a replica of the feather insignia will be made to be as close as possible to the original. In the future, it will serve as an important didactic tool in the Mexica Hall of the MNA. Therefore, the insignia was examined in detail and individual steps in the craft were reproduced as mock-ups in the conservation laboratory in Vienna. A visual artist will make the replica based on conservation research and his own visual examination during a residency at the Weltmuseum Wien. Since the replica is understood to be an object made with reference to scientific findings, the process will also enable current knowledge on this ancient craft to be reviewed and expanded upon.

When feathers are only present in small fragments, it is very difficult to identify the bird species non-destructively. The feathers identified on the insignia offered the opportunity to test whether it is possible to draw conclusions about biopigments and structural

colours using multiband imaging (MBI) in combination with fibre optic reflectance spectroscopy (FORS). In the field of ornithology and animal behaviour, spectroscopic studies to qualify and quantify feather colour are widely accepted [2–4]. In cultural heritage, FORS and MBI are already well-established methods to study dyes and pigments in textiles and paintings [5–8] but are rarely applied to featherwork, except for by Daher [9] or Pearlstein [10]. However, ultraviolet-induced visible luminescence imaging (UVL) has become an important tool for the light sensitivity assessment of keratin [11], for feather cleaning studies [12], and for feather identification [13].

2. Historical Background

2.1. The Art of Featherworking–Amantecayotl

Various historical sources were used in this research. The most important source for the craft of the *amantecas* is the so-called Florentine Codex [14], or Historia General de las cosas de Nueva España, written between 1575 and 1577 in the city of Tlatelolco by Bernardino de Sahagún and a group of local informants, indigenous collaborators, and local painters. It is a twelve-volume encyclopaedia covering the life, nature, religion, philosophy, history, and culture of the ancient Nahuatl-speaking people of Central Mexico. Book IX (chapter 18–21) is dedicated to the *amantecayotl*. *Amantecayotl* is a specialised craft in which naturally coloured and dyed feathers are glued to a paper support or tied together.

The individual processes of feather selection and preparation by *amantecas* are vividly documented. Three types of *amantecas* operated in two kinds of settings. The *calla amanteca* produced military paraphernalia and sold their products in the markets [15]. The *tecpan amanteca* were associated with the imperial palace; they made luxury gifts and elaborate costumes worn in ceremonies, festivals, and combat [16,17]. A third group, the *calpixcan amanteca*, produced the most precious objects for the Mexica sovereign [18]. All three types of *amantecas* were closely linked to the nobility, as the use of feather paraphernalia and other luxuries was limited to the ruling class [19]. We do not know whether these *amantecayotl* categories were maintained during colonial times.

The Mesoamerican tradition in feather art was promoted by the Spanish missionaries after the *Conquista* and mostly consisted of Christian devotional images and liturgical luxury items for the European royalties, nobles, and leaders of Catholicism. The feather mosaics made by New Spain *amantecas* with depictions of Christ, the Virgin Mary, and saints had already reached Europe, Asia, and Africa as well as the north and south of the American continent at the end of the 16th century [20].

2.2. The Art of Dyeing Feathers Red

The "Memoria sobre la naturaleza, cultivo y beneficio de la grana" by José Antonio de Alzate y Ramírez from 1777 [21] is considered one of the most remarkable studies and the first essay on American cochineal (*Dactylopius coccus*), the breeding and harvesting of this insect, and the use of this dye in New Spain. Cochineal was a tribute paid by many indigenous people, first to the Aztecs and later to the Viceroyalty of New Spain. None of the red dyes from the Old World—kermes (*Kermes vermilio*), Polish cochineal (*Porphyrophora polonica*), and lac (*Kerria lacca*)—could compete with the deep red colour derived from the dye extracted from cochineal (*Dactylopius coccus*) [22]. The dye was in great demand among the Spanish elite for dyeing fabric, and until 1785, the end of the mercantile system, large quantities of the cochineal production was destined for export to Spain [23].

In the Florentine Codex, indigenous informants use various names for the red colour, such as "chili-red" [24] (51v), "scarlet red" [24] (58r), or "red like fresh blood" [24] (217r). Feathers were not only dyed red with cochineal (*Dactylopius coccus*) [24] (216r–217r) but also yellow with, for example, Barba de león (*Cuscuta tintoria* Mart. Former

Enghelm., a variety of the parasitic plant dodder) [24] (217v) or the petals of the sunflower *Cosmos sulphureus* [24] (217r).

In the past, dyers used, and still use, a variety of plants and minerals for the dyeing process in Mexico. The wool is pre-treated for degreasing in a solution of *tequesquite* water [25], *tequesquite* being a natural mineral salt containing compounds of sodium chloride, sodium carbonate, and sodium sulphate.

Natural dyes can generally be used for direct dyeing, but permanent results are only obtained with tanning agents or mordant dyes. Mordanting with metal salts binds the dye to the fibre, improves the colour fastness, and makes the colour more radiant. In addition, depending on the mordant, different shades can be achieved with the same dye [26]. One of the most common mordants was an aluminium-based salt; the feather dyers added alunogen, $Al_2(SO_4)_3 \cdot 17H_2O$), an aluminium sulphate mineral, and then saltpetre (nitrate of sodium or potassium) to the dyebath [24] (65r) in a meta-mordanting process. Alunogen occurs naturally as a rare mineral found in volcanic environments and was used for refining colour and for washing [24] (219v). *Tezhuatl* leaves [27] from a shrub (*Miconia* sp.), which are used as a herbal mordant, are another aluminium-containing source [28]. The leaves are boiled together with alum and *tlaliyac* (copperas, i.e., iron(II) sulphate) to dye not only wool, silk, or feathers but also *tochomitl* (rabbit hair) red [24] (218v). The feather dyers of the past had most likely experienced that an orange-red colour is achieved by adding acidic material to the cochineal dye bath, e.g., the leaves of wood sorrel (Oxalis spp.), which contain soluble salts of oxalic acid [27,29,30], and that the use of alkalis (such as soda ash) results in a blue-red to bright purple colour.

3. Identification of Naturally Coloured and Dyed Bird Feathers for Making a Replica of a Colonial Feather Insignia from Mexico

This paper presents experimental research to characterize bird feathers and their colourants on the insignia based on historical sources, visual examination, and spectral imaging. In order to create an authentic replica, it is crucial to work with feathers from the same bird species. This ensures that the specific characteristics of the feathers, such as colour and texture, can be accurately reproduced. The second part of the project is experimental research on the dyed feathers present. This includes methods for identifying red-dyed feathers and the development of recipes for dyeing contour feathers in two shades of red. Colour measurements were not performed; the red feather colour was assessed visually by direct comparison with the original object. It was much more about concentrating on the practical part and learning as much as possible about traditional dyeing processes and materials for colour matching.

3.1. Feather Insignia: Naturally Coloured Bird Feathers

The naturally coloured feathers of the insignia were identified by visually comparing them with bird skin collections at the Natural History Museum in Vienna and the Pabellón Nacional de la Biodiversidad at UNAM in Mexico City as part of this research project. Additionally, the identification of the feathers was guided by historical sources such as the Codex Mendoza [31]. Most of the naturally coloured feathers are derived from parrots from the family Psittacidae. The long blue wing feathers are from the scarlet macaw (*Ara macao*); they are blue on the dorsal and yellow-orange on the ventral side. The decoratively glued dark-green, yellow-green, and yellow feather tips are from an *Amazona* (parrot) species. The iridescent green feather tips may originate from the domestic wild turkey (*Meleagris gallopavo*) or Muscovy duck (*Cairina moschata*).

The yellow feathers with orange speckles for the petal design were deliberately placed as accents by *amantecas* (Figure 2). Initially, it was assumed that these were colour accents

that were subsequently applied with a dye. However, microscopic examination confirmed that this is a natural colour variation common to the plumage of *Amazona* species (lesser wing covert, head).

Figure 2. Flower motif: yellow feathers and orange speckles, red and pink feathers.

Each part of a naturally coloured feather (shaft, barbs, barbules) can display different colours, and the colour mechanisms in the keratin structure play a role of varying importance in colour rendition. Feather colours originate from biopigments (carotenoid, psittacofulvin, melanin, porphyrin, turacin, turacoverdin), structural, and iridescent structural colours. In contrast to the biopigment colours, the structural colours are created by light scattering at the interfaces of biomaterials—keratin and melanin—and air, each of which has a different refractive index [32]. Most blue, violet, and green colours are a combination of structural colours and biopigments that are created in the barbs. The iridescent colour is produced in the barbules by coherent scattering of light by layers of keratin and melanin granules [33]. Melanin is an effective absorbent of UV and IR radiation [34].

Most of the insignia feathers are from parrots, which derive their colour from the yellow, orange, and red biopigment psittacofulvin. The colour of green parrot feathers is a combination of yellow psittacofulvin in the cortex, melanin granules in the medulla, and the keratin structure (Figure 3) [35]. Psittacofulvin is restricted to the order Psittaciformes (parrots, cockatoos, lories, and lorikeets) [36] and is a useful marker for identifying these birds. It can exhibit a natural bio-luminescence when exposed to a UV source, and this feature can aid in the identification of bird feathers [36]. However, and this has been noted elsewhere [12,37], it is not possible yet to make a clear distinction between luminescent and non-luminescent psittacofulvin chromophores of similar composition.

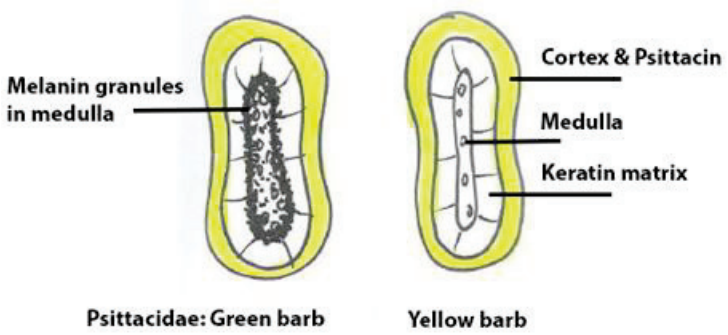


Figure 3. Cross section of a green and yellow Psittacidae barb. Drawing by Renée Riedler, based on Tinberg et al. [38].

The list of birds used by the *amantecas* for their featherwork, which are symbolically coded [39], covers around 20 species [40–42]. These birds were raised in captivity and their

feathers were collected, sold, or given as a tribute. The Codex Mendoza [30] is the primary source on how feathers and feathered objects reached the city of Tenochtitlan, the capital to the Aztec empire, and circulated there. Some of the most colourful feathers belong to bird species living in ecosystems located far from Tenochtitlan; they would have arrived there as commercial goods or tribute from tropical areas south of the empire and along the coast of the Gulf of Mexico. We do not have information about how feathers arrived in the workshops of the convents in New Spain.

3.2. Examination of Dyed Bird Feathers

An important first step was to identify the feathers, both in terms of bird species and colourants, that form the insignia. While most of the vibrant colours are created by biopigments in combination with organized keratin structures as outlined in the introduction, the pink and red feathers are dyed. The colour of the red feathers is a combination of red dye and most likely psittacofulvin biopigments, which are responsible for the yellow, orange, or red colours specific to parrots. Although these dyed feathers resemble naturally red feathers, there are three characteristics that indicate the presence of dye: The feathers have a red vane, a brown shaft, and a pink plumulaceous part, which is usually white, brown or grey in other birds. Another distinguishing feature is the even red colouration on both sides of the feather, while undyed feathers only show the colour on the ventral side. A final hint is the glossy red spots of undissolved dyestuff scattered all over the feather. Glossy red spots are also found on the pink-dyed feathers.

Based on historical sources, visual examination, and scientific studies on two comparable objects (feather shields at the WMW, inv. no. 43.381 and at Chapultepec Castle, inv. no. 10-92265) [43], the authors of this paper considered that there is a high probability that the feathers are dyed with American cochineal (*Dactylopius coccus*). The colour of the red dyed feathers is still vibrant; the authors of this paper anticipate only minor changes in hue and saturation. Insect-derived dyes such as cochineal are fairly light-stable, with fading rates that remain below that of blue wool 3 [44,45], and feathers containing psittacofulvin biopigments were found to be of medium sensitivity [9]. However, the feathers dyed pink are in very poor condition. This is indicated by a severe loss of barbules, which is to be expected given their age and the fact that they have been exposed to chemical and thermal processes during dyeing. Light damage is also visible in the many white spots on the otherwise pink feathers. There are no reliable records of previous exposure to light but it is known that the insignia was part of the collection of Archduke Ferdinand II of Tyrol (1529–1595) at Ambras castle (Innsbruck), where most of his items were kept in cabinets. The insignia was brought to Vienna in the late 19th century and has been on display for long periods of time ever since.

4. Materials and Methods

4.1. Multiband Imaging (MBI)

In order to support our research with accessible and non-destructive equipment, the research team used multiband imaging (MBI) in combination with fibre optic reflectance spectroscopy (FORS). The requirements for the MBI equipment were that it should remain within a limited budget and that it should be mobile (Table 1).

All images were acquired with a Nikon (Vienna, Austria) D850 camera body modified for “full spectrum” (sensitivity between about 360 and 1100 nm). A Nikon Nikkor 50 mm f/1.8D AF lens was used for all the photos. The camera was operated in fully manual mode and tethered to a computer, using the software ControlMyNikon 5.6 to allow sharp focusing. The camera for MBI takes five images, with the filters (UV-VIS-IR) and light sources being changed manually. The CHSOS Robertina technical photography filters set

"https://chsopensource.org/technical-photography-filters-set/" (accessed on 14 February 2024), reference targets, and radiation sources summarised in Table 2 were used. Post-processing procedures of the VIS, IRR, UVL, and UVR images and the creation of IRRFC and UVRFC images were carried out using Adobe Photoshop CS6. The workflow is based on the Charisma protocol [46] and a flowchart provided by Cosentino [8].

Table 1. Equipment for multiband imaging (MBI) at the Weltmuseum Wien.

Camera	Modified Nikon D850 Camera, internal filter disassembled (360–1000 nm)
	• Visible-reflectance (VIS), ultraviolet-reflectance (UVR), infrared-reflectance (IRR) • UV-induced Vis luminescence (UVL) • 2 false colour images (IRRFC, UVRFC)
Filter	• CHSOS Robertina TF filters set (UV/VIS/IR)
Radiation source	• UV LED 365nm SableLED® lamps • Tungsten, Quenox 5000 K, 60 W • Halogen, Osram 6444Os, 12 V, 50 W
Target	• RMI Conservation target • CHSOS MBI-MSI calibration card • Teflon target (PTFE)
Software	• ControlMyNikon • Adobe Photoshop Lightroom • Adobe Photoshop CS6

Table 2. FORS (fibre optic reflectance spectroscopy) setting.

Spectrometer	Detector	Spot Size	Angle	Lamp	Software
Gorgias by CHSOS (Viagrande, Italy), 350–900 nm	Toshiba TCD1304DG	Ø 1 mm	45°	10 W halogen lamp	F. Menges "Spectragryph—optical spectroscopy software", Version 1.2.16, 2022, http://www.effemm2.de/spectragryph/

4.2. Fiber Optic Reflectance Spectroscopy (FORS)

Fiber optic reflectance spectroscopy (FORS) uses fibre optics for directing the white light onto a small spot (typical diameter about 1 mm) to be analysed. The light reflected by the surface can be collected by the same fibre bundle using different angles (typically between 45 ° and 90 °) of detection and varying spectroscopic ranges from the UV to the near IR regions.

The Gorgias reflectance spectrometer for art by Cultural Heritage Science Open Source "CHSOS, https://chsopensource.org/reflectance-spectroscopy-system/; Table 2" (accessed on 14 February 2025) used in this study is made of a 10 W halogen lamp and a Toshiba TCD1304DG linear array detector offering a range of detection in the visible region from about 350 to 900 nm. It is equipped with an optic fibre of 7 × 600-micron core fibres (6 excitation fibres, 1 collection fibre) surrounded by a stainless steel tubing for extra strength. The fibre is 1 m long and it has a 45 ° adapter for reflectance measures.

FORS measurements were taken of the differently coloured feathers of the colonial insignia as well as examples of all the dyed and undyed reference feathers using the 45° setting and measurement times between 0.5 and 1 s per spectrum; single spectra were recorded. Spectra evaluation was performed using the OpenSource software Spectragryph (https://

www.effemm2.de/spectragryph/about.html), which is capable of generating first derivatives of the FORS spectra for determining inflection points besides the absorption maxima.

4.3. Scanning Electron Microscopy with Energy Dispersive X-ray Detection (SEM-EDX)

Scanning electron microscopy with energy dispersive X-ray detection (SEM-EDX) was used to verify the composition of selected materials used during the dyeing experiments, i.e., alum and *tequesquite* from the Sonora market (see supplementary spectra).

The SEM examinations were carried out in cooperation with the University of Applied Arts Vienna, Institute of Conservation, on the carbon-coated samples using a JEOL JSM-IT200 scanning electron microscope equipped with a tungsten cathode and a JEOL SDD EDX detector. Applying the high-vacuum mode and an excitation voltage of 20 keV, a maximum resolution of up to 3 nm can be achieved.

4.4. Feather Dyeing: Materials and Recipes

For the preliminary dyeing studies in a laboratory setting in Vienna, commercially available material was purchased as outlined in dye books and manuscripts [26,29] (Table 3). The feathers were mordanted with alum and dyed with cochineal or dyed without any mordant. Subsequently, variables such as different mordants, e.g., tin(II) chloride, and pH values were explored, and further experience was gained in feather dyeing workshops in Mexico. Experimental dyeing studies conducted in Vienna incorporated dye recipes and additives which had been explored and collected in Mexico.

Table 3. Supply for feathers, dye, and mordant.

Feather	Material	Source
Chicken	White, semi-plumaceous	www.atelier-renato.at; feathers imported from China
Chicken	White, semi-plumaceous	www.moonlightfeather.com
Goose	White, pennaceous "shoulder feathers"; translucent vane	www.atelier-renato.at; feathers from a local farm in Austria
Scarlet macaw	Red, pennaceous	Natural History Museum Vienna; birdskin
Turkey	White, plumaceous	www.moonlightfeather.com
Dye		
Cochineal	Cochineal (silver grey) from Canary Islands, contains 18–22% carminic acid	Kremer Pigmente #3040
	Cochineal (red) from Peru	La Nopalera farm (Tlapanochestli), San Bartolo Coyotepec, Oaxaca
	Cochineal (red)	Schoenfaerberey®
Mordant		
Alum	Potassium aluminium sulphate, $KAl(SO_4)_2 \cdot 12H_2O$	Kremer Pigmente #64100.12100.136
	Naturally occurring mineral, aluminium sulphate resp. alunogen, $Al_2(SO_4)_3 \cdot 17H_2O$	Sonora market, Mexico City
	Tezhuatl leaves (plant based Al salt)	Oaxaca
Tin(II) chloride	$SnCl_2$	Neuber's Enkel
Copper(II) sulphate	$CuSO_4$	Museum stock, unknown supplier
Iron(II) sulphate	$FeSO_4$	Museum stock, unknown supplier

Feathers: For our experimental dyeing protocols, we used five types of feathers (Table 3). All feathers were in good condition, which was confirmed by conducting a simple water repellence test: a water droplet was not absorbed by the feather but rolled off after the feather was slightly twisted. It is therefore assumed that they had been only minimally pre-treated (e.g., gentle cleaning).

Dyestuff: For this study, we used American cochineal (*Dactylopius coccus*) purchased in Oaxaca (Mexico) and from two different European suppliers (Table 3). The cochineal insects were prepared in different ways before dyeing: grinding, soaking overnight, or removing the waxy coating by soaking the insects in an alcohol solution (ethanol:H_2O = 1:3) for one minute; these modifications did not visibly change the dyeing result.

Recipes: With regard to the amount of material, liquor ratio, and dyeing time, we tried to adhere to proven recipes [26,29] to ensure a certain comparability of the results. Demineralised water was used as the solvent throughout, and the maximum temperature was limited to 70–80 °C to protect the integrity of the feathers [47].

Mordant: A dye series with various water-soluble metal salts (based on aluminium, iron, and copper) has been produced. Alum (potassium aluminium sulphate), aluminium sulphate (alunogen), and plant leaves containing aluminium [48] were included in the study. Alunogen was purchased from the Sonora market, which was established in the 1950s. It is one of the most emblematic and popular markets in Mexico City, where you can find traditional raw materials that are not available in other markets.

Although tin(II) chloride was not yet known at the time, it was included in the dye series, along with other mordants, to determine a range of colours that could be achieved on the feathers. It produces bright orange-red colours when combined with cochineal. In addition, experiments were carried out with *tezhuatl* leaves, a plant-based mordant. The leaves were collected by the weavers Victoria Villaseñor Oviedo and Carlos Barrera Reyes in San Mateo del Mar, Oaxaca. Mrs. Oviedo recalled that her mother used them for dyeing with cochineal. The leaves were boiled in water for an hour and the resulting liquid was taken to Mexico City to experiment with it as a mordant.

pH value: For the dyeing process itself, six dye liquors with pH values from 3 to 8 [49] were prepared. The pH was measured with a pH/mV Hand-Held Meter (Wissenschaftlich-Technische Werkstätten GmbH). The colour of carminic acid in solution appears light orange at low pH, changes to red in the weakly acidic and neutral range, and turns violet in the alkaline range. The dye liquors were used in combination with alum and tin(II) chloride, as these mordants produce the desired red hues. The pH was adjusted with acetic acid (CH_3COOH) and sodium hydroxide (NaOH) solutions.

Additives: Citric acid and lemon juice were added to the alum mordant (pH 2.5) and the dye bath. Dyers in Mexico add lemon juice at the end of the cochineal dye bath to obtain a range of colours from red to orange. This practice is widespread in Los Altos de Chiapas, as with the Gómez Pérez family from Chacoma Tenejapa and the Pérez Hernández family from San Andrés Larráinzar. Lemon was not available until after 1493, when it was introduced to America by Christopher Columbus. Another acid used to supplement the alum mordant was tannic acid, which did not affect the pH but did influence the colour hue.

Tequesquite, a salty crust that forms when marshes dry up, from a medicinal shop at Sonora market was purified before use. The undissolved granular material was filtered off and the clear solution evaporated until a white powder remained, containing the soluble fraction of the natural mineral salts, i.e., compounds of sodium chloride, sodium carbonate, and sodium sulphate. Feathers soaked in alkaline solutions such as *tequesquite* are severely damaged and the resulting colour is not red but a light pink. Traditionally, *tequesquite* was used as a mordant [50], because in its naturally occurring, unfiltered form, it also contains

small amounts of Al and Fe, which are only present in trace amounts after the purification (dissolution and filtering) process (see supplementary SEM-EDX spectra).

5. Results and Discussion

5.1. Multiband Imaging (MBI)

Used in MBI mode, the camera captured four images (Figure 4) of each feather colour (Table 4), and during the following image processing, additional UVR and IRR false colour images (UVRFC and IRRFC) were generated, respectively.

Figure 4. Multiband images (MBI) and false colour images: Set-up by Weltmuseum Wien (see details in Figure 5).

UV-induced visible luminescence imaging (UVL): The pink feathers emit pink luminescence in the UVL image (a). This is typical for a red dye such as cochineal on a keratin substrate. Feather keratin alone shows a white to blue UVL [11,12]. The red feathers seen in the visible image absorb UV and appear very dark in the UVL image. This can be explained by a higher concentration of the dye (b) in combination with the presence of biopigments (c); both also obscure the UVL of the keratin. The yellow (d) and yellow-green feathers (e) show UV bioluminescence, which is typical for some yellow parrot feathers [12,36]. However, when the melanin concentration is high, as in the dark green feathers (f), this usually quenches the UVL. The keratin of the light-blue feathers (h) emit a light blue colour in the UVL image.

Infrared-reflected imaging (IRR) and infrared-reflected false colour (IRRFC): The feather keratin is largely transparent to IR radiation, as suggested by the light appearance of the IRR image. The feathers containing melanin appear significantly darker, and the other colourants also have an influence on the observed reflection behaviour. This difference in transparency/reflectance behaviour is evident from the IRRFC image. In the IRRFC image, some red dyes like cochineal appear orange (a, b, c). The yellow and yellow-green parrot feathers with psittacofulvin biopigment (d, e) appear white and light blue, respectively, in IRRFC. The colour difference between both images is most likely due to the presence of melanin in the yellow-green feathers. In general, it is noticeable that structural and iridescent structural feathers appear in various purple colours in the IRRFC image (e, f, g, h).

UV-reflected imaging (UVR) and UV-reflected false colour (UVRFC): The feathers absorb UV radiation to varying degrees. The red-dyed (c) and the green iridescent feathers (g) absorb the most and the light blue feathers (h) the least UV radiation. The differences in reflectance behaviour, resulting from different pigments and structures, are also evident from the UVRFC image. In the UVRFC image, some red dyes like cochineal appear olive green (a, b, c). The yellow (d), yellow-green (e), and dark green (f) parrot feathers with psittacofulvin biopigment appear in various shades of purple in the UVRFC image. The colour difference is most likely due to the different melanin content in the feathers. Structural blue appears bright blue and green iridescent feathers appear a dark blue in the UVRFC image (g, h).

Table 4. Summary of the main observations made from the MBI images of the feather insignia (Figures 4 and 5).

#	Location of Colour	Bird Spec.	UVL	IRRFC	UVRFC	Pigment
a, b	Pink barbs, pink barbules	unknown spec.	Pink shades	Light orange	Olive	Dye
c	Red barbs, red barbules	unknown spec.	Dark red	Orange	Dark olive	Dye, biopigment
d	Yellow barbs, yellow barbules	*Amazona* spec.	Bright yellow	White	Purple	Psittacofulvin
e	Yellow-green barbs, translucent barbules	*Amazona* spec.	Bright yellow-green	Light blue	Purple	Psittacofulvin, melanin, structural colour
f	Dark-green barbs, brown barbules	*Amazona* spec.	-	Light purple	Dark purple	Psittacofulvin, melanin, structural colour
g	Brown barbs, iridescent-green barbules	Turkey or duck	-	Dark purple	Dark violet	Melanin, iridescent-structural colour
h	Light-blue barbs, translucent barbules	Scarlet macaw (*Ara Macao*)	Light blue	Light purple	Light blue	Melanin, structural colour

Although it is not possible to confirm the presence of cochineal in the pink and red feathers without applying additional methods such as FORS or high-performance liquid chromatography (HPLC), the false colours detected in the IRRFC and UVRFC images, together with the low levels of luminescence observed in the UVL image, give strong hints to the presence of either an insect-based red dye or a plant-based dye present at high

concentrations [7]. As plant dyes commonly used in Europe, such as madder, or similar local Mexican species (for example, *Relbunium* spp.) are not known to have been used for feather dyeing in Mexico in that period, the most likely candidate for an insect-based dye would be cochineal, as its use and availability at the period is well-known [21–24].

For a better understanding of the red feathers, MBI images of a macaw feather, a cochineal dyed macaw feather and dyed chicken feathers were obtained (Figures 6–8), and the main observations are summarized in Table 5.

Figure 5. (**a**–**h**) Details of multiband images (MBI) of chevrons with feathers from different bird species.

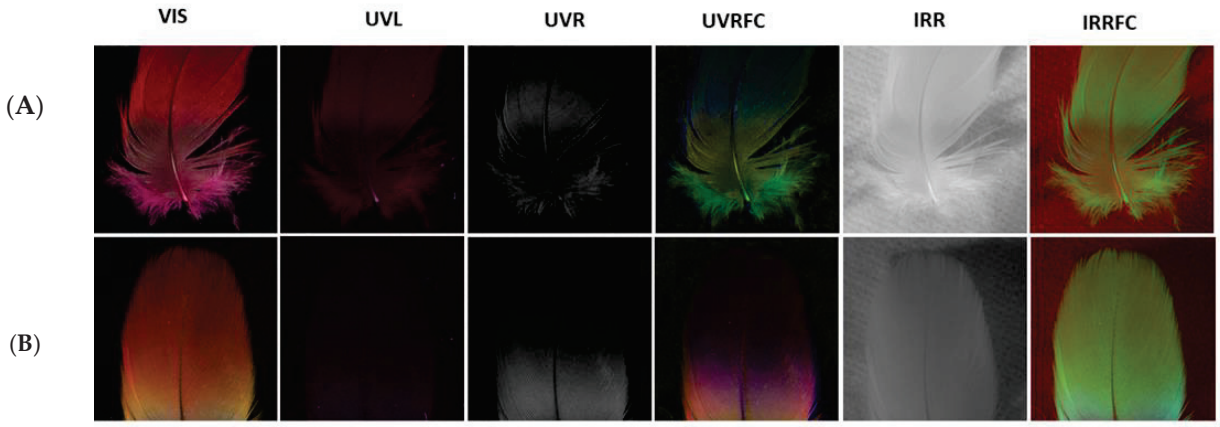


Figure 6. Multiband images (MBI) (VIS, UVL, UVR, UVRFC, IRR, and IRRFC) on black background of a cochineal-dyed scarlet macaw feather and alum mordant (**A**) and naturally coloured scarlet macaw feather (**B**).

UV-induced visible luminescence imaging (UVL): The dyed macaw feather emits red (Figure 6A) and the dyed chicken feathers show red to purple (Figures 7 and 8) luminescence in the UVL image. The red colour observed is the fluorescence of the keratin through the filter of the dye. The undyed macaw feather appears dark in the UVL image.

Infrared-reflected imaging (IRR) and infrared-reflected false colour (IRRFC): The feather keratin is largely transparent to IR radiation, as suggested by the light appearance of the IRR image (Figures 6A, 7 and 8). The colourants also have an influence on the observed reflection behaviour. This difference in transparency/reflectance behaviour is

evident from the IRRFC image. The macaw feathers appear yellow in colour (Figure 6A,B) and the dyed chicken feathers an orange colour (Figures 7 and 8) in the IRRFC image. The white chicken feather remains white in the IRRFC image (Figure 7a).

Table 5. Summary of the main observations made from the multiband images (MBI) in Figures 6–8.

	Bird Spec.	UVL	IRRFC	UVRFC	Pigment
Figure 6A	Scarlet macaw	Pink and red	Yellow and orange	Olive, green, and blue	Alum, cochineal, psittacofulvin
Figure 6B	Scarlet macaw	-	Yellow	Pink and purple	Psittacofulvin
Figure 7a	Chicken	White	White	Yellow	White structural colour
Figure 7b	Chicken	Pink	Light orange	Yellow and olive	No mordant, cochineal
Figure 7c–h	Chicken	Red to purple	Orange	Green	Alum, cochineal, pH 3–pH 8
Figure 8a′–f′	Chicken	Red	Orange	Green	Tin(II) chloride, pH 3–pH 8
Figure 8g′	Chicken	Red	Orange	Green	Alum, cochineal, tannic acid
Figure 8h′	Chicken	Red	Orange	Olive	Alum, cochineal, citric acid

UV-reflected imaging (UVR) and UV-reflected false colour (UVRFC): In contrast to white feathers, dyed, and biopigmented feathers absorb most of the UV radiation. The differences in reflection behaviour resulting from the different pigments and structures are also clearly visible in the UVRFC image. In the UVRFC image, the dyed macaw feather (Figure 6A) has a green downy part, an olive-coloured vane, and a blue tip. The colour of the undyed macaw feather in the UVRFC image ranges from pink at the base to purple closer to the tip. The white feather appears yellow (Figure 7a), and the colour of the unmordanted dyed feather is a mixture of yellow and olive. The dyed chicken feathers appear in olive and green hues (Figures 7 and 8).

For comparison purposes and to investigate whether it is possible to distinguish between carotenoid and psittacofulvin biopigments, MBI was performed on a random selection of available feathers (Figure 9, Table 6) with known biopigments [51]. We identified two problems: firstly, the background colour affects the colour of the spectral images generated for translucent feathers. To solve this problem, two feathers were placed on top of each other. Secondly, the age of the feathers and their state of preservation are different, which affects the intensity of the bioluminescence.

UV-induced visible luminescence imaging (UVL): The white and yellow feather of the sulphur-crested cockatoo (*Cacatua galerita*) (Figure 9A′) and the yellow feather of the blue and yellow macaw (*Ara araurana*) (Figure 9E′) emit a bright orange luminescence in the UVL image, which is typical for many parrots [52]. Both feathers were documented shortly after they were collected from the bird, which might have an impact on the intensity of the bioluminescence. The yellow tail feather of the montezuma oropendula (*Psarocolius montezuma*) (Figure 9D′) with carotenoid pigmentation appears in a light yellow colour in the UVL image, similar to the VIS image. Stains from soiling are visible at the base of this feather. The roseate spoonbill (*Platalea ajaja*) (Figure 9B′) and the scarlet ibis feather (*Eudocimus ruber*) (Figure 9C′) appear in similar colours in the UVL image, less so in the VIS image. Although unavoidable stray light somewhat distorts the colour appearance in this image and was taken into account, it did not influence the interpretation. The green parrot (Figure 9F′), the

scarlet macaw (*Ara Macao*) (Figure 9G'), and the brown (Figure 9H') feathers do not emit luminescence in the UVL image due to their melanin content.

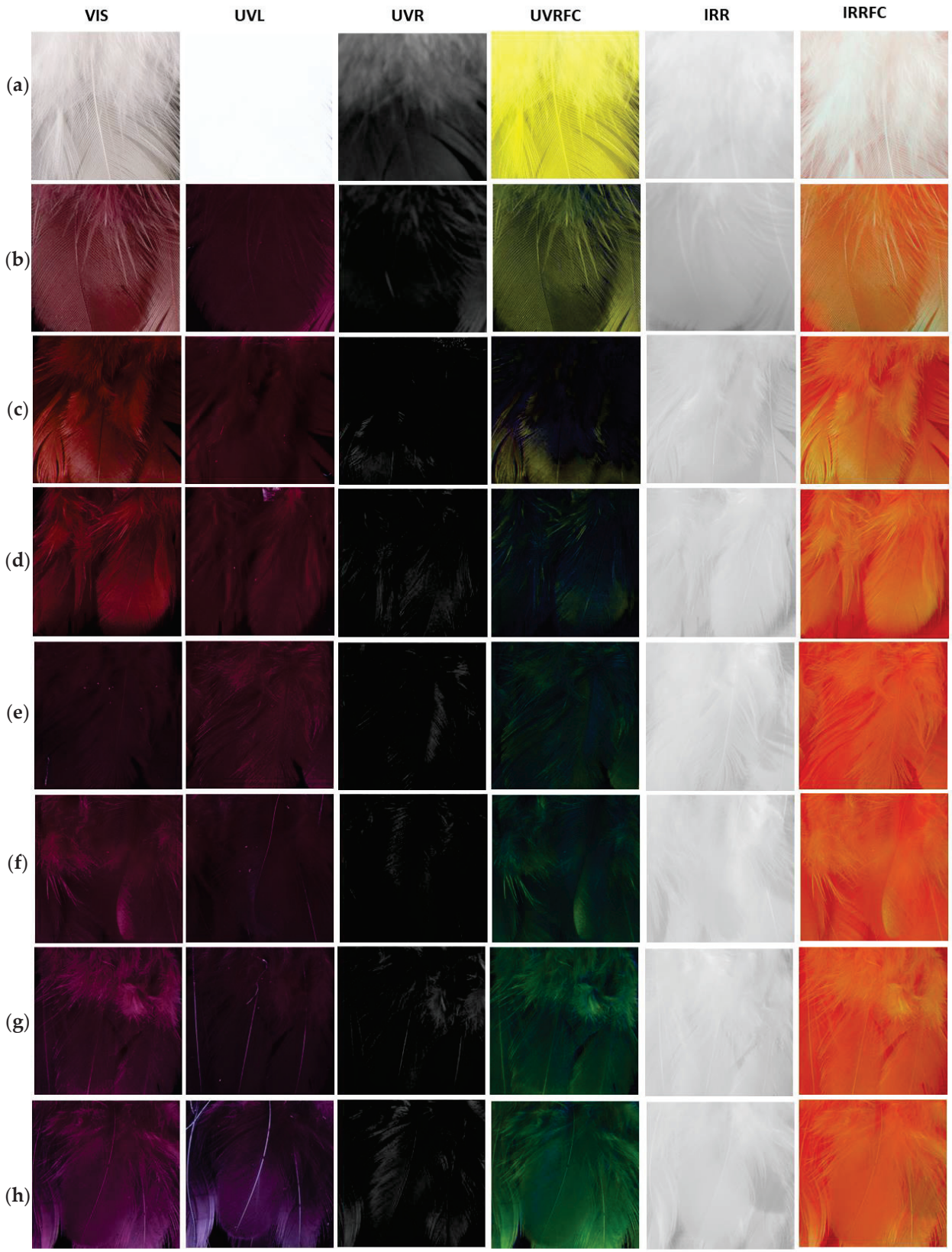


Figure 7. Multiband images (MBI) of white feathers (**a**), cochineal-dyed feathers without mordant (**b**), and cochineal-dyed feathers with alum mordant, pH 3–pH 8 (**c**–**h**).

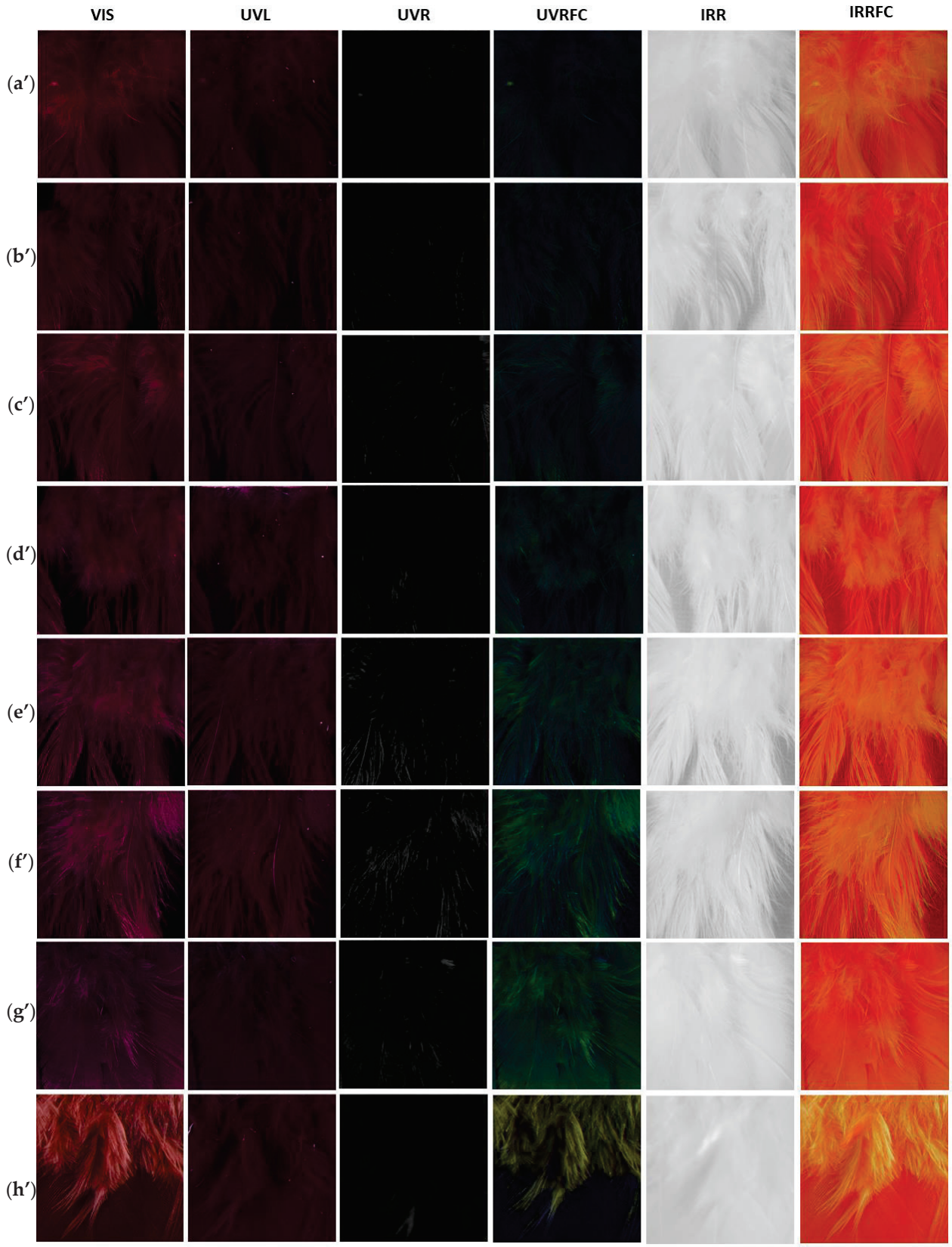


Figure 8. Multiband images (MBI) of cochineal-dyed feathers and tin(II) chloride mordant, pH 3–pH 8 (**a′**–**f′**); cochineal-dyed feathers and alum mordant, tannic acid (**g′**); cochineal-dyed feathers and alum mordant, citric acid (**h′**).

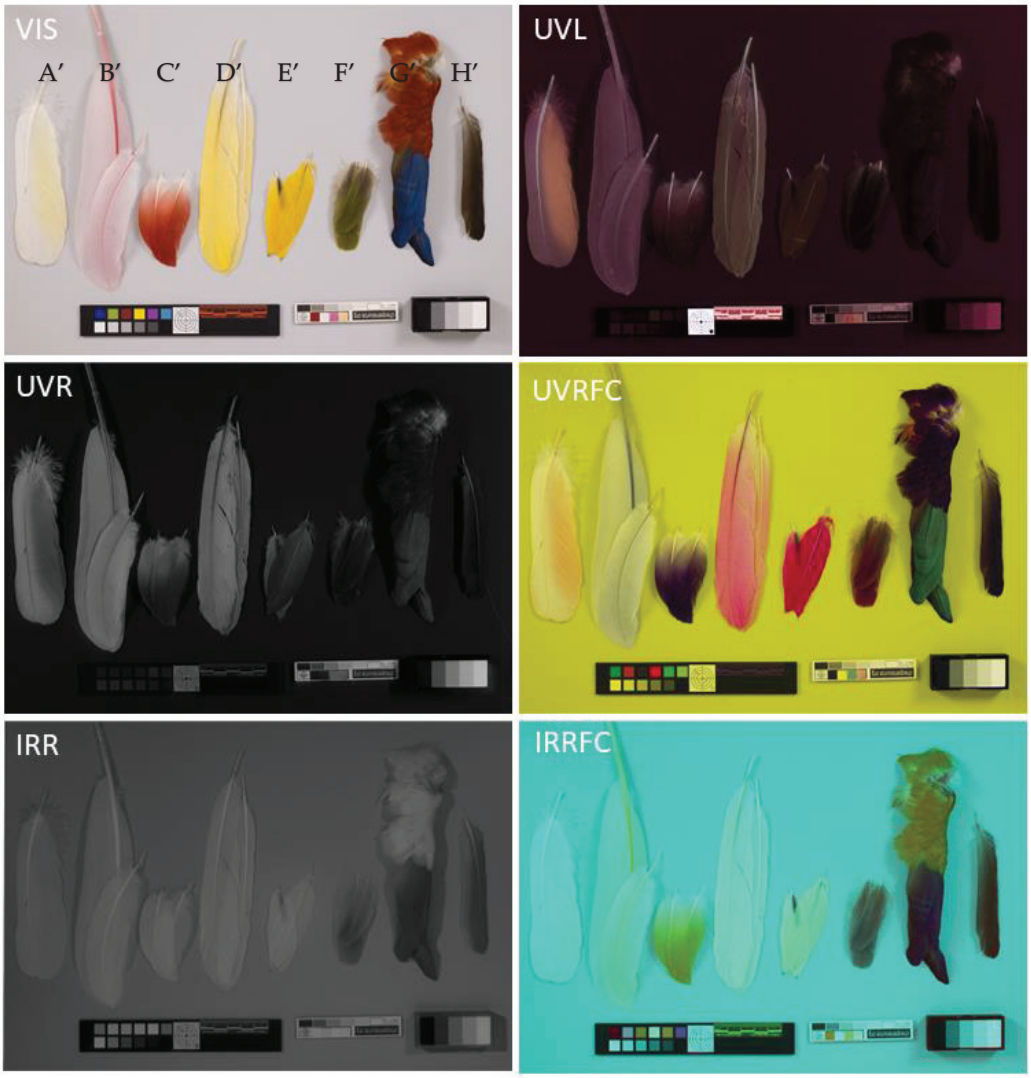


Figure 9. Multiband images (VIS, UVL, UVR, UVRFC, IRR, and IRRFC) of a feather selection representing a range of biopigments on a neutral grey background. From left to right: Sulphur-crested cockatoo (**A′**), roseate spoonbill (**B′**), scarlet ibis (**C′**), montezuma oropendula (**D′**), blue and yellow macaw (**E′**), unspec. parrot (**F′**), scarlet macaw (**G′**), and brown feather (**H′**).

Table 6. Summary of the main observations made from the Multiband images (MBI) in Figure 9.

#	Bird Species	Pigment	VIS	UVL	UVRFC	IRRFC
A′	Sulphur-crested cockatoo (*Cacatua galerita*), coll. 2023	Psittacofulvin	Light yellow	Dark yellow	Pale orange	White
B′	Roseate spoonbill (*Platalea ajaja*), coll. 2007	Carotenoid	Light pink	Light pink	Light blue	Light yellow
C′	Scarlet ibis (*Eudocimus ruber*), coll. 2007	Carotenoid	Orange	Dark orange	Dark violet	Dark yellow
D′	Montezuma oropendula (*Psarocolius montezuma*), coll. 2007	Carotenoid	Yellow	Light yellow	Light purple	Light yellow
E′	Blue and yellow macaw (*Ara araurana*), coll. 2023	Psittacofulvin	Dark yellow	Orange	Dark purple	Light yellow
F′	Parrot, n.d., taxidermy	Psittacofulvin, melanin	Green	-	Dark purple	undef.
G′	Scarlet macaw (*Ara Macao*)	Psittacofulvin	Red	-	Dark violet and pink	Orange
	Scarlet macaw (*Ara Macao*)	Melanin	Dark blue	-	Turquoise	Dark violet
H′	Brown wing feather, n.d.	Melanin	Brown	-	Brown	Brown

Infrared-reflected imaging (IRR) and infrared-reflected false colour (IRRFC): The feather keratin is largely transparent to IR radiation, as suggested by the light appearance of the IRR image. The melanin-containing keratin appears significantly darker, and the other pigments have little to no influence on the observed reflection behaviour. Some difference in transparency/reflectance behaviour is evident from the IRRFC image: the feathers based on psittacofulvin or carotenoid biopigments appear white (Figure 9A') or yellow in different levels of brightness (Figure 9B'–E') or orange (Figure 9G'). The colour of the green feather (Figure 9F') in the IRRFC image is an indefinable mixture of greys. The blue part of the scarlet macaw wing (Figure 9G') shows brown, but also some blue hues, and the brown feather (Figure 9H') appears light brown in the IRRFC image. The brown colours in the IRRFC images are indicative of their melanin content.

UV-reflected imaging (UVR) and UV-reflected false colour (UVRFC): The feathers absorb UV radiation to varying degrees. The white part of the cockatoo (Figure 9A'), the pink spoonbill (B'), and the yellow oropendula feather (D') reflect the most UV radiation and the green parrot (F'), the red macaw (G') and the brown feather (H') the least. The differences in reflectance behaviour, resulting from different pigments and structures, are also evident from the UVRFC image.

The yellow part of the cockatoo feather appears in a pale orange in the UVRFC image (A'). This colour differs significantly from the colour of the yellow macaw (E') and green parrot feather (F'), which appear in a dark purple colour.

It should be noted that the cockatoo belongs to a different bird family (Cacatuidae) to the macaw and unknown parrot (green feather). The spoonbill appears in a subtle blue (B') and the scarlet ibis in a dark purple (C'). The third feather based on carotenoid pigmentation, the yellow oropendula feather, displays a pink-magenta colour in the UVRFC image (D'). The red macaw feathers appear in a dark purple (G'), the blue macaw in turquoise (G'), and the brown (H') in a very similar brown colour in the UVRFC image.

5.2. Fiber Optics Reflectance Spectroscopy (FORS)

A usual way of plotting the absorption information inherent in FORS reflectance spectra is using the log(1/R) coordinates, known as apparent absorption. Here, the absorption bands clearly discriminate the carotenoid-based yellow colour of the montezuma oropendula reference feather (Figure 10, spectrum c) from the yellow colour of the chevron (Figure 10, spectrum a) and flower petal feathers within the colonial insignia (Figure 10, spectrum b). The carotenoid-based yellow feather of the oropendola has absorption peaks at approximately 404, 430, 457, and 487 nm, whereas the spectra of the insignia's yellow feathers show broad absorption bands around 450 and 475 nm [9]. The main difference is the lack of structure in the spectra from the yellow areas of the insignia compared to the reference spectrum (carotenoid). As the yellow feathers have been identified as being from a parrot species, it is likely that the pigment is a psittacofulvin, based also on comparison to work including reference spectra by Tinbergen et al. [38].

In the same way, an insect-based dye such as cochineal can be identified by its absorbance maxima around 525 and 560 nm (Figure 11a) and an inflection point at approximately 590 nm (Figure 11b) [5,53]. Using the first derivative plot for our FORS spectra, the inflection point for the feathers of the original insignia could be detected at 607/608 nm (Figure 11b, spectra a and b), which is in good accordance with the alum-mordanted cochineal-dyed chicken feather, applying pH 4 (Figure 11b, spectrum d). Changing the pH value (e.g., to pH 3) during the dyeing experiments leads to a clear shift in the inflection point of the corresponding FORS spectrum for the dyed chicken feathers (Figure 11b, spectrum c) to a higher wavelength. By using tin(II) chloride as a mordant instead of alum at pH 4 and 3, the inflection points are shifted to lower wavelengths, i.e., between 590 and 600 nm (FORS data shown in the Supplementary Material). It is well known that loss of

spectral structure is a function of dye concentration [7], and this is the case for the spectra shown in Figure 11a.

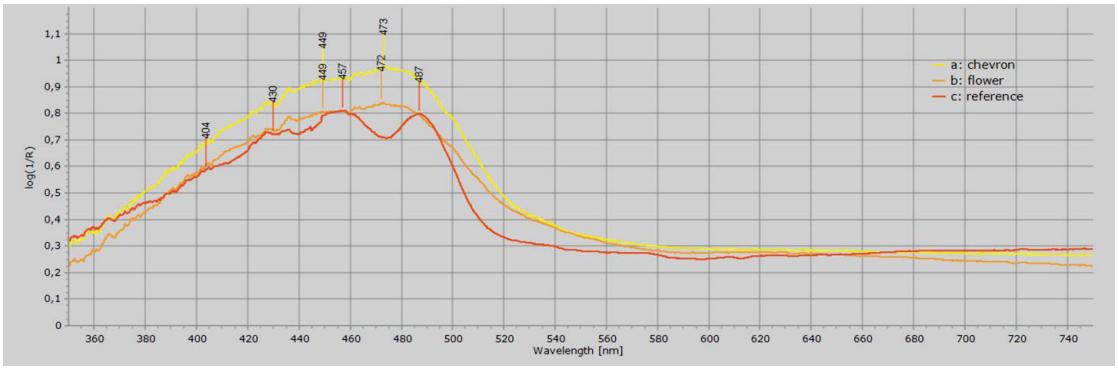
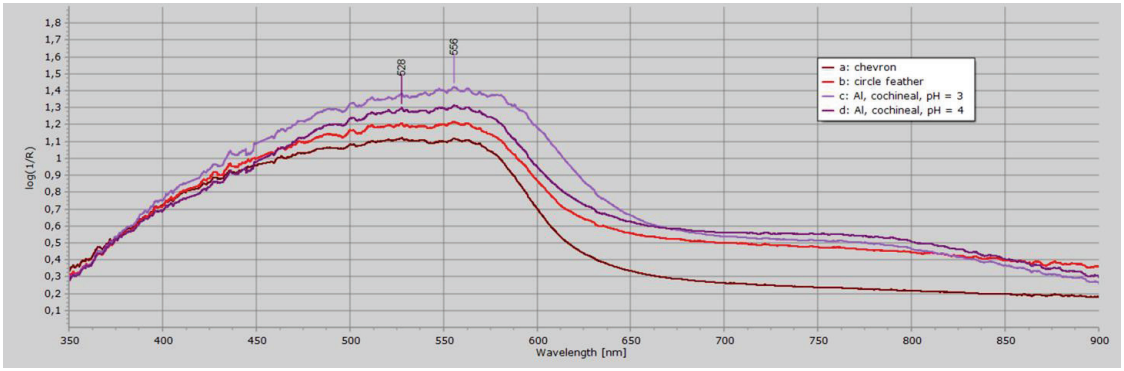
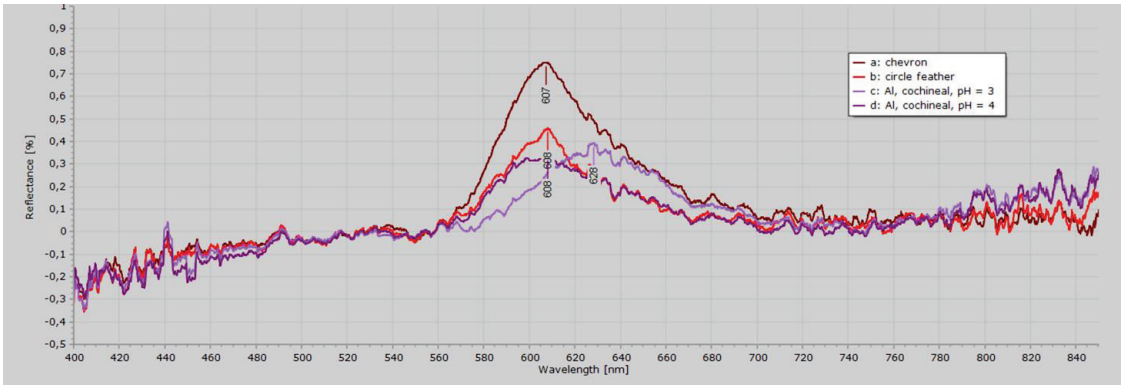


Figure 10. FORS spectra plotted in log(1/R) coordinates: the yellow feathers of the insignia (a: chevron; b: flower) show clearly different spectra compared to the carotenoid-based yellow feathers of the montezuma oropendula tail (c: reference).



(**a**)



(**b**)

Figure 11. (**a**) FORS spectra plotted in log(1/R) coordinates: Red-dyed feathers of the colonial insignia (a: chevron; b: circle feather) compared to alum-mordanted cochineal-dyed chicken feathers (c: Al, cochineal, pH 3; d: Al, cochineal, pH 4). (**b**) First derivative of FORS spectra as shown in (**a**). The inflection point of the spectra for the red-dyed feathers of the colonial insignia (a, b) closely matches the inflection point of the spectrum for the alum-mordanted/cochineal-dyed chicken feather applying pH 4 (d). Changing the pH from 4 to 3 in the dying experiments clearly shifts the inflection point in the corresponding spectrum (c).

5.3. Dyeing for Making a Replica: Observations

The colour of the red- and pink-dyed feathers for the disc and chevron design was approximated by focusing on the effects of different chemicals and pH levels. The aim was to create a recipe for the pink-coloured feathers and one for the red-coloured feathers based on a visual comparison with the original object.

Feathers: Two types of feathers from different sources were used: chicken feathers and goose shoulder feathers. Since the feathers come from different sources, they were cleaned in different ways, possibly with cleaning agents. We cannot rule out the possibility that some preen oil was still present. A colour difference (with and without mordant) (Table 7a–d) can be attributed to the different structure of the two types of feathers because one can rule out the possibility of substances remaining on the feather after exposure to the dye bath (with and without mordant bath).

Table 7. Recipes (a–r): Feather colour variation based on the type of feather, the basic dye recipe, the mordant and additives.

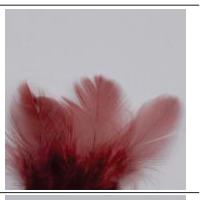
Recipe #	Feather	Recipe	Mordant	Additives	Image
a	Goose	Kirby, van Bommel, Verhecken 2014	without mordant		
b	Chicken	Kirby, van Bommel, Verhecken 2014	without mordant		
c	Goose	Kirby, van Bommel, Verhecken 2014	alum $KAl(SO_4)_2 \cdot 12H_2O$		
d	Chicken	Kirby, van Bommel, Verhecken 2014	alum $KAl(SO_4)_2 \cdot 12H_2O$		
e	Chicken	Kirby, van Bommel, Verhecken 2014	copper sulphate	pH 4	
f	Chicken	Kirby, van Bommel, Verhecken 2014	iron sulphate	pH 4	

Table 7. *Cont.*

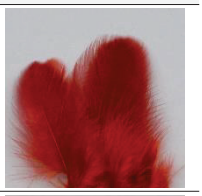
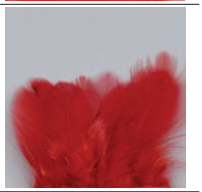
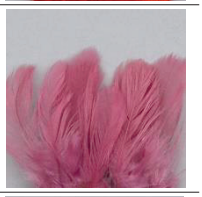
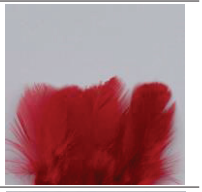
Recipe #	Feather	Recipe	Mordant	Additives	Image
g	Chicken	Kirby, van Bommel, Verhecken 2014	Alum $KAl(SO_4)_2 \cdot 12H_2O$	pH 4	
h	Chicken	Kirby, van Bommel, Verhecken 2014	Tin(II) chloride	pH 4	
i	Chicken	Kirby, van Bommel, Verhecken 2014	Alum $KAl(SO_4)_2 \cdot 12H_2O$	Cream of tartar	
j	Chicken	Arroyo Ortiz 2020	*Tequesquite*		
k	Turkey	Barrera Reyes 2023	Alum *tezhuatl*		
l	Chicken	Arroyo Ortiz 2020		Citric acid	
m	Chicken	Arroyo Ortiz 2020	Alum $KAl(SO_4)_2 \cdot 12H_2O$	Citric acid	
n	Chicken	Arroyo Ortiz 2020	Alum $KAl(SO_4)_2 \cdot 12H_2O$ tequesquite	Citric acid	
o	Chicken	Arroyo Ortiz 2020	Alum $KAl(SO_4)_2 \cdot 12H_2O$	Tannic acid	

Table 7. *Cont.*

Recipe #	Feather	Recipe	Mordant	Additives	Image
p	Chicken	Kirby, van Bommel, Verhecken 2014	Alunogen $Al2(SO_4)_3{\cdot}17H_2O$		
q	Blue and yellow macaw	Kirby, van Bommel, Verhecken 2014	Alum $KAl(SO_4)_2{\cdot}12H_2O$		
r	Scarlet macaw	Arroyo Ortiz 2020	Alum $KAl(SO_4)_2{\cdot}12H_2O$	Citric acid	

Cochineal: The use of different cochineal products and preparation methods had no visible influence on the colour. Soaking the feathers overnight, variations in the dyeing time of up to Table 7h, and re-soaking in the dye bath as well as a second dye bath did not affect the result.

Mordant: Dyeing feathers with cochineal and alum ($KAl(SO_4)_2{\cdot}12H_2O$) without additives produced a bluish-purple hue, which was significantly different from the desired red hues of the insignia feathers. Pre-mordanting with alunogen ($Al_2(SO_4)_3{\cdot}17H_2O$) resulted in a more reddish hue (Table 7p) and tin(II) chloride produced bright orange colours (Table 7h). Copper and iron sulphate created shades of purple (Table 7e–f).

pH-value: The pH of the dye bath played a crucial role in determining the final colour. In acidic conditions, the carminic acid dye bath turned red, whereas in alkaline conditions, it turned blue-violet. In order to achieve a red colour, it was expedient to dye with pH 4 (Table 7g).

Supplementary additives: Supplementary additives such as tannic acid in combination with alum produced a dark red hue with a blue tinge (Table 7o), and citric acid shifted the colour towards an orange hue (Table 7l). However, the most accurate red, closest to the insignia feathers, was obtained by dyeing yellow (Table 7q) or orange (Table 7r) macaw feathers with cochineal and alum.

6. Conclusions

Multiband imaging of bird feathers: We demonstrated the use of multiband imaging (MBI) techniques to investigate biopigments and structural feather colours in birds. The study showed both the potential and the limitations of this method for non-invasive analysis of feather colours. When prior knowledge of the bird species is available, as it is for the insignia, specific patterns can be recognized in the MBI images that are related to the type of biopigments. The study struggled to differentiate between colours based on carotenoids and psittacofulvins. Additionally, it was challenging to find a pattern across feathers from different bird families that had psittacofulvin-based colouration. This suggests that birds from different families exhibit distinct MBI patterns although they share the same biopigment. A more comprehensive study that includes a systematic study of

feathers across genera, families, and species in combination with a study of the molecular composition of the biopigments would be required for more reliable conclusions.

What can be said with certainty is that several factors have influenced the outcome of MBI imaging: the state of preservation of the feathers, their structural features, the type and concentration of biopigments present in the feathers, and the type and concentration of dye.

Experimental research: Feather dyeing with cochineal: The formal design of the central motifs (butterfly and flower) is influenced by the European style of the time, but aspects of Mesoamerican origin prevail, among which the predominant use of red stands out. Depending on the context, pre-Hispanic cultures of Mexico assigned a symbolic meaning to the red colour. It can symbolize death and the underworld, or war, blood, and sacrifice; red can also refer to the ancestral time, the earth, and the force of light [54,55]. In this insignia, the presence of red, perhaps intentionally, permeates some of these indigenous concepts. Therefore, the replica project placed a particular focus on the dye study. As already demonstrated in many studies, cochineal is capable of producing a wide range of colours that are influenced by various factors, such as the chemical composition of the dye, the concentration, the type of fibres, the mordant used, and additives [56]. The main goal of this research was to develop a sound understanding of dyeing techniques and to work with materials that may have been used in the past and which are still known and used today.

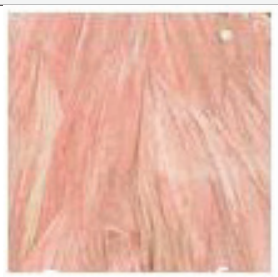
For the pink colour, dyeing with cochineal without mordant proved to be the most effective, as it yielded pink goose and chicken feathers that matched the corresponding colours on the insignia (Table 7a,b). However, a dyeing recipe with mordant (Table 7j,k) will be chosen for the replica to ensure the colour remains permanent, even if the hue will vary. Another possibility would be to add potash to the dye bath with cochineal to achieve a pink colour for alum-dyed materials [26].

Dyeing chicken feathers with mordant and cochineal at pH 4 (Tables 7g and 8) came closest to the desired red colour but was less saturated and lacked luminosity. The perfect colour match, also in terms of luminosity and saturation, was achieved by dyeing a yellow and orange macaw feather (Table 9q,r). However, given that approximately 3600 feathers had to be dyed for the replica, this was not realistic as there were insufficient resources available.

Table 8. Recipe for the best colour-matching of red-dyed feathers (see Table 7g).

Mordant bath	1.8 g feathers 90 mL demineralized water 0.36 g potassium aluminium sulphate Dissolve the alum in water. Add the feathers and heat the mordant bath to max. 70–80° C, then maintain the temperature for one hour. Stir occasionally. Rinse thoroughly with water.
Dye bath	1.8 g mordanted feathers 110 mL demineralized water 0.22 g cochineal (carefully ground) pH 4 (adjusted with acetic acid CH_3COOH) Put the cochineal in a polyester mesh bag and soak it in water. Raise the temperature to 100° C and boil for one hour. Remove the bag, add the feathers, and adjust the temperature to max. 70–80° C. Maintain the temperature for one hour. Stir occasionally. Rinse thoroughly with water. Absorb water with blotting paper and blow-dry (with cold air).

Table 9. Dyed bird feathers which best match the pink, rose-coloured and orange-red feathers of the colonial insignia (a, b, q, r) and the undyed parrot feathers in comparison (s, t).

Recipe # (See Table 7)	Colonial Insignia	Dyed Sample	Insignia and Dyed Sample
a Pink (goose feather)			
b Rose (chicken feather)			
q Orange-red (yellow feather of blue and yellow macaw)			
r Orange-red (orange feather of scarlet macaw)			
Detail of insignia compared to undyed parrot feathers			
s scarlet macaw			
T blue and yellow macaw			

The recipe in Table 8 has only been used on a small scale so far; the next step is to carry out the dyeing process on a large scale to test the reproducibility. It is emphasized that working with natural dyes is associated with uncertainties, especially when repeating dyeing processes. Another important point is that the feathers used must be of comparable quality, size, and structure.

The research highlights that while it will not be possible to exactly replicate the dyeing process for feathers, the project has provided valuable insights into materials, techniques, processes and the significance of particular shades of red on pre-colonial and colonial feather objects.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/heritage8030085/s1, Figure I. SEM-EDX spectrum of "alum"—most probably alunogen—from Sonora market, clearly showing the presence of aluminium sulphate instead of potassium aluminium sulphate. Figure II. SEM-EDX spectrum of uncleaned, i. e. unfiltered, tequesquite purchased from Sonora market. Figure III. SEM-EDX spectrum of cleaned tequesquite. The insolvable components based on Si, Ca, Mg, Al and Fe are mostly removed during the cleaning process. Figure IVa. FORS spectra plotted in log(1/R) coordinates: Red dyed feathers of the colonial insignia (a: chevron; b: circle feather) compared to tin(II) chloride mordanted/cochineal dyed chicken feathers (c: Sn, cochineal, pH 3; d: Sn, cochineal, pH 4). Figure IVb. First derivative of FORS spectra as shown in Figure IVa. The inflection point of the spectra for the red dyed feathers of the colonial insignia (a,b) diverge from the inflection point of the spectra for the tin(II) chloride mordanted/cochineal dyed chicken feathers applying pH 3 and 4 (c,d).

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Conflicts of Interest: The authors declare no conflicts of interest.

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New Evidence of Traditional Japanese Dyeing Techniques: A Spectroscopic Investigation

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Abstract: The Japanese textile tradition is renowned for its intricate designs achieved through a variety of dyeing techniques, including *kasuri*, *shibori*, and paste-resist dyeing. These techniques are often combined within a single textile, resulting in exceptionally elaborate creations. Our paper delves into the technical aspects and complexities of these methods, highlighting the dynamic interplay between tradition and innovation in Japanese textile production. Our scientific endeavour focused on some textiles dating between the 19th and 20th centuries and belonging to the Montgomery Collection of Japanese folk art. Employing non-invasive techniques such as visible reflectance spectroscopy and ER-FTIR spectroscopy, we uncovered key insights into the materials and methods utilized in the creation of these textiles. Our analysis revealed a diverse array of pigments and dyes, including plant-derived, inorganic, and synthetic variants. These findings illuminate the cultural syncretism between traditional Japanese practices and the adoption of new materials from the West, underscoring the dynamic nature of textile production in Japan. Furthermore, ER-FTIR spectroscopy elucidated the predominant use of cotton as the primary fibre in the textiles, aligning with historical records of Japan's role as a major producer of cotton yarn. Analysis of white areas within the textiles revealed evidence of resist-paste dyeing techniques, particularly *tsutsugaki* and *katazome*, through the absence of dye penetration and the characteristic appearance of white lines. Confirmation of indigo dyeing techniques (*aizome*) was achieved through ER-FTIR spectroscopy, providing reliable identification of indigo and Prussian blue in various shades of blue present in the textiles. Additionally, the detection of Western-derived dyeing method (*utsushi-yūzen*) and free-hand painting (*kaki-e*), offers insights into the diversity of dyeing practices employed by Japanese artisans. The presence of proteinaceous materials and synthetic dyes observed in some textiles has implications for conservation practices, suggesting the need for tailored approaches to ensure the preservation of these culturally significant artifacts. Overall, these scientific results shed new light on the materials, techniques, and cultural contexts underlying Japanese textile production, advancing our understanding of this rich artistic heritage and informing future research endeavours in textile science and conservation.

Keywords: Japanese textiles; dyeing techniques; historical textiles; ER-FTIR spectroscopy; visible reflectance spectroscopy

1. Introduction

Textiles have long played a vital role in Japan culture and have never been considered inferior to painting or sculpture [1]. In particular, the survival of textiles from the premodern period is due to donations to temples and shrines of precious robes worn by high-ranking Buddhist monks, aristocrats, and samurai, such as *kosode* (small-sleeved *kimono*), *kesa* (vestment), *ban* (banner), *uchi- shiki* (altar cloth), and *maku* (lintel curtain). The Shōsōin treasure, kept in the Tōdaiji temple at Nara, has long contained brilliant examples of historical textiles since the 8th century [2]. Folk textiles are conserved there as well, giving evidence of the great importance attributed to handicraft objects by Japanese people [3]. The term *mottainai* ("don't waste") is often related to the field of textiles and is additional proof of the high value given to textiles. Folk was used to repurpose rags by turning them into patches, for example. The high residual value of worn-out clothes reflected the craftmanship of the brand-new textiles. The activity of weaving a textile, as well as a basket, has carried a deep cultural importance in Japanese culture. The ability of the weaver is to give an aesthetically pleasant shape to shapeless matter. The weave is also soaked with sacral significance, being a metaphorical representation of the bond with the divinities [4].

Even the dyeing of the yarns was charged with symbolic meaning. It was a common belief that dyes could imbue a fabric with special powers [3,5]. These beliefs were probably related to the medicinal properties of the plants the dyes came from; according to Japan's indigenous Shinto religion, spirit-gods (*tama*) were housed in the natural compounds showing a particular power.

The choice of the colour was also charged with added significance derived from the Chinese cosmological system which has been adopted in Japan since the 7th century. According to this system, every colour should be combined with other colours according to a precise five-colour scheme (*goshoku*), which are a reminder of, respectively, a cardinal point, a natural element, a season, a planet, and a musical note [3,5].

A focus on the most renowned Japanese dye—indigo—is useful to frame the complexity of symbolic meanings attributed to dyes and the Japanese people's perception of different colours [6]. Indigo (*ai*) was obtained from the fermented leaves of Japanese persicaria (*Polygonum tinctorium Ait.*), an annual plant native to Japan. It was also widely used by the lower classes thanks to the feasibility of the dyeing process. Nevertheless, obtaining a dark hue was labour and time intensive, so even in the richest samurai armours indigo was largely adopted. A lot of different hues could be obtained, and each colour had its own identity, with a precise name and significance. Dipping the yarn in the dye bath several times was believed to make the fibre itself stronger, and to keep away snakes because of the strong smell indigo has [3]. Similarly, indigo-dyed textiles were assumed to be useful in case of stomach illnesses, fever, and snake bites.

1.1. Materiality and Manufacturing of Japanese Textiles

Traditionally, commoners' garments and every-day textiles were obtained from a variety of plants including ramie (*Boehmeria nivea* L.), hemp (*Cannabis sativa* L.), wisteria (*Wistaria floribunda Willd.*), mulberry (*Broussonetia kazinoki Sieb.*), oak (*Broussonetia papyrifera* L.), and arrowroot (*Puerarua hirsuta Thunb.*) [3]. These 'bast' or plant-stem fibres (called *asa* in Japanese language) have been fundamental to Japanese tradition, as all textiles were made from these native plant fibres until the introduction of silk, cotton, wool, and later, synthetics [7]. Silk was considered a precious yarn, initially imported from China, while cotton was introduced in Japan in the 16th century, and quickly became very common as cotton textiles were softer and their production was easier.

Initially, Japanese textiles were shaped by Chinese techniques and styles, but successively, Japanese manufacturing characteristics were established. A wide array of colours was employed, including blue, green, purple, red, and yellow [8]. In particular, dyeing methods such as *aizome* (indigo dyeing) and *benizome* (safflower dyeing) were developed [1,9]. On top of indigo and safflower, a huge variety of different plants were used to obtain dyes. Secondary colours were generally obtained by dyeing one colour over

another [10]. The dyeing was achieved by dipping the fibres in hot water solutions rich in the colouring principle, previously obtained by the maceration and decoction of petals, seeds, leaves, branches, and roots from a great variety of plants [11–14]. Except for vat or direct dyeing, the yarn generally underwent a prior mordanting step with tannins or inorganic salts containing aluminium, iron, or copper ions, which made the fibre–dye bond stronger and more durable, even influencing the final hue of the textile [13–15]. A complete discussion about dyes and mordants has been done elsewhere [12].

Japan's textile tradition is known as one of the world's most dynamic, especially due to the extraordinary complexity of the designs obtained, combining a huge variety of dyeing techniques. The majority of methods were based on "resisting", that is preventing the diffusion of the dye towards specific regions of the fibres [3,16,17]. It could be done either on the threads prior to weaving, or on the surface of the woven fabric. These two design methods are referred by Japanese people by using the terms *saki-zome* (dyed before) or *ato-zome* (dyed after) [3]. A combination of different techniques could be applied, as well as the surface of the finished fabric could be decorated by painting with dyes and inks (*kaki-e*) [3].

Basically, two main methods can be recognized, according to the way the resisting is obtained [3,18]. By wrapping, knotting, and folding, *kasuri* and *shibori* are obtained. The first is done on the threads, while the second is performed on the woven textile. When indigo is used, the result is a white-on-blue motif, characterized by a geometrical design.

Paste-resist dyeing is used to "resist" or prevent the dye from reaching all the cloth, thereby creating a pattern and ground. White areas can be left intentionally white or receive a different colour afterwards. The Japanese tradition encompasses several paste-resist techniques, used alone or in combination, allowing to obtain figurative designs and multiple-coloured textiles [3]. Generally, sticky rice paste (*furonori*) is used, which prevents the diffusion of the colour in the treated parts of the textile. It can be applied multiple times in different areas to allow the use of different colours. The techniques mainly differ according to the way the design is obtained. In *katazome*, a paper stencil (*katagami*) is used to apply a *furonori* paste onto fabric, and then the fabric is dyed. The areas covered by the paste remain undyed, creating a pattern. Traditional *katazome* patterns often feature geometric shapes, nature-inspired motifs, or repeating patterns. *Yūzen* is a decorative dyeing technique often used in the creation of *kimono* [3,16]. It involves hand-painting or applying rice paste-resist to fabric using a cone-shaped tool. After the design is drawn with a water-soluble dye and left to dry, colours are applied, allowing to obtain intricate and colourful designs, often depicting nature or traditional motifs. *Tsutsugaki* is a freehand resist-dyeing technique where a rice-paste mixture (*furonori*) is applied to fabric by a paper cone ending with various shaped metal tips to obtain lines that are flat, round, thick, and thin. The technique derives from *yūzen*, but the cone tip is generally larger, and less refined patterns are obtained. *Tsutsugaki* creates bold, expressive lines and designs. After the application of dyes, steam is used to fix the colours. After dyeing, the paste is washed away, and the design emerges with white outlines. Another variation of *yūzen* is the *katayūzen* method, where the dye is directly applied to the textile using a brush through a paper stencil (*katagami*). This strategy allowed one to significantly reduce the time and labour associated with the manufacturing of a decorated textile, thus lowering the costs [3,16].

Many textiles are multi-coloured with an indigo ground colour. To obtain such results, the secondary colours are applied first, fixed, and then covered with a thick layer of paste. The fabric is dipped several times in the indigo dye bath and let in the air every time to oxidase the molecule. A final hot water bath removes the rice paste residue [3].

Kaki-e is not strictly a dyeing technique, but it is frequently encountered for highly decorated textiles, such as hanging scrolls (*kakemono*) [19], hand scrolls (*emakimono*) [20], sliding doors (*fusuma*), or folding screens (*byōbu*) [21]. *Kaki-e* is a free-hand painting technique, either monochrome or polychrome, executed on the fabric using brushes [22]. Monochrome pieces typically use *sumi-e*, made from soot mixed with glue derived from fishbone or animal hide. Polychrome pieces use pigments derived from natural ingredients,

such as minerals, shells, corals, and semi-precious stones like malachite, azurite, and cinnabar [12]. It is probable that lake pigments, which are organic dyes extracted from plants which are turned into a powder, were once used as well. A hide glue solution, called *nikawa*, serves as a binder for these powdered pigments. The same painting materials were identified in a number of works dealing with *ukiyo-e* prints analysis [23–28].

Paintings on paper and textiles are fragile artworks, whose integrity has to be preserved using non-invasive techniques of analysis. When possible, a multi-analytical approach is applied, including different techniques such as X-ray Fluorescence, reflection Fourier Transform Infrared (FTIR) spectroscopy, Raman, Ultraviolet-Visible (UV-Vis) reflectance spectroscopy, and hyperspectral imaging (HSI) [20,23,25,27,29–32]. In particular, FTIR spectroscopy is a promising method for fibre recognition alternative to microscopic observation [33,34]. External Reflection (ER) FTIR spectroscopy has been successfully used to non-invasively analyse a wide variety of artistic materials and different supports, such as illuminated manuscripts [30,35], easel paintings [36,37], textiles [38,39], and photographs [12]. Thus, ER-FTIR spectroscopy is adept at providing information about the chemical composition of fibres, binders, and pigments.

It is obviously advantageous that these techniques can be applied non-invasively, as sampling is not always feasible. However, due to the lack of separation of the colorants, the results are not always conclusive. In some cases, only High-Performance Liquid Chromatography-Mass Spectrometry (HPLC-MS) is able to reveal the exact composition of the dye. This ability is particularly important when identifying synthetic dyes, due to the high variety of similar compounds within a class [23,40]. Nevertheless, identifying the dye class rather than the specific dye molecule is sometimes sufficient, for example, when determining whether synthetic or natural dyes are present and understanding how objects were created and treated [32,41]. For instance, UV-Vis reflectance spectroscopy is a widely used technique that can provide preliminary, if not conclusive, information about the identity of pigments and dyes [24,42–46]. Specific literature demonstrated that the technique is trustworthy as far as (a) pure colours are considered or (b) a large set of reference spectral data is collected from several mock-up samples dyed with known raw materials. The main limitations to the direct identification of dyestuffs arise from the concentration of dyes on the fibres and the mixtures of different colorants. When synthetic dyes are investigated, the exact identification cannot generally be obtained, due to the high variability within a class [32,41]; yet, identifying the dye class could be sufficient to confirm the proposed dating of the textiles.

1.2. Aim of the Study

This study aimed to comprehensively investigate the dyeing techniques and materials used in Japanese folk textiles, with a focus on providing scientific insights into their composition and production methods. The research utilized a significant collection of historical textiles, with the constraints of on-site and non-invasive analyses. By applying non-invasive spectroscopic techniques, such as visible reflectance spectroscopy and ER-FTIR spectroscopy, we aimed to identify the diverse array of pigments and dyes utilized in Japanese folk textiles, as well as the primary fibre materials employed in their construction. Particular attention was given to the technical aspects and materiality of the dyeing techniques. By analysing the application of these methods within individual textiles, we aimed to bridge the gap between traditional textile scholarship and modern scientific analysis, providing a holistic understanding of Japanese textile heritage.

2. Materials and Methods

2.1. Reference Materials

A custom-made database of Japanese dyes and pigments applied to paper was built and analysed by visible reflectance spectroscopy as a reference. In total, 31 traditional materials, 11 synthetic materials, and 25 mixtures of two dyes and/or pigments were chosen and tested based on a previous thorough bibliographical search [12]. Dyes were bought as

powdered or raw materials from Pigment Tokyo (Japan) and extracted according to a recipe tested in a previous work [12]. Extracted dyes and pigments were subsequently mixed with a 3% *w*/*w* solution of animal glue and alum ($KAl(SO_4)_2$) and applied with different concentrations on white drawing paper (Fabriano, weight 180 g/m^2). As for the mordant, only alum was considered as it is definitely the most cited one in the specific literature. For each dye, pigment, or mixture, 3 to 5 different concentrations were considered to account for concentration-induced variability.

2.2. The Montgomery Collection of Japanese Folk Art

The seven objects examined in this study belong to the Montgomery Collection of Japanese folk art, collected over more than fifty years by collector Jeffrey Montgomery. It stands as one of the most significant private collections of Japanese folk art, encompassing textiles, furniture, ceramics, sculptures, and paintings [3,47]. Displayed in numerous exhibitions worldwide, the Collection was hosted at the MUSEC in 2021–2022 and analysed during that period.

Various types of textiles are represented in the Collection, dating predominantly from the late Edo to the Taisho era (from the second half of the 19th century to the 1920s). A common textile type is the *futonji*, a decorated cover traditionally included in a bride's trousseau. Part of the traditional Japanese bedding set, known as a *futon*, it typically comprises a padded mattress and a quilted bedcover. A *futonji* could be repurposed as a smaller wrapping cloth (*furoshiki*), usually square, utilized for wrapping and/or transporting goods. Traditional materials include silk and cotton, with attention given to the aesthetics of *furoshiki* and how it is folded to enhance the design pattern.

Various types of *kimono*, the iconic traditional Japanese garment, are also present. *Hitatare* was the most common and iconic style of clothing worn by the samurai. A *hanten* was a short winter coat, which started to be worn, especially by the common people, in the 18th century, during Japan's Edo period (1603–1867).

Specialized fabrics were used for furnishing purposes, such as making *byōbu* (literally 'wind wall'), folding screens composed of several panels adorned with decorative painting and calligraphy. *Byōbu* were employed to partition interiors and enclose private spaces, among other uses.

The analysed objects of the Montgomery Collection are depicted in Figure 1, accompanied by brief descriptions indicating object number, type, dimensions, and dating for each object. The analysed areas were visually selected to encompass the full range of colors, and analysis of the white substrate was also conducted.

Analyses were conducted using both techniques in the same area whenever possible. However, there were instances where collecting ER-FTIR spectra was not feasible due to limitations in the maximum height accessible to the instrument. Conversely, certain areas were not analysed by reflectance spectroscopy due to its non-contactless nature, and the condition of the area discouraged surface contact.

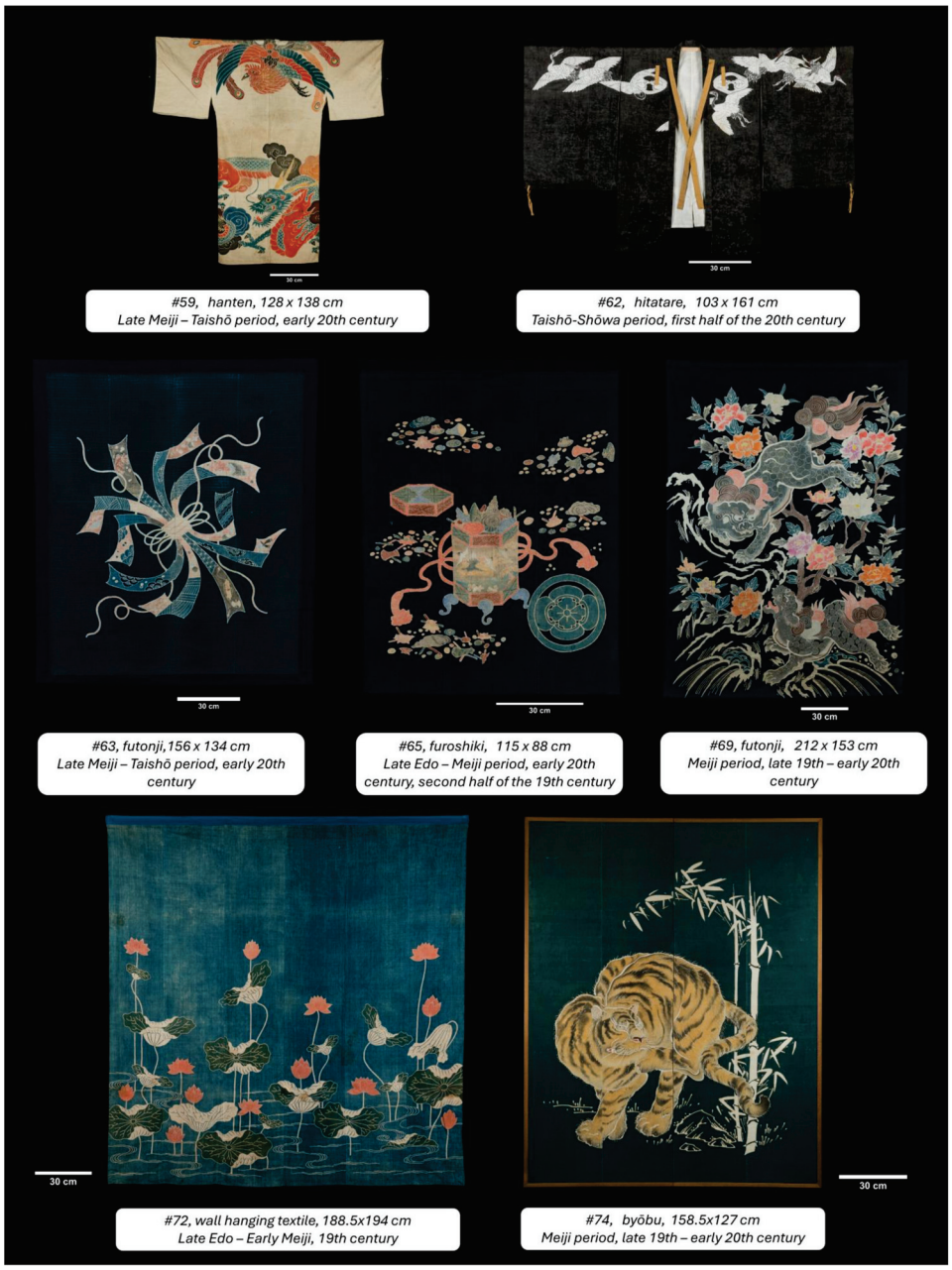

Figure 1. Photographs and details of the objects under study from the Montgomery Collection.

2.3. Visible Reflectance Spectroscopy

Visible reflectance spectroscopy of coloured areas was carried out using a portable Lovibond® SP60 spectrophotometer (Lovibond, Dortmund, Germany), equipped with an integrating sphere. The standard illuminant used was standard daylight, D65, using a CIE 1964 10° standard observer. The calibration of the instrument was performed on the reference, which consisted of a disk of white ceramic for white and a trap (dispersion cone) for black. The wavelength range of measure was from 400 to 700 nm with 10 nm acquisition step, d/8°, SPIN (Specular-Included) and a circular area of 8 mm diameter was analysed (8 mm viewing/12 mm illumination). The spectra were compared with a custom-made database of Japanese dyes and pigments, including 31 traditional materials, 11 synthetic materials, and 25 mixtures of two dyes and/or pigments. For each dye, pigment, or mixture, 3 to 5 different concentrations were considered.

2.4. External Reflection Fourier Transform Infrared Spectroscopy

ER-FTIR measurements were conducted on site using an Alpha Bruker FTIR portable spectrophotometer (Bruker, Billerica, MA, USA) configured in external reflection mode, allowing for contactless measurements, equipped with a DTGS detector. Spectra were collected within the range of 7500 to 375 cm^{-1}, utilizing a resolution of 4 cm^{-1} and averaging 200 scans. Periodic background measurements were obtained using a flat gold mirror. The instrument was positioned in front of the target area, with the optimal distance determined by focusing via the built-in camera. Subsequent fine adjustments were made via software to maximize signal intensity directly in the interferogram. On average, the working distance from the surface ranged from 1 to 1.5 cm. Spectral data were processed using pseudo-absorbance (log (1/R); where R = reflectance) as the intensity unit. The spectra of the samples were interpreted by comparison with a custom-made reference database and with the literature.

2.5. Data Treatment and Elaboration

Spectragryph optical spectroscopy software, Version 1.2.15, was utilized for visualizing and manipulating visible reflectance and ER-FTIR spectra [48]. Standard Normal Variate (SNV) processing was employed on either the entire spectrum or specific segments to correct the baseline and normalize the signal. This approach involves subtracting the mean spectrum from each individual spectrum, thereby removing information about absolute intensity while allowing for the discernment of subtle differences in the band shape [34]. Visible reflectance spectra were also subjected to second derivative when needed to facilitate the comparison of similar features. The simulation of pigment mixtures [23,49] though the linear combination of two spectra was calculated using the "Add" function in Spectragryph software, after being normalized. The y values of the two spectra were added to obtain the final spectrum. Origin Pro 2018 software (OriginLab Corporation, Northampton, MA, USA) was used for data plotting.

3. Results

3.1. Visible Reflectance Spectroscopy

Visible reflectance spectroscopy was used to study the coloured areas. Figures 2–5 show the spectra of different parts of the samples, grouped by colour, along with the spectra of the references.

Red area spectra exhibit an inflection between 570 and 610 nm (Figure 2). Two areas of different textiles (59_2, 69_2) show a good correlation with the reference sample of Ponceau red 2R (acid red 26), so the use of this synthetic compound or a similar one belonging to the same family (aryl azo dyes) can be proposed. The inflection point was found at 590 nm. The spectrum of the other red area 59_1 can be attributed to the pigment red ochre. The spectral curve of the sample matches well with the reference spectrum; the pigment can also be easily recognized in the second derivative graph, which shows a maximum at 560 nm and a minimum at 590 nm.

Yellow areas give evidence of the use of different dyes, although their identification is considered quite problematic due the similarity of their spectra (Figure 3). In area 59_8, the presence of *yamahaji* can be proposed, as the spectrum of the sample clearly matches the reference spectrum. *Yamahaji* is a traditional Japanese dye based on the flavanonol fustin, extracted from the wood of Japanese sumac (*Toxicodendron vernicifluum*) [12,50]. In sample 69_5, the yellow parts were probably achieved using a synthetic dye from family of arylide, or Hansa, yellow [51]. The second derivative graphs obtained from the spectra of the sample and the reference (Hansa yellow PY3) both show a maximum at 480 nm and a minimum at 510 nm. The slight differences in the reflectance spectrum are attributed to the varying concentrations of the dye on the support [42], as proved by Figure S1.

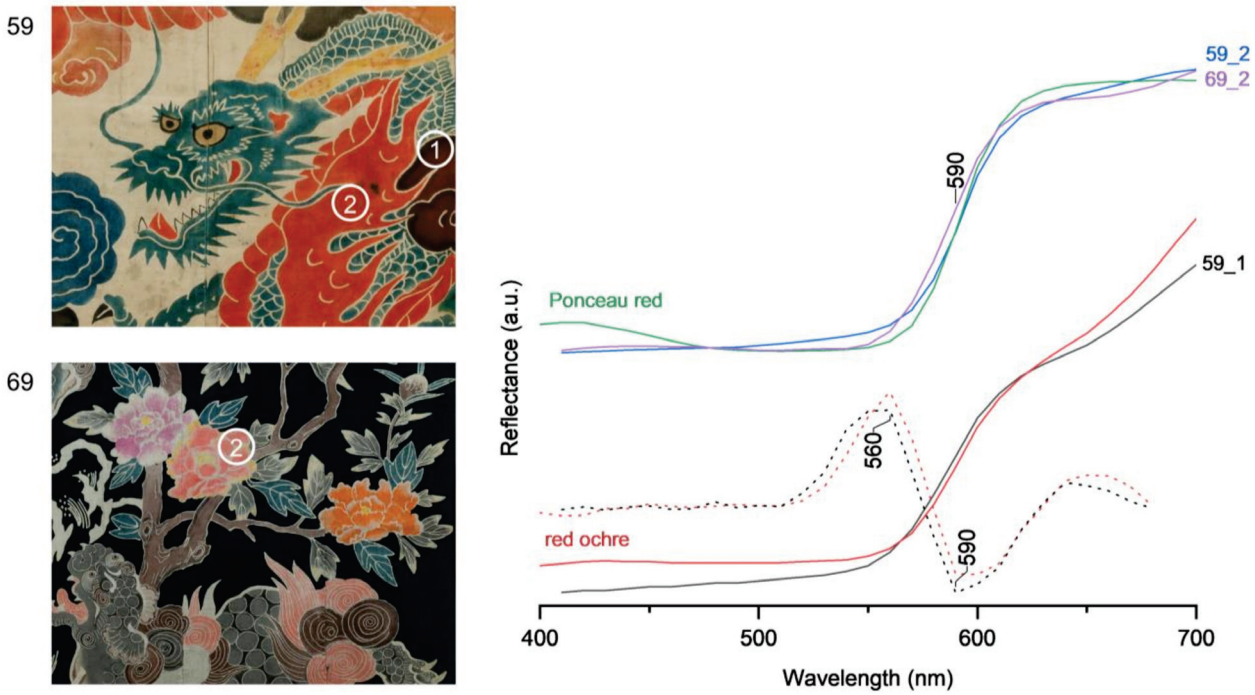

Figure 2. On the left, regions of interest from objects 59 and 69, indicating the location of the sampling points under discussion. On the right, results of visible reflectance spectroscopy performed on the same areas (red). Solid lines represent the spectra of the samples (on the right) and references (on the left); second-derivative plot of the spectra are drawn with dashed lines.

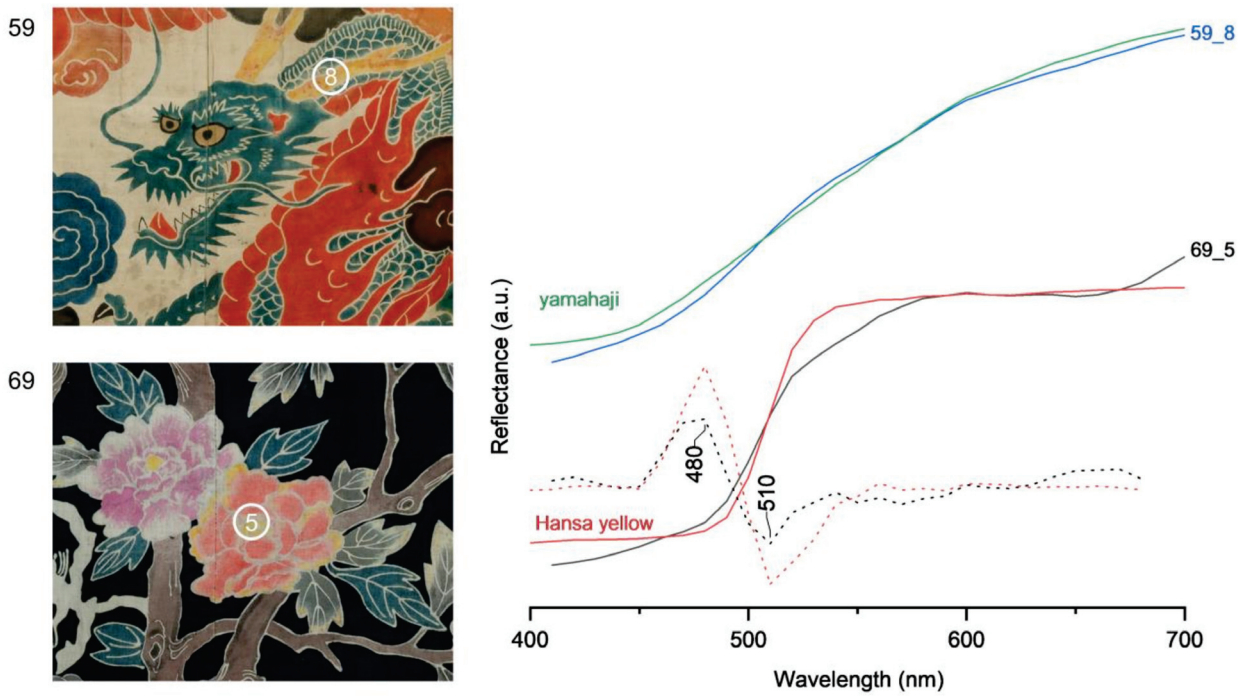

Figure 3. On the left, regions of interest from objects 59 and 69, indicating the location of the sampling points under discussion. On the right, results of visible reflectance spectroscopy performed on the same areas (yellow). Solid lines represent the spectra of the samples (on the right) and references (on the left); second-derivative plot of the spectra are drawn with dashed lines.

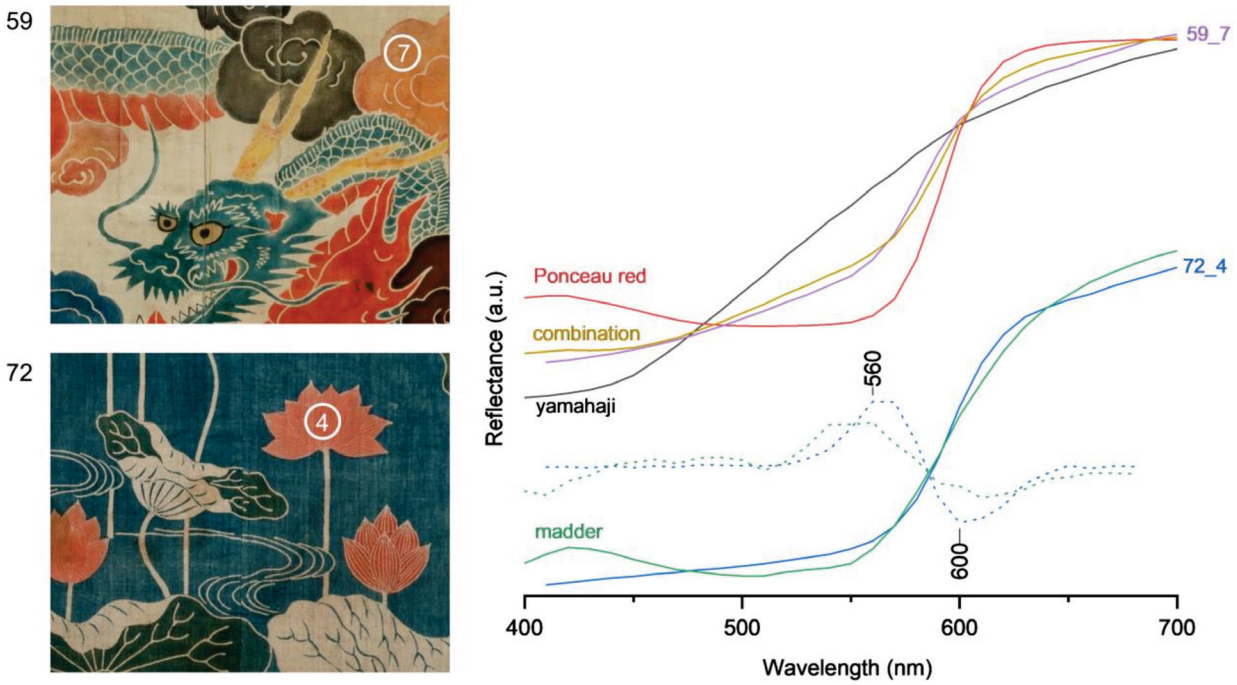

Figure 4. On the left, regions of interest from objects 59 and 72, indicating the location of the sampling points under discussion. On the right, results of visible reflectance spectroscopy performed on the same areas (orange–red). Solid lines represent the spectra of the samples (on the right) and references (on the left); second-derivative plots of the spectra are drawn with dashed lines.

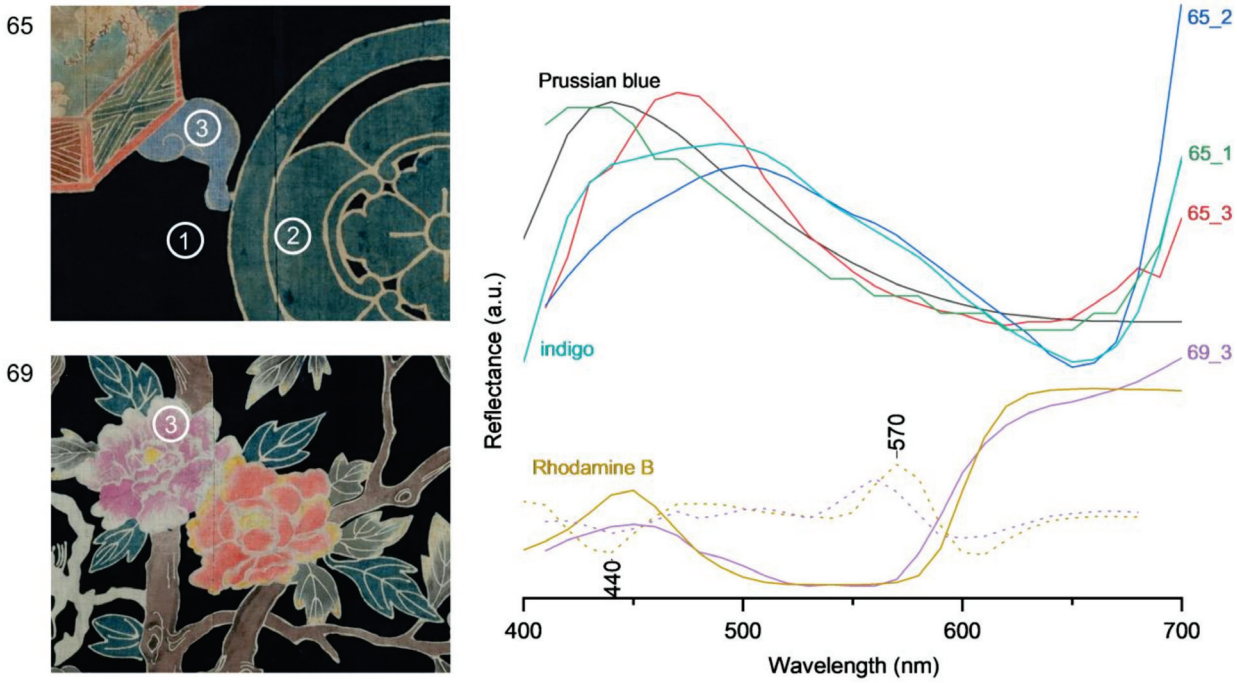

Figure 5. On the left, regions of interest from objects 65 and 69, indicating the location of the sampling points under discussion. On the right, results of visible reflectance spectroscopy performed on the same areas (purple and blue). Solid lines represent the spectra of the samples (on the right) and references (on the left); second-derivative plot of the spectra are drawn with dashed lines.

The study of orange–red parts in objects 59 and 72 encountered some challenges. The orange area 59_7 gave a negative result when compared with realgar, one of the few known orange pigments. It was hypothesized that a mixture of yellow and red dyes might have been used, as orange dyes are uncommon. A mixture of Ponceau Red 2R and *yamahaji* was tested since both were identified as pure dyes in other parts of the same textile. Instead of preparing a mock-up sample of the resulting dye, a linear combination of the two spectra was calculated, as a linear mixing model has proven to be quite successful for the unmixing of pigment mixtures [23,49]. In Figure 4, the spectra of the two pure dyes are shown alongside their linear combination. The calculated spectrum closely matches the sample spectrum.

Sample 72_4 is a red area with some thin white lines across the dyed surface. It was not possible to exclude the white parts from the acquired area. Its spectrum imperfectly matches the reference spectrum for madder, as evidenced in the second derivative graph.

Figure 5 shows the spectra of purple and blue areas. The spectrum of the purple area 69_3 matches quite well with Rhodamine B (basic violet 10), as evidenced in the second-derivative graph (maximum at 570 nm and minima at 610 and 440 nm). Discrepancies can be explained based on the hypsochromic shift, as it happened with Hansa yellow [42]. The spectra of different concentrations of Rhodamine B are shown in Figure S2 as a proof. The use of this synthetic compound or a similar one belonging to same family (triarylmethane dyes) can be proposed.

The three spectra of the blue areas taken from object 65 demonstrate the variability associated with blue hues. Only the spectrum 65_2 closely matches the reference spectrum for indigo. The spectrum of 65_3 resembles that of Prussian blue, but its maximum is red-shifted relative to the reference, preventing its identification. Similarly, the spectrum of area 65_1 is similar to Prussian blue spectrum, but it differs at higher wavelengths.

3.2. ER-FTIR Spectroscopy

ER-FTIR spectroscopy was performed on both coloured and non-coloured areas of the same textile. At least one non-coloured part from each textile was analysed to characterize the bulk material. All the spectra are similar; the plots of samples 59_3 and 69_8 are shown in Figure 6, alongside the spectrum of a cotton reference. The reference spectra of hemp and viscose were evaluated as well but were excluded from the discussion as the sample spectra did not exhibit any of the peaks attributed to lignin or modified cellulose [34]. The spectral features of the cotton reference spectra precisely coincide with those of the analysed areas. By evaluating only peaks that do not show significant shifts between ATR and external reflection modes, in accordance with a previous paper [34] we assigned peaks at 1043 and 1021 cm^{-1} to C-O stretching located in secondary and primary alcohols, respectively. Vibration at 895 cm^{-1} is due to C-O-C symmetric stretching in plane. The C-C ring breathing band at 1155 cm^{-1}, which is characteristic of cellulose in ATR mode, is inverted at 1166 cm^{-1} in reflection mode. The strong peak at 1105 cm^{-1}, attributed in ATR mode to C-O-C glycosidic bond, is inverted in the reflection mode. C-H bending at 1430, 1365, 1315 cm^{-1}, and C-H rocking at 1000 and 985 cm^{-1} do not show spectral changes. We report the same for CH_2 wagging at 1335 cm^{-1} and CH_2 twisting at 1280 cm^{-1}. A peak at 1205 cm^{-1} is assigned to C-OH and C-CH bending. The bending vibration of OH group appears as a broad band centred at 1640 cm^{-1} and at 3300–3100 cm^{-1}. The shoulder at 1730 cm^{-1} (marked with an asterisk) can be related to the ageing of the fibre, as previously reported [34].

The spectra of the coloured parts closely resemble that of cotton, although a considerable number of spectra show major differences compared to the bulk material (Figure 6). The peaks appearing in the region of amides I and II (1760–1500 cm^{-1}), as well as the peaks at 1163, 1080, and 1030 cm^{-1}, indicate the presence of a proteinaceous material [38]. These signals match a reference sample of animal glue [52]. The spectral features of animal glue are evident in the spectrum of sample 59_1, giving evidence of a considerable amount of glue. The broad OH stretching band, which in cotton is dominated by the peak of the

intramolecular hydrogen bonding [34], strictly resembles the same band as it appears in animal glue, centred at 3320 cm^{-1} and attributed to amide A [38]. The same peaks exhibit a lesser intensity in sample 69_1, resulting in a spectrum that shows features of both the features of glue and cotton.

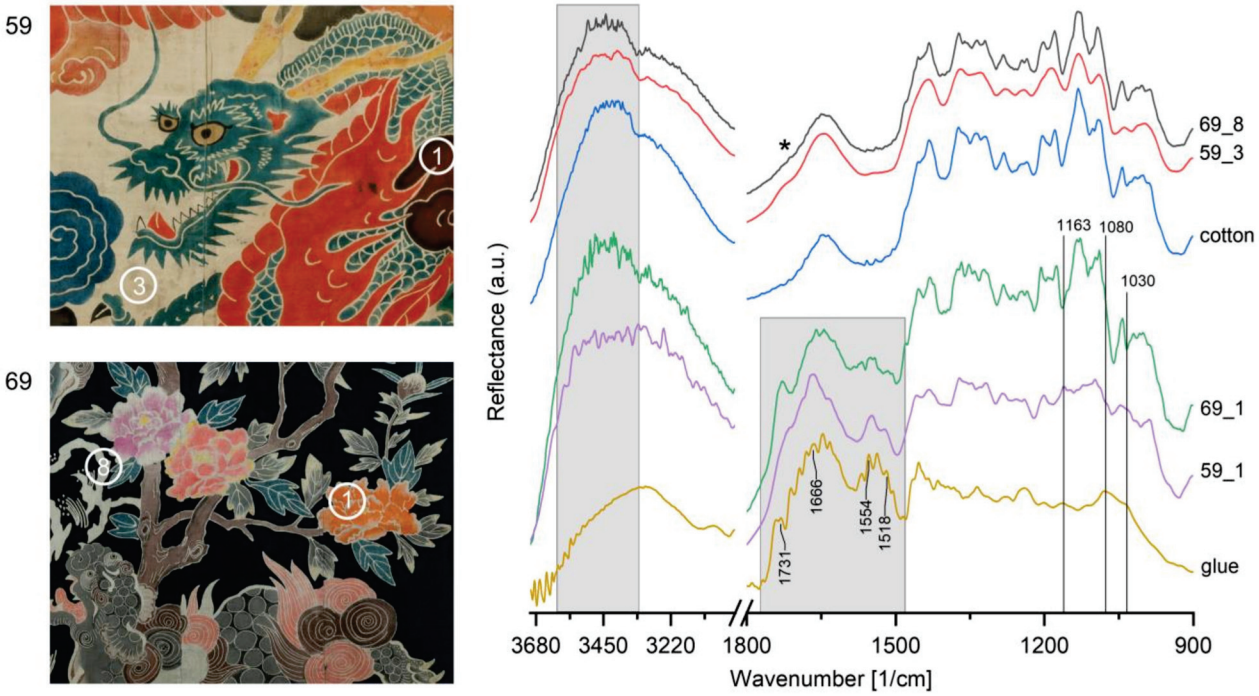

Figure 6. On the left, regions of interest from objects 59 and 69, showing the location of the sampling points under discussion. On the right, ER-FTIR spectra of the same areas, together with the reference spectra for cotton and animal glue. The regions of the spectra showing major differences are highlighted. The asterisk marks the shoulder at 1730 cm^{-1}.

Upon closer inspection, some spectra reveal minor peaks associated with specific pigments and dyes. Indigo and Prussian blue are easily identifiable using ER-FTIR spectroscopy, as illustrated in Figure 7. In object 63, three distinct shades of blue can be differentiated. The typical features of indigo dye, at 1634 and 1614 cm^{-1} [53], are prominent in the area 63_3, which appears very dark, and are present with reduced intensity in sample 63_2. Other characteristic marker bands for indigo are detected at 1462 and 1482 cm^{-1}, but they coincide with absorptions due to the cellulosic substrate. Although sample 63_1 appears dark, it does not exhibit any of the diagnostic bands of indigo, suggesting that a different type of dyeing was used in this area.

In sample 65, the diagnostic features of indigo are evident in the dark background (sample 65_1). These features are less pronounced in sample 65_2 due to the less intense hue (not shown). For samples 65_3 and 65_5, a different shade of blue and different shades of green were employed. In both cases, the spectral features of Prussian blue, with its distinctive peak at 2098 cm^{-1}, appear in the spectra [12,36].

In Figure 8, additional materials related to the use of specific pigments are illustrated. The spectrum of sample 59_1 displays peaks indicative of illite at 3620, 1026, 825 cm^{-1} and of quartz at 1161, 1145, 792 cm^{-1} [54,55]. Illite, a type of clay, can exhibit various colours depending on the type of iron oxide it contains. Quartz is also commonly associated with these materials. Given that the analysed area is red, it is reasonable to assume the presence of iron (III) oxide [56]. The peak at 1098 cm^{-1} is indeed characteristic of red ochre [55]. For the sample 74_3, peaks corresponding to kaolin are identifiable at 3697, 3622, 1114, 1092, 1020, 912, 796 cm^{-1} [54,55]. Pure kaolin is white, becoming yellowish due to the presence of limonite [55]. This possibility aligns with the off-yellow colour of the analysed area. The

peaks marked with asterisks (3320, 1666,1554, 870 cm^{-1}) indicate the use of animal glue as a binder.

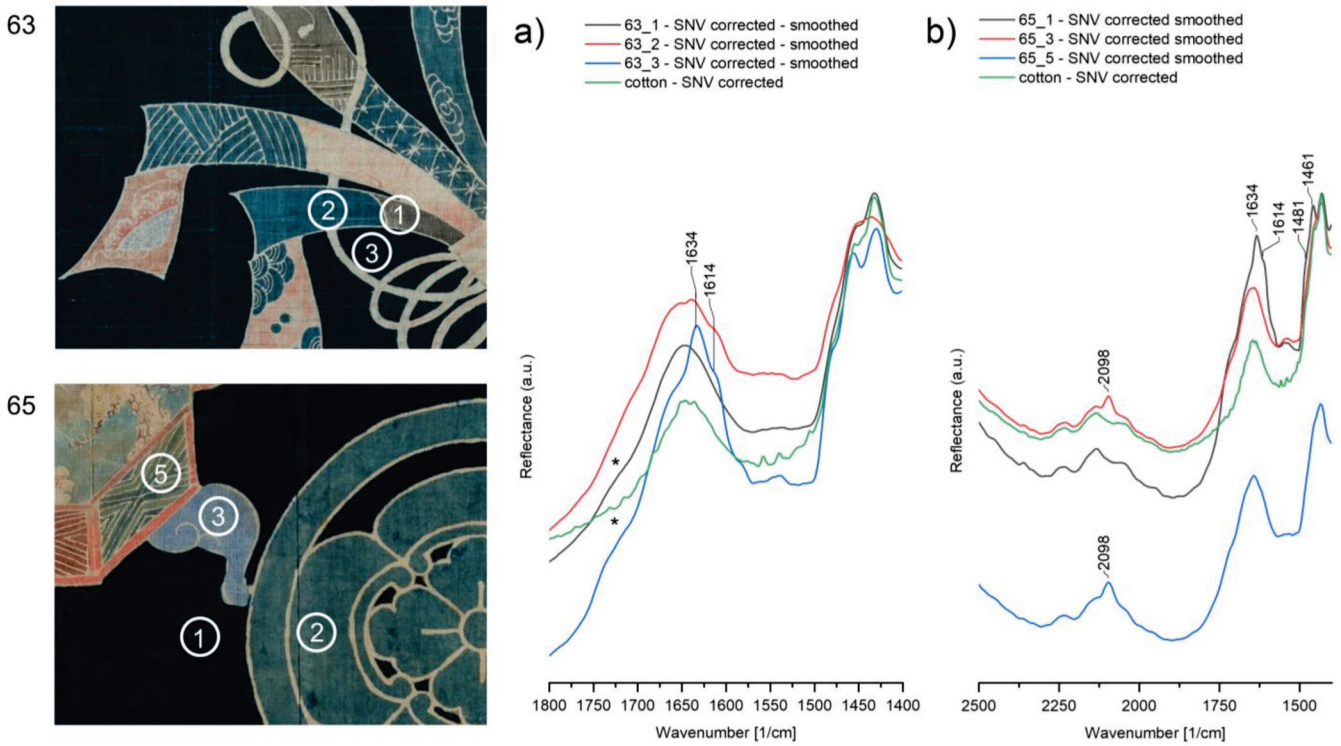

Figure 7. On the left, regions of interest from objects 63 and 65, showing the location of the sampling points under discussion. On the right, ER-FTIR spectra of the same areas, together with the reference spectra of cotton. The asterisk marks the shoulder at 1730 cm^{-1}.

Table 1 summarizes the main findings obtained from the analysis of the Montgomery Collection. An overview of the identified pigments or dyes is provided in Table S1 along with their spectral features.

Table 1. Summary of the main binders, pigments and dyes identified. NA means that this point of analysis was not analysed using both the techniques. Tentative identifications are marked with an asterisk (*).

Textile	Colours	Binder Identified by ER-FTIR Spectroscopy	Dyes and Pigments Identified by ER-FTIR Spectroscopy	Dyes and Pigments Identified by Reflectance Spectroscopy
***kimono*—59**	maroon	animal glue	red ochre	red ochre
	red	animal glue		Ponceau red 2R *
	black	animal glue	Prussian blue, indigo	
	orange			yamahaji, Ponceau red 2R *
	yellow	NA	NA	yamahaji
***kimono*—62**	black			
***futonji*—63**	light black			
	light blue		indigo	
	blue (ground)		indigo	
***futonji*—65**	blue (ground)		indigo	
	pale blue		indigo	

Table 1. *Cont.*

Textile	Colours	Binder Identified by ER-FTIR Spectroscopy	Dyes and Pigments Identified by ER-FTIR Spectroscopy	Dyes and Pigments Identified by Reflectance Spectroscopy
	light blue	animal glue	Prussian blue	
	red	animal glue		NA
	green	animal glue	Prussian blue	NA
***futonji*—69**	orange	animal glue		
	red	animal glue		Ponceau red 2R *
	purple	animal glue		rhodamine B *
	blue (ground)		indigo	
	yellow	animal glue		hansa yellow *
	green			
	grey	animal glue		NA
***futonji*—72**	blue (ground)		indigo	
	red	animal glue		akane *
	green			
***byobu*—74**	green		indigo	
	yellow	animal glue	yellow ochre	yellow ochre
	red	NA	NA	yamahaji, Ponceau red 2R *

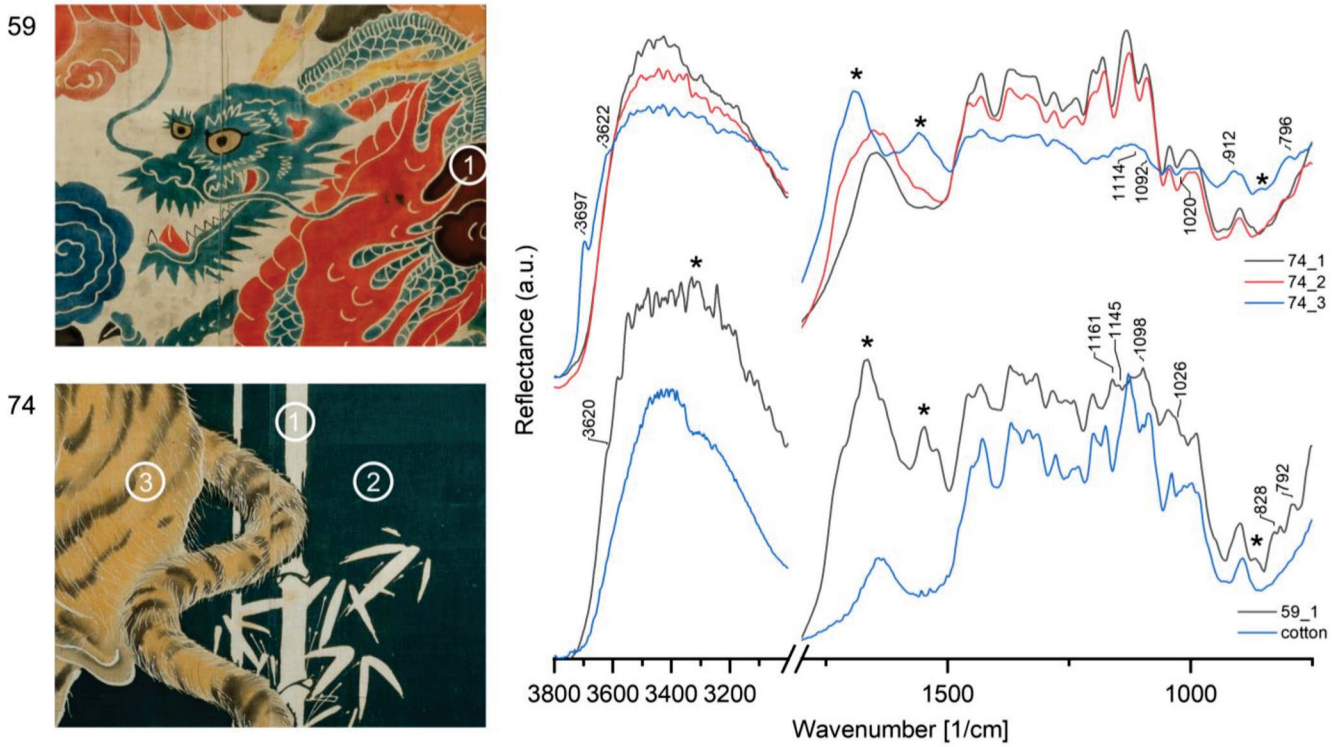

Figure 8. On the left, regions of interest from objects 59 and 74, showing the location of the sampling points under discussion. On the right, ER-FTIR spectra of the same areas, together with the reference spectra for cotton. The asterisks mark the peaks attributable to animal glue (3320, 1666, 1554, 870 cm^{-1}).

4. Discussion

The results obtained from the current study enrich our knowledge about the materiality of Japanese textiles. As shown by Table 1, the majority of the materials investigated were successfully identified, either as a specific component or at least within their general class. However, microdestructive techniques would be necessary for the precise identification of each compound.

Cotton was identified as the support in all the analysed areas. Cotton occurrence is not obvious considering that the major yarn used for the manufacturing of *kimono* was silk. Due to its cost and to the prohibition for commoners to use this precious fibre until the Meiji era (1868–1912), folks generally used bast fibres for weaving, such as hemp and ramie, which were known collectively as *asa*. Cotton plant started to be cultivated in Japan in the 16th century. For a long time, it was considered a luxurious and expensive material. The widespread occurrence of cotton in the Montgomery Collection is in line with the proposed dating of the artworks to the end of 19th century. It is known that due to the industrialization of Japan coinciding with the beginning of Meiji era, Japan became one of the world's largest producers of cotton yarn and cloth [57].

Indigo dyeing—*aizome*—is a well-known Japanese technique, so it was not surprising to detect indigo in the majority of the blue areas of the Collection. ER-FTIR spectroscopy showed great performance in detecting indigotin, especially in the dark blue areas. Indigotin is equally detected when mixed with other dye to create green hues. Conversely, visible reflectance spectra are strongly influenced by the hue of the blue, preventing reliable identification. For example, ER-FTIR results showed that areas 65_1 and 65_2 are dyed with indigo, but the reflectance spectrum of area 65_1 does not match with the reference spectrum. It appears as a very dark blue. The very high concentration of indigo, which makes its detection very feasible by ER-FTIR spectroscopy, prevents identification by reflectance spectroscopy. This concentration-dependant issue is a renowned limitation of reflectance spectroscopy [42].

Another issue with reflectance spectroscopy is the identification of Prussian blue. For example, Prussian blue was easily identified by ER-FTIR spectroscopy in area 65_3, but the reflectance spectrum (Figure 5) does not agree with the FTIR attribution due to a significant shift in the absorption maximum of the sample spectrum compared to the reference. This shift is probably due to the colour coverage. The literature reports that mixing malachite green with a white pigment, such as lead white, induces a red shift effect in the absorption maximum [58]. A similar effect probably occurs in blue-dyed textiles, as the off-white cotton support alters the appearance of the blue colour [28]. This issue likely affects the spectrum of sample 72_4 as well, which imperfectly matches the reference spectrum for madder due to the presence of some white areas in the analysed part.

The detection of indigo provides insight into the skilful use of *aizome* techniques to achieve various hues of blue in different areas of the textile. For instance, objects 63 and 65 display indigo-dyed regions with differing shades of blue (Figure 7). This effect was likely achieved by dipping the textile in the dye bath multiple times, protecting lighter areas with *furonori* [3]. Indigo was also found in a green area of object 74, suggesting this hue was achieved by dipping the textile in different dye baths (Figure 8).

Another traditional technique, *tsutsugaki*, was identified indirectly. Objects 63 and 65 feature uneven white lines, indicative of the use of the *tsutsugaki* tube. Although no traces of *furonori* paste were found on the textile surface, the absence of any white paint in these areas confirms that they were protected from absorbing indigo rather than being coloured. The width of the white lines and the complex pattern further suggest the use of this technique.

Detecting indigo also facilitates the recognition of other colorants that could be mistaken for indigo. In objects 62 and 63, a black dye unrelated to indigo was identified, suggesting the use of a technique involving tannin and iron salts, typical of the Asiatic area [59]. Prussian blue was found in objects 59 and 65, an unexpected material for textiles. The presence of animal glue as a binder clearly appears only in the analysed areas in object

59. While Prussian blue has been used in Japan since the early 19th century, it was primarily known for colouring woodblock prints (*ukiyo-e*) [28]. To the best of our knowledge, there are no references about its use for textile dyeing in Japan. In the West, it became a significant artists' pigment in the 18th century and a low-cost alternative to indigo for textiles in the first half of the 19th century, once a method to fix it directly onto fibres was discovered [60]. This result was achieved either by solubilizing the pigment in an alkaline solution before application or using binders such as gum, oil, or albumin.

The detection of proteinaceous material applied to most of the coloured areas, including those with Prussian blue, explains the use of pigments and dyes that lack affinity for cellulosic fibres. While the presence of animal glue (gelatin) has been suggested, other proteinaceous materials cannot be ruled out, especially when the spectral features of glue are not very intense. Variability in the types of proteinaceous material is evident in the spectra shown in Figure 6. It is well known from the literature that Japanese paintings on paper and silk were made using watercolours obtained by mixing animal glue (*nikawa*) with powdered pigments or precipitated dyes (lakes pigments) [21]. Gelatin could act as a binder, but also as a mordant. Commonly, the lack of affinity of cotton for the natural dye is improved by the mordanting technique that consists of treating the fabric with metal salts. These mordants form metallic complexes with dye and cotton improving dyeing. Because protein fibres like wool and silk were known to have good dyeability, efforts were made, as early as the half of the 19th century, to animalize cotton by depositing protein material onto it to make it more dyeable. In a dyeing and tissue-printing handbook dating to 1882 [61], albumen, animal gelatin, and wheat or rice proteins are listed as common proteinaceous materials for treating cotton before applying the dye, or to be mixed with dye and printed onto the dye. The dye would then be fixed by steaming or other methods. Protein mordanting was used, for instance, for dyeing cotton with early synthetic dyes, as they could not directly bond to cellulosic fibres [62]. Fukatsu-Fukuoka [63] reports that since 1879, a modified technique called *utsushi-yūzen* began to replace the traditional *yūzen-zome*. In this new technique, synthetic dyes or "aniline" were mixed with starch paste, traditionally used only for resisting dyes on fabric. It is likely that the rice protein in the paste facilitated the dye fixation to the cotton textile [64]. The dyed paste could be applied to the fabric through stencils, a method traditionally used for paste-resist dyeing of cloth (*kata-yūzen*). When the dyed fabric was steamed, the dye penetrated the fabric while the paste remained on the surface, simultaneously dyeing and resisting other dyes.

This process was similar to calico printing, although albumen was preferred over wheat proteins [65]. The detection of synthetic dyes in object 69, along with signals indicating a proteinaceous material, supports the use of the *utsushi-yūzen* technique. The precise history of synthetic dye introduction helps date objects 69 and 59, where such dyes were found. Ponceau red 2R was found in a Japanese print dated 1889, a few years after its discovery by H. Baum in 1878 [25]. Rhodamine B was discovered in 1887 [32] and Hansa yellow was first synthetized in 1909 [51]. HPLC-MS would be the only method capable of precisely identifying synthetic dyes, given the high variety of similar compounds within a dye class. However, the identification of the dye class through reflectance spectroscopy is sufficient to confirm the proposed dating of the textiles. The detection of synthetic dyes used on textiles aligns with the use of these new "aniline" dyes, as attested in a number of previous studies on *ukiyo-e* prints and hand-painted photographs from the same period [12,23,25].

In objects 59, 65, and 74, the extensive use of opaque pigments (such as red and yellow ochre and Prussian blue) mixed with animal glue suggests a deliberate attempt to achieve a pictorial effect. The detection of glue-based paint aligns with the typical materials used for colouring paper screens (*byōbu*) [21], woodblock prints (*ukiyo-e*) [66], and hand scrolls (*emakimono*) [20]. Free-hand painting on textiles is known as *kaki-e* [22] and can be combined with other dyeing techniques for obtaining the desired decoration.

Object 59 exemplifies this dual identity of the textiles, midway between a cloth and a painting. This object has been found to contain a traditional dye (*yamahaji*), a synthetic dye (a Ponceau red), and several inorganic pigments. The absence of proteinaceous materials associated with *yamahaji* suggests that a traditional dyeing technique was used for the yellow parts, aligning with the pale hue typical of natural dyes, as opposed to the brighter and opaquer synthetic and inorganic ones. An aqueous solution of Japanese sumac wood (*Toxicodendron vernicifluum*), the source of *yamahaji*, was likely applied to the textile. For the red parts, a mixture of Ponceau red and proteinaceous material—hypothetically glue or rice paste—was used. The orange part is particularly interesting, as it has been probably obtained by mixing a traditional dye (*yamahaji*) with a synthetic one (a Ponceau red). This finding, along with the detection of the *utsushi-zome* method, attests to a high level of syncretism between Western and Japanese material culture. For the black part, a mixture of glue, Prussian blue, indigo, and probably carbon black (*sumi*) was found; for the maroon part, red ochre was mixed with *sumi* and glue. The design reminds one of the *tsutsugaki* technique, although the use of stencils (*kata-zome*) to speed up the dyeing process cannot be ruled out. It is probable that once applied onto the textile all the colours were fixed by steaming.

The dyeing techniques used for these textiles significantly impact their conservation practices. Loosely bound dyes as well as proteinaceous materials, such as animal glue, are vulnerable to damage from wet cleaning [67,68]. Additionally, these materials are susceptible to biological attack, as glue can become a culture medium for microorganisms following hydrolysis, serving as a nutrient source [69].

5. Conclusions

This paper presents the results of a groundbreaking study on the dyeing techniques used in the manufacturing of Japanese folk textiles. Seven textiles from the Montgomery Collection of Japanese folk art were analysed using non-invasive techniques to detect traces of dyes and other materials related to their production.

The visible reflectance spectra of several coloured areas of the textiles were compared with spectra from a custom-made database of Japanese dyes and pigments applied to paper. The comparison enabled the identification of numerous dyes and pigments, including plant-derived, inorganic, and synthetic colorants, either as specific component or at least within their general class. Their use, even within the same textile and in mixed forms, indicates a high level of cultural syncretism between traditional Japanese techniques and new materials introduced from the West.

ER-FTIR spectroscopy confirmed that cotton was the primary yarn used in these textiles. This finding is consistent with Japan's status as one of the world's largest producers of cotton yarn at the beginning of the 20th century. The analysis of white areas in the textiles revealed that these parts were not dyed. This evidence, along with the distinctive shape of the white lines, supports the use of resist-paste dyeing techniques based on *furonori* paste, specifically *tsutsugaki* and *kata-zome*.

Indigo dyeing (*aizome*), which was an educated guess before the analyses, was confirmed for the majority of the blue areas. Compared to reflectance spectroscopy, ER-FTIR spectroscopy provided more reliable detection of indigo, even in light and dark blue areas that are challenging to identify with reflectance spectroscopy. ER-FTIR spectra also revealed instances where blue areas were not dyed with indigo but obtained with Prussian blue, an uncommon finding for Japanese textiles.

This study found that many coloured areas contained proteinaceous material, which was used with both pigments and dyes. In some instances, the textiles were used as canvases with opaque pigments mixed with animal glue, employing a pictorial technique known as *kaki-e*. This study provides the first scientific confirmation of *kaki-e* on cotton. In other cases, the presence of proteinaceous material, which could be either animal glue or rice proteins, could be related to the application of a new technique called *utsushi-yūzen*. This technique involves using a paste of *furonori* and aniline dye mixed together, another

evidence of cultural syncretism. The detection of proteinaceous materials and synthetic dyes has implications for conservation practices, as these textiles may be more sensitive to water and biological attacks.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/heritage7070171/s1, Figure S1. Visible reflectance spectra of Hansa yellow mock-up samples (a) and their second derivative (b). Different concentrations of the dye are evaluated, from 1 (more concentrated) to 5 (less concentrated). The dilution of the dye becomes apparent through the hypsochromic shift; Figure S2. Visible reflectance spectra of Rhodamine B mock-up samples (a) and their second derivative (b). Different concentrations of the dye are evaluated, from 1 (more concentrated) to 5 (less concentrated). The dilution of the dye becomes apparent through the hypsochromic shift; Table S1. Summary of the ER-FTIR and visible reflectance spectroscopy results for the colorants. Peaks at 3320, 1666, 1554, 870 cm^{-1} indicate the presence of a proteinaceous binder. Tentative identifications are marked with an asterisk (*). Original values of the reflectance spectra are marked with a dagger (†).

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Technology of Dyeing beyond Text

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Abstract: A major source in the research on Baltic cultural history (Latvia, Estonia), including studies dedicated to the clothing of local inhabitants, are the drawings and descriptions of Johann Christoph Brotze (1742–1823), which date back to the turn of the 18th and 19th centuries. They contain references to dyes and dyeing methods used by local peasants. The information recorded by J. C. Brotze, although fragmentary, is valuable because researchers lack documentary sources about the dyeing methods used in the 18th century in the territory of present-day Latvia. Additional research yields more extensive information about the contents of the descriptions. The current article will describe the experimental method that enabled the establishment of the specific dyeing technique, which, using *Bixa orellana* L., was employed to obtain the particular orange color referred to in the descriptions.

Keywords: natural dyes; *Bixa orellana* L.; J. C. Brotze; traditional clothing; Vidzeme region of Latvia

1. Introduction

A major source in the research on the Baltic history of culture (Latvia, Estonia), including the studies dedicated to clothing of the local inhabitants, are the drawings and descriptions of Johann Christoph Brotze (1742–1823), which date back to the turn of the 18th and 19th centuries. They contain some references to dyes and dyeing methods used by the local peasants. The information recorded by J. C. Brotze, although fragmentary, is valuable, because researchers lack documentary sources about the past dyeing methods used in the 18th century in the territory of present-day Latvia. Additional research provides more extensive information about the contents of the descriptions. The information found in J. C. Brotze's collection constitutes the basis of the current article; hence, an insight must be provided into the background of J. C. Brotze and the origins of the manuscript he left to posteriority. Brotze was born in Görlitz, Saxony. His ancestors came from the territory of contemporary Czech Republic, the religious community of the Moravian Brethren, although Brotze himself did not belong to it. Although his family was impoverished, Johann Christoph Brotze earned a living as a technical draftsman and acquired his education at the Görlitz Gymnasium and at the Universities of Leipzig and Wittenberg [1] (pp. 8–10). In 1768, he moved to Riga, which at that time was a part of the Livonian Governorate of the Russian Empire, and started working as a tutor in the Baltic German family Von Vegesack. However, a year later, he became a teacher at the Riga Imperial Lyceum and worked there as a pedagogue for 46 years, and in 1801 he became the rector of this lyceum [1] (p. 10). At the same time, he learned the Latvian language of the local peasants and was a keen cultural historian and researcher of the Baltic region. Brotze's own testimony that he studied "the language of this land [i.e., Latvian]" [1] (p. 10) is essential, because it affirms that the author could have obtained the information contained in the comments to the drawings directly from the local peasants, thus increasing the historical reliability of this material. Brotze's digitally available biography states: "Brotze belongs to the so-called school of polymaths—Renaissance men of the late humanist movement and considered the collection and processing of historical sources to be his main task. Brotze collected historical materials, drew everything that he considered to be important: people, buildings, coins, coats of arms, city plans, technical innovations, etc., moreover, recorded everything with

great precision and always added written explanations to the drawings, which sometimes comprised a few lines, but occasionally took up several pages" [2]. J. C. Brotze died in 1823 and was laid to rest in Riga [1] (p. 27).

He left an immense amount of material, which consists of written messages, drawings and redrawings, including coats of arms and plans. The vast heritage includes the collection of cultural-historical drawings and descriptions in 10 volumes, "Sammlung verschiedener Liefländischer Monumente, Prospecte, Münzen, Wappen etc.". The author collected materials for these volumes between 1770 and 1818, both in Riga and during his travels in the Baltic provinces of the then Russian Empire (the territory of present-day Latvia and Estonia) [3].

Among other things, the aforementioned descriptions contain references to natural dyes and mordants that local peasants used to dye their clothes. This information had not attracted the attention of previous generations of researchers. Likewise, it must be noted that Brotze repeatedly depicted yellow/orange aprons as part of peasant clothing, although such apparel is not present in museum holdings.

The purpose of this paper is to collect the evidence left by Brotze concerning the aforesaid aprons and the dye used to obtain their orange color, and to test the reliability of these records against other written sources. To obtain further information about the dyeing technique, dyeing experiments were used to obtain the tangerine-orange color indicated in the description. Practical dyeing experiments, using *Bixa orellana* L., and their results constitute an essential part of the study. They were carried out to ascertain the reliability of Brotze's records, as well as to establish the dyeing technology used. The results of the research yield more substantial knowledge about the circulation of information (the combined use of modern (new) and traditional information) in the social class of peasants, who formed the largest part of society in the Baltics during the researched period.

2. Materials and Methods

The research is based on an interdisciplinary approach, combining the research methods of the humanities and natural sciences. Analyzing the information provided by the written sources and illustrations created by contemporaries about peasant clothing in the territory of present-day Latvia in the late 18th and early 19th century, it is possible to obtain new information in the research on the history of traditional clothing. Drawings of clothing from previous centuries, created by eyewitnesses, and the texts explaining these drawings are a particularly valuable source of knowledge in the history of clothing for a period from which relatively few, if any, practical objects survive. Along with information about the history of clothing, these texts contain evidence of using natural dyes for dyeing textiles. Practical dyeing experiments carried out by the author were also used to prepare the article.

2.1. Published Written and Iconographic Sources

Very little is known about the history of clothing in Latvia in the 18th century. Since only some pieces of traditional clothing from this period have reached the holdings of the museums (moreover, the dating of these specimens is usually determined quite approximately), the research uses mainly descriptions and drawings, which, unfortunately, provide only fragmentary, mosaic-like evidence of the development of the historical clothing worn by Latvian peasants. An essential source of the article is Johan Christoph Brotze's collection of drawings and their descriptions, "Sammlung verschiedener Liefländischer Monumente, Prospecte, Münzen, Wappen etc.", created at the end of the 18th century and the beginning of the 19th century. The manuscript is stored in the UL Academic Library and is also available electronically [2]. The part of this collection that refers to the territory of Latvia, together with scientific comments, was published in four volumes between 1992 and 2007 [4–7]. The texts explaining the drawings are published in the German language corresponding to the original, accompanied by the translation into Latvian.

To obtain a broader historical picture, as well as to evaluate the degree of reliability of the descriptions of the drawings, the information provided by Brotze was compared with

the testimonies found in other written sources about the cultural and historical evidence, which are of interest on this occasion: yellow women's aprons and a plant used for dyeing with the German name 'Orlean'.

The written sources used in the study, along with the descriptions of J. C. Brotze's drawings, also include the late 18th and early 19th century periodicals in Latvian and German languages. Since the periodicals in the German language in the territory of Latvia appeared earlier than those in the Latvian language, the German press of Riga contains valuable information about the goods imported into the Baltic provinces of the Russian Empire at the end of the 18th and the beginning of the 19th century, and the activities of merchants in Riga. For the current article, the periodicals "Rigische Anzeigen" [8–12], "Rigasche Zeitung" [13–16], "Rigasche Stadtblätter" [17–19], and others [20,21] have been used.

2.2. Unpublished Written Sources

The set of written sources created in the 20th century comprises the ethnographic expedition materials of the Monuments Board, stored in the collection of the National History Museum of Latvia (NHML). They consist of questionnaire-type ethnographic object description pages, as well as free-form written information. This article mainly draws upon the information about dyeing with plant-based dyes, which can be found in the section "Dyeing, washing, bleaching" (LNVM ZAE folder 47) [22] and "Female folk dress" (ibid., folder 35) [23]. The materials of the ethnographic expeditions were used to gain a broader insight into the dyeing methods used by the peasants. A study published in Riga in 1935 and dedicated to ancient Latvian dyeing methods was also used for this purpose [24].

3. Results

3.1. Records Concerning Yellow/Orange Aprons

J. C. Brotze drew yellow aprons and provided written information about them with reference to various places in Vidzeme. Dark yellow or orange-yellow aprons can be observed in a drawing that may have been made around 1794: "Clothing in the manors of Gaujiena and Trapene" (Figure 1). The color of these aprons is noted in the description of the drawing: "Die Weiber tragen alltägl[ich]einen schwarzen Rock, Orangefarbne Schürze, und hellgraues Leibchen mit langen Schößen, deßen Näthe und Ränder öfters mit bunten Schnüren oder bunter Wolle brodirt sind"—"Women commonly wear a black skirt, an orange apron and a light grey bodice with long sleeves, the seams and edges of which are often embroidered with colored cords or colored woolen threads" [7] (p. 313). Yellow aprons are worn by three of the five female figures depicted (one is shown with her back to the viewer, while the body of another is concealed behind other figures).

Similar aprons are also shown for the peasant women of the Rūjiena area (Figure 2). In the description of this drawing, J. C. Brotze indicated not only the color of the aprons, but also the dye with which it was obtained: "(. . .) die Röcke färben siemit Birken-Erlenrinde und Vitriol schwarz, und die Schürzen mit Orlean orangefarben; doch tragen sie auch andere"—"They dye their skirt black with birch and alder bark, and vitriol, and their aprons with Orlean orange, but they also wear other ones" [6] (pp. 436–437). Although the author of the drawings refers to the orange color, the coloring in the drawings appears golden yellow. (Discussing this question in more detail would be the topic of another study, which would analyze historical names of colors).

In a very small drawing of a female figure in the foreground of the view of Jeru Manor in 1800, an orange-yellow apron can also be seen (Figure 3). Here, the artist focused on the landscape and did not comment on the outfit of the depicted figure [6] (pp. 432–433).

Figure 1. Clothing in the manors of Gaujiena and Trapene, [2] bm06005a (https://www.acadlib.lu.lv/broce/lielbildes/sejums_nr6/bm06005am.htm (accessed on 4 March 2024)).

Figure 2. The peasants of the Rujiena area, [2] bm08008a (https://www.acadlib.lu.lv/broce/lielbildes/sejums_nr8/bm08008am.htm (accessed on 4 March 2024)).

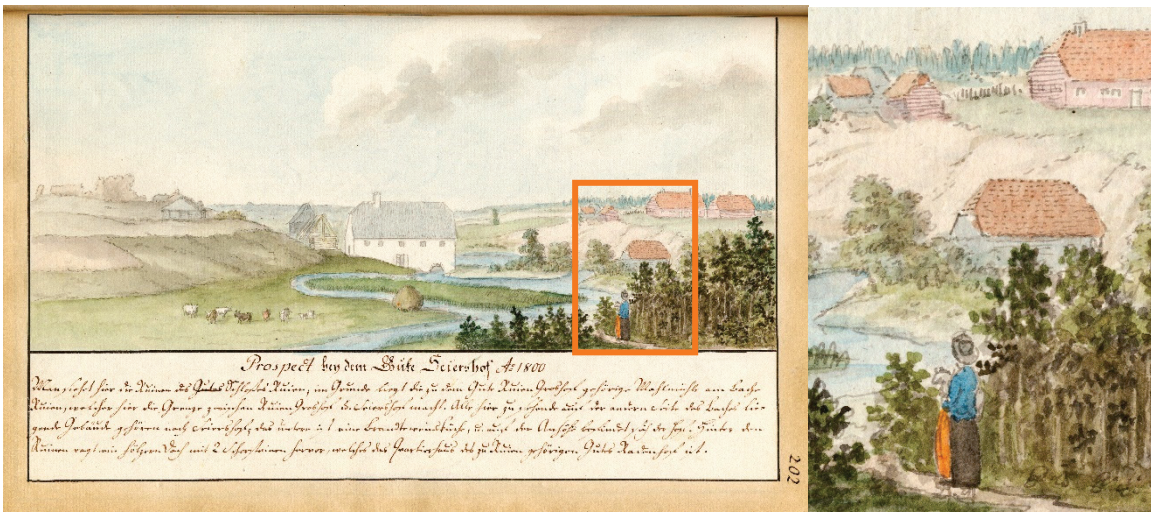


Figure 3. View of Jeru manor, [2] bm08202a (https://www.acadlib.lu.lv/broce/lielbildes/sejums_nr8/bm08202am.htm (accessed on 4 March 2024)).

These drawings by J. C. Brotze and their descriptions convey that at the end of the 18th century, in various parts of Vidzeme, Latvian peasant women wore yellow aprons of a rather intense color in addition to aprons of other colors. The article will explore and ascertain the dyestuff used to obtain the orange color, which has not been noted in other sources (regarding the territory of Latvia) until now.

3.2. Orlean

The evidence left by J. C. Brotze about clothing in late 18th century, in addition to drawing attention to the color of the aprons, which has not been noted in other publications, also indicates the dyestuff used for its production: orlean, or in English—annatto, which is obtained from the seeds of the shrub *Bixa orellana* L. [25,26]. It is also used as a dye for violins and other stringed instruments [27]. However, it is much more widely used as a food coloring (E 160b) and flavoring [28,29] (Annatto, Bixin, Norbixin (E 160b) is authorized as a food additive in the European Union (EU) in accordance with Annex II to Regulation (EC) No. 1333/2008 on food additives, and specific purity criteria have been defined in the Commission Regulation (EU) No. 231/2012). It is still occasionally used for textile dyeing, as evidenced by some dyers' blog posts on the internet, such as Franklin's post on 3 October 2015 [30].

In the 1930s the ethnographer Ādolfs Karnups translated the text written by J. C. Brotze in German, "die Röcke färben sie mit Birken-Erlenrinde und Vitriol schwarz, und die Schürzen mit Orlean orangefarben" [6] (pp. 436–437), slightly differently from the contemporary version: "They dye their skirts black with birch and alder bark, and vitriol, and their aprons—in orange of Orléans" [31]. Here, the word 'Orlean' is interpreted as signifying a place name (Orléans—a city in France). Unfortunately, Ā. Karnups had not additionally considered the content of this quote and provided no further comments.

Seeking a more accurate translation of the word 'orlean', the 18th-century Riga German press yielded a confirmation that it was used at that time to denote a dye, not a place name. The word 'orlean' emerges from 1785 to 1846 in merchants' advertisements together with other textile dyeing substances (German: Farben) [8–21]. The term 'Farben' as a designation of a substance which is a part of a specific group was used at that time only for substances used for dyeing textiles. If annatto was initially specified as belonging to dyes (Farben), then in the second half of the 19th century, it emerges in association with foreign spices, which indicates its use in cooking.

The customs list of imported goods of the Russian Empire dating back to the 1830s and 1840s show that orlean (annatto) was a medium-cost product. Its import duty was half that of the very widely used indigo, which was required to obtain the dark blue color.

Comparatively much more expensive was cochineal, which was used to produce a bright red or pink color. However, the common madder or dyer's madder (*Rubia tinctorum* L.), another source of the red color, was half the price of annatto. Thus, for example, in 1831, an import duty of 1 ruble had to be paid for one pound of annatto, 2 rubles for indigo, 10 rubles for cochineal, and only 50 kopecks for dyer's madder [14].

The lists of imported goods from the beginning of the 19th century also reveal the quantities of dyestuff brought into the region: in 1809, 14,189 ½ pounds of annatto, 4642 pounds of cochineal, and 50,630 ¾ pounds of indigo were imported [17]. However, two years later, in 1811, the amount of annatto imported had almost doubled: 29,403 pounds of this dye were imported. Comparatively, 57,596 ½ pounds of indigo and 5666 ½ pounds of turmeric were also imported that year, also referred to by the descriptive term 'Farben'—dyes [19] (see Table 1).

Table 1. The quantity of imported dyestuff in the port of Riga in 1809–1811 *.

Year	Dyestuff/Farben	Amount (Pounds)	Sources
1809	Cochenille	4642	Specification der im 1809 ten Jahre in Riga eingeführten Waaren. *Rigasche Stadtblätter*, 1810, 9, p. 3. [17]
	Indigo	50,630 ¾	
	Orlean	14,189 ½	
1810	Cochenille	7456 ½	Specification der im 1810 ten Jahre in Riga eingeführten Waaren. *Rigasche Stadtblätter*, 1811, 1, p. 8. [18]
	Indigo	11,569 ½	
	Orlean	3105	
	Kurkumma	25,061 ½	
1811	Indigo	57,596 ½	Specification der im 1811 ten Jahre in Riga eingeführten Waaren. *Rigasche Stadtblätter*, 1812, 4, p. 2. [19]
	Orlean	29,403	
	Kurkumma	5666 ½	

* The terms denoting dyestuff have been provided in the original transcription of the source document.

The publications found in the press indicate that at the time when J. C. Brotze made the drawings, annatto ('Orlean') was a textile dyestuff well-known in German society, also known by the author of the drawings himself. However, this does not mean that this particular dyestuff was used by the peasants of Vidzeme. Nevertheless, such a possibility cannot be precluded.

3.3. Dyeing Experiments

The analyzed written sources indicate that in the late 18th and early 19th century, the peasants of the Vidzeme (Livonia) province of the Russian Empire had the opportunity to purchase and use the imported foreign dye *Bixa orellana* L. for dyeing their clothing. Meanwhile, these written sources do not provide indication as to the applied dyeing method. Although the information on dyeing with *B. orellana* can already be found in the scientific literature [25,26,32], practical dyeing experiments based on local ethnographic material about other plants were carried out to establish which dyeing technique best matched the color tones in the drawings.

3.3.1. Dyeing Experiment I

In the dyeing experiment, dried, crushed seeds of *Bixa orellana* L. were used (Figure 4). The ratio of initial dyestuff (plant) to fiber weight was 1:1.

The ground seeds were soaked in cold water for 12 h. Then, the liquid was slowly heated to boiling point and boiled for 1 h. Then, the dyestuff was strained to separate plant particles, and cooled. The resulting liquid was orange-brown in color (Figure 5).

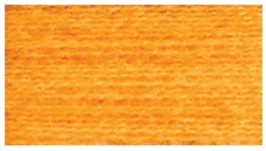
Figure 4. Whole and ground seeds of *Bixa orellana* L. Photo: A. Karlsone.

Figure 5. Dye solution from *Bixa orellana* L. Photo: A. Karlsone.

Both plant (flax and cotton) and animal fiber (wool yarn) were dyed in seed annatto dye solution to test how different materials reacted with this dye.

Linen and cotton threads pre-treated in two different ways were used: (1) boiled without mordant, and (2) mordanted by using alum (8 g $KAl(SO_4)_2$/100 g fiber). The wool yarn used in the experiment was of two types—unmordanted, and mordanted with alum and cream of tartar (8 g $KAl(SO_4)_2$ + 7 g $KC_4H_5O_6$/100 g fiber). The materials prepared for coloring were immersed in the cooled (25–30 °C) dye liquid for several (~3) hours. After that, heating of the dye liquid was started. The solution was heated to 90 degrees, and heating continued at this temperature for 1.5 h. Different materials colored markedly differently (Table 2, the first column of color samples).

Table 2. Tones of colors obtained by dyeing with *Bixa orellana* L.

	Dyed in Plain Water with Heating	**Modified with Alkaline Solution (Lye)**
Wool without mordant		
Wool mordanted with alum	 	
Linen mordanted with alum	 	 
Cotton mordanted with alum		

Since none of the obtained color tones corresponded to the designation 'orange', based on the accumulated dyeing experience, it was decided to try to change the color shade by after-treatment of the fiber with lye—an alkaline solution obtained from wood ash. The dyed, but still wet, samples were rinsed in a warm alkaline solution (55 °C) of pH 10–12. As a result, the color of plant fiber changed from a cream tone to an orangish color, while the color of wool fiber changed from distinctly yellow to a golden yellow-brown color (Table 2, the second column of color samples).

It was found that orlean/annatto dyestuff binds to the fiber without the mediation of the mordant, which corresponds to the information found in the scientific literature [25,28] (p. 193). Respectively, the unmordanted yarn dyed as well or even more intensely than the mordanted one. Furthermore, the unmordanted yarn reacted more actively to the after-treatment of the fiber in an alkaline solution—the obtained color tone was brighter for linen and cotton, as well as wool.

Although initially the dyestuff solution was prepared in a ratio of 1:1 (plants: material to be dyed), during the dyeing process, it became evident that the dyestuff saturation in the liquid was high, and it was possible to dye a larger amount of fiber in it. As a result, two times as much fiber was dyed, with the obtained color tone maintaining a similar intensity. This means that the amount of orlean/annatto required is only half the weight of the fiber to be dyed, which is a relatively small amount.

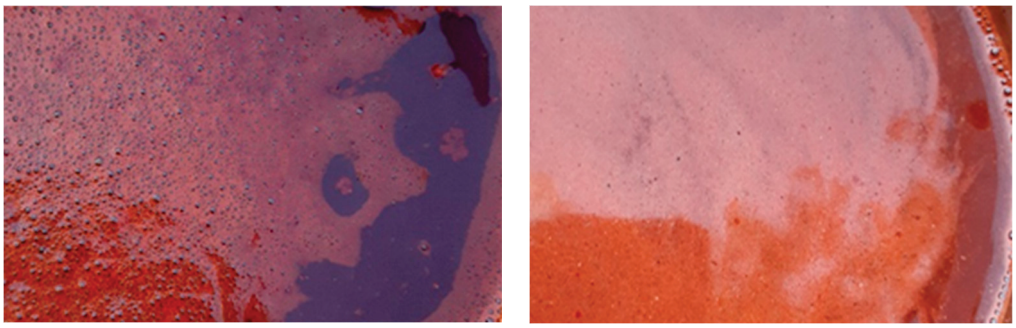
In order to ascertain whether the Latvian peasants were familiar with the method of dyeing with the use of alkaline solution (lye), corresponding recipes were sought in the ethnographic material.

Both the materials collected by the Monuments Board and stored in NHML [33] and the book of Martha Bieleinstein [24] describe dyeing techniques, when plants (*Agrimonia eupatoria* L., *Alnus glutinosa* (L.) Gaertn., *Calluna vulgaris* (L.) Hull, *Juniperus communis* L., *Ledum palustre* L., *Potentilla erecta* (L.) Raeusch., *Prunus avium* L., etc.) are doused with a strong (pH not specified) lye solution and heated in it, thus obtaining a dyestuff solution [24] (pp. 137–139).

In previous dyeing experiments, the author of the article had already used these notes to test them in practice. As a result, it was found that an essential part of the process was left out of the record: the plants mentioned by Martha Bielenstein [24] (pp. 137–139) should not only be heated in the alkaline solution, but also soaked in it beforehand. Depending on the type of plant used to obtain dyestuff, the soaking process can take several days or even a week. This length of time is determined by how quickly the alkaline liquid becomes pH neutral in interaction with the substances present in the plants. This is necessary in order to ensure that the animal fiber (wool yarn) is not damaged during the subsequent dyeing process, which involves heating.

3.3.2. Dyeing Experiment II

In order to test the results of the dyeing technique recorded in the ethnographic materials with the imported plant *Bixa orellana* L., a second dyeing experiment was carried out. Only fabrics of plant fiber (linen and cotton) were dyed in it. The ratio of the dyestuff to the weight of the fiber was 2:3 (to ascertain that the obtained color tone would be sufficiently bright). Two parallel dyeing experiments were carried out: (1) by soaking the plant material (seeds of *B. orellana*) producing the dyestuff in water; and (2) by soaking the plant material producing the dyestuff in an alkaline (pH 12) solution. Ground *B. orellana* seeds were soaked for about 3.5 days (87 h), then slowly heated and boiled for 1.5 h. Already during the soaking process, the color of the liquid differed: the alkaline solution was significantly darker (Figure 6). After heating, the color difference was even more pronounced (Figure 7).

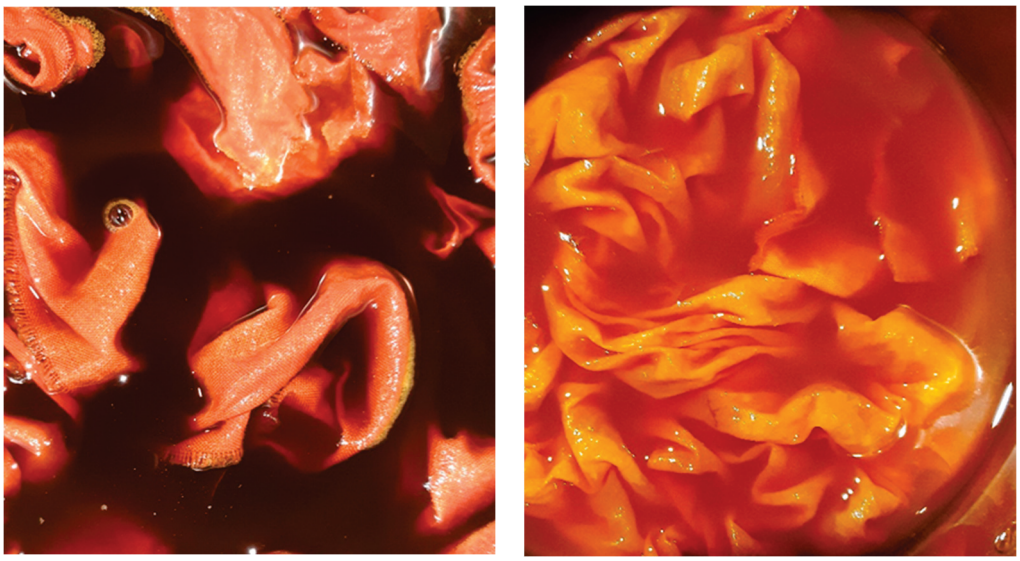


(**a**) (**b**)

Figure 6. The color of the liquid in which ground *Bixa orellana* L. seeds are soaked: (**a**) in an alkaline solution; (**b**) in water.

Before dyeing, pieces of linen and cotton fabric were boiled in a liquid with added detergent (1 tablespoon per 6 L of water) to ensure that the fiber was as clean as possible. The clean and wet fabrics were then soaked in the cooled dyestuff solution (Figure 8), and after several hours, the heating was started. As before, the liquid was gradually heated to a boiling temperature, and then the material to be dyed was heated at the boiling temperature for about 1 h. Then, it was left to cool in the dyestuff solution and rinsed (Figure 9). As a result, much brighter and more saturated color tones were obtained than in the first experiment (Figure 10).

Figure 7. Dyestuff solutions obtained from *Bixa orellana* L.: (1) on the left—from the plant soaked in lye (alkaline solution); (2) on the right—from the plant soaked in water.



(**a**) (**b**)

Figure 8. Fabrics prepared for dyeing are soaked in a boiled and strained dyestuff solution: (**a**) liquid prepared with alkali; (**b**) the liquid prepared in water.

Figure 9. Pieces of fabric dyed with *Bixa orellana* L. during the rinsing process.

Figure 10. Fabric samples dyed with *Bixa orellana* L. From the left: (1) linen fabric and (2) cotton fabric dyed in a liquid obtained by soaking the plants producing the dyestuff in water. Next: (3) linen fabric and (4) cotton fabric dyed in a liquid obtained by soaking the plants producing the dyestuff in an alkaline solution.

The color obtained with alkali (as the fabric dried, the fiber became about half as light—as is usually the case with textiles of plant origin) is sufficiently specific to be described exactly as the tangerine-orange color mentioned by J. C. Brotze.

Based on in-depth studies of written sources about the tradition of using the plants to produce dyestuff in Latvia [34] and the author's more than 15 years of practical experience in dyeing with nature-derived substances, it can be said that there are no other known plants that would have been used in the territory of Latvia, with which fibers of plant origin could be dyed in this color. This could confirm the hypothesis that orlean/annatto has not only been known as a dyestuff to J. C. Brotze, but could also have been used by Vidzeme peasants to obtain a tangerine-orange colored apron. Moreover, as proved by means of the practical experiment, when dyeing a small piece of clothing, such as an apron, or the amount of yarn required for it, a relatively small amount of plant producing the dyestuff is required. However, it is precisely the fact that money has been paid for this dyestuff that bestows upon a garment dyed in this color the meaning of particular luxury.

4. Conclusions

From the findings presented in this paper, we can conclude that Johann Christoph Brotze mentioned a real dye used for dyeing peasant aprons worn as festive attire. The plant *Bixa orellana* L. indicated as dyestuff was available in the Vidzeme governorate of the Russian Empire, and peasants could buy it because only a small amount of dye was needed for dyeing. Practical experiments further demonstrated that alkali was utilized in the dyeing process in the 18th century. It is highly probable that the plant used as the source of dye was soaked in alkali before dyeing, thereby obtaining a brighter orange color. Moreover, the tone of the linen fabric dyed in the experiments corresponds to the one seen in Brotze's drawings. Additionally, a technology not mentioned in the written source has been uncovered, as illustrated in Figure 11.

Figure 11. Reconstruction of clothing according to J.C.Brotze's drawing, apron dyed with *Bixa orellana* L. using the dyeing method described in the article with the use of alkali. Photo: M. Karlsons.

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An Unknown 18th-Century Flemish Dyers Manuscript from Antwerp (1778–1802)

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Abstract: This paper presents a historical analysis of a rare dyer's manuscript, preserved within the Museum of Industry in Ghent, Belgium. The manuscript, originating from a dyer in late 18th-century Antwerp, includes an extensive collection of recipes. The study will enable researchers to better grasp the practices of traditional dyeing techniques and materials in the region during that time. The manuscript focuses primarily on the dyeing of woolen fabrics. Approximately 90 of the 132 recipes utilize red dyes. Recipes for dying orange, brown, black, blue, and green colors are also described. The document mentions the use of madder, brazilwood, redwood, and cochineal. To create a variety of red shades, the dyer describes how fabrics were treated with different mordanting compounds, with alum and tin as the main ingredients, and how the dyeing solutions were prepared. The resulting colors include 'madder red', 'formal red', 'crimson', 'scarlet', 'Turkish red', 'fire color' and 'flesh color'. In addition to the dyeing recipes, the manuscript contains various accounting documents and correspondences between the dyer, customers, and suppliers. Lastly, over 100 original, colored samples are attached to the described recipes. In this paper, the artifact's contents will be disclosed, comprising recipes with attached samples and correspondence. Findings resulting from archive research will be included, contextualizing and placing the dyer in their urban and social context. The paper concludes by discussing its potential limitations and provides avenues for possible future research.

Keywords: dyer's recipe book; 18th century; natural dyes; Antwerp; wool; color terminology

1. Introduction

This anonymous 18th-century manual was recently donated to the Museum of Industry in Ghent[1] and offers a rare and valuable glimpse into the dyeing practices of the time. A local school of textile design[2] donated it as part of a broader collection composed mainly of late 19th-century documents. This manuscript differentiates itself from the rest of the collection by being the only one from Antwerp and from the last quarter of the 18th century. It reports dyeing formulae, samples dyed with the described recipes, first-hand notes, and correspondences related to commercial activities. Within the museum, the manuscript was digitalized and introduced as part of the collection, but no further research or in-depth analysis of the contents was conducted. The discovery of an 18th-century dyer's manual containing practical dyeing instructions, matching samples, and a conspicuous amount of information related to the business is a rare and relevant finding. Artifacts of this kind are exceptionally rare, and only a small number are available to us today [1]. A manuscript of this sort offers us an original perspective on the world of dyeing at the time, shedding new light on these practices, which often were kept as secrets of the trade [2]. Furthermore, it is known that the Low Countries, and, specifically Antwerp, were renowned for the quality and variety of dyed textiles. Nevertheless, direct sources from the Low Countries are scarce, and even though, in the last decade, more have come to light and been analyzed, the general panorama remains largely unexplored and in need of detailed research [3].

Through a first evaluation and translation from the 18th-century Dutch, the relevance of this discovery becomes clear, offering an in-depth insight into the dyeing practices and activities of a dyer within the walls of Antwerp in the 18th century. This finding is relevant for an understanding of local know-how and the working of society at that time, as well as in the broader context of research in the practical art of dyers. This paper seeks to provide a detailed overview of the contents of the manuscript, including recipes (Figure 1), accounting notes (Figure 2), and correspondences. Furthermore, by analyzing the contents and conducting research within the Antwerp archives[3], we were able to trace and further contextualize the dyer, placing the business in the reality of its time and granting us a broad view of the workings of such an enterprise. Through this contribution, we aim to begin addressing the gap in the existing knowledge regarding dyeing practices within the Lowlands and further expand the actual knowledge base.

Figure 1. To dye Orange with madder and turmeric. pp. 35–36.

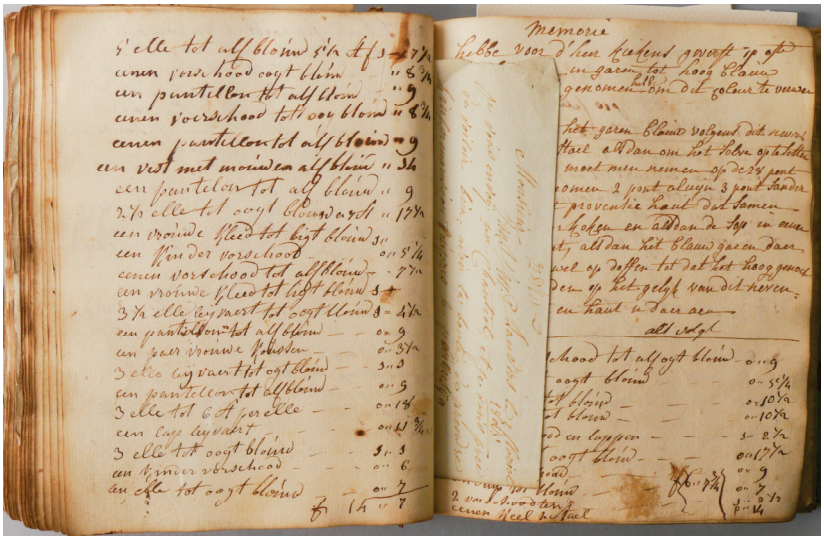

Figure 2. Example of recipes and pricing of product pp. 105–106.

2. Discussion

2.1. Historic Placement

The manuscript was donated in 2020 to the Museum of Industry in Ghent by a local textile school, without any contextual information. It was part of the collection preserved within the institution, but it lacked links to the rest of the artifacts, especially when it came

to relevant elements for our research. The manuscript itself had no clear indications about the manufacturer it belonged to or who the compiler might have been. Despite this absence, an examination of the artifact's contents yielded very valuable information.

The geographical provenance was quickly determined as Antwerp, primarily through the addresses found in the correspondences. Another pivotal component in the identification process was a small map (Figure 3) contained within the manuscript, depicting the presumed location of the manufactory in the cityscape. Several features surrounding the building were named, the most pertinent reference being the indication of the 'Oude Leeuwen Rui', which persists as an existing road in today's city network and allowed us to considerably narrow the geographical scope.

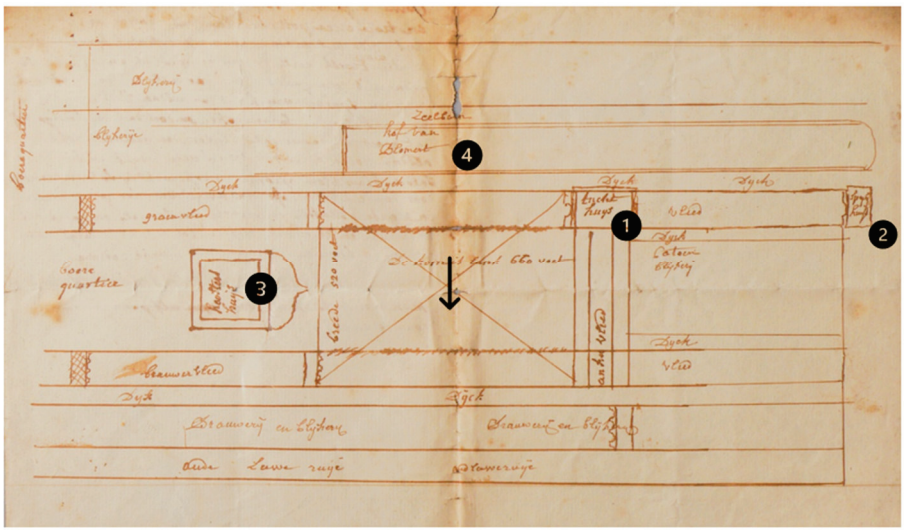

Figure 3. The map contained within the dyer's manuscript. (1) Tuchthuis (Penal structure), (2) Unnamed property, (3) Hanseatish huis (Hanseatic house), (4) Blommaert's property.

Another crucial element is presented in (Figure 4)[4], conserved in one of the city archives, containing a segment of the systematic land registers for the year 1800. This map facilitated the correlation of the remaining locations outlined in the manuscript's drawn map, including Tucht-huis (Penal structure), Ankervliet, Oude Leeuwenrui, Hanseatisch huis (House of the Hansa), and others.

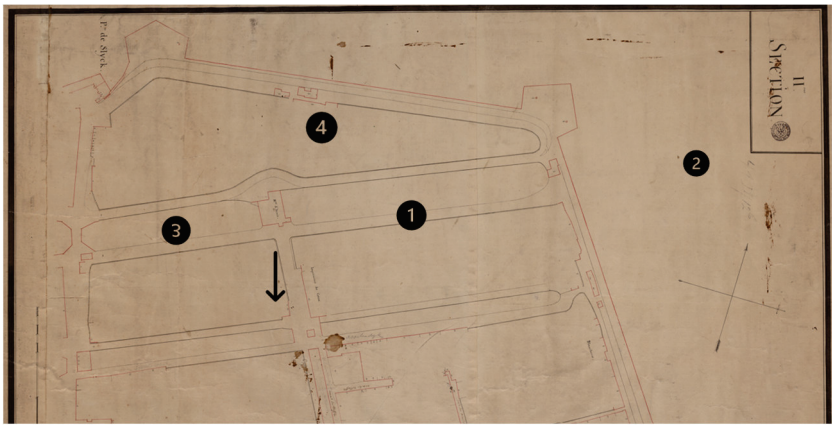

Figure 4. Section 2 of the map of Antwerp in ca.1800. (1) Tuchthuis (Penal structure), (2) Unnamed property, (3) Hanseatish huis (Hanseatic house), (4) Blommaert's property.

As a result, the dyer's establishment could be precisely located within the old city. Further validation arose as the name indicated on the manuscript's map for the domain north of the dyer (Blomaert) aligns with the one documented in the 'Gevelplan', associated

with it (Figure 4). This 'Gevelplan', detailed the names of the owners of various buildings and domains within the city walls. However, despite these confirmations, the name of the manufacturer remained elusive, as this building is listed as the property of 'La Commune', signifying the city itself.

Subsequent research revealed that it was common practice for city magistrates to stipulate long-term rental agreements or grant permission for manufacturers to use public or city-owned buildings, particularly for activities or industries they sought to promote. [4] Dyeing, unlike spinning and weaving, posed a series of challenges when looking for a suitable location. The specialized and heavy equipment required, including large kettles and furnaces, often necessitated their integration into the building's structure, making relocation impractical or impossible without substantial investment. Consequently, buildings housing dyeing operations were less likely to undergo repurposing between multiple rental contracts or companies [4].

Further evidence of the dyer's presence is documented in the 'Wijkboeken' (Figure 5), also preserved within the Felix Archief [5]. These books contain records of legal acts about buildings in specific neighborhoods, organized by period. Numerous dyers are mentioned throughout the books and pages (e.g., De Blauwe Hand, Ververij de Schaapskooi). However, it remains challenging to determine which of these is the manufacturer in question [6].

Figure 5. Pages from the 'Wijkboeken', holding account for the neighborhood of the manufacturer.

Also interesting is the proximity of the dyer to a penal institution. Although seemingly unrelated, the so-called tucht- or rasp-huizen (grind-houses), were common correctional institutions in which criminals were engaged in labor [7]. Often, these structures provided manpower for tasks related to the textile/dyeing industry, such as the chipping of dyewoods, for example, redwood and brazilwood [8]. While historical records attest to this practice, specific details regarding this particular instance were not found.

2.2. Historic Context

Although the exact name of the dyer remains undetermined, the timeframe (1778–1802) and location, situated at the corner between the 'Ankervliet' and 'Tuchthuis' are clear. These buildings were situated in a segment of the north-eastern city expansion initiated in the 15th century along the Schelde River [4]. Over time, this area evolved into the renowned 'Verversrui' or 'Dyer's Canal', owing to the concentration of many dyeing-related enterprises. Key factors driving this evolution were the availability of clean water and the central position within the city [4].

2.3. Socio-Economic Context

During the 18th century, Antwerp and the rest of the Austrian Netherlands witnessed important political and economic evolutions [9]. The first half of the century had been a period of stagnation, marked by instability and limited growth which also affected

the local textile industry. Small textile manufacturers had become outdated through lacking investments. Moreover, they were often outcompeted by large, modern, and more complex companies in the Northern Dutch Republic and other cities in the empire. In these competing organizations, all activities were centralized within company-owned buildings, which were systematically monitored and sealed from the outside world for daily operations. This allowed these foreign enterprises to efficiently increase their output, making it impossible for the smaller companies of the south to survive [10].

Nevertheless, in the second half of the century, the economy of the southern region benefitted from a stable political climate and economic growth. In combination with some state-driven measures and private investment, this led to a period of flourishing for the local textile industry [11]. Conspicuous investments were set directly into the creation of new companies, and the old, small-scale local enterprises were replaced by modern industries that could produce at the same pace and price as their competitors. One of the first companies established by these investments was 'Compagnie Beerenbroek', a textile printing enterprise. The company was founded in 1753 and obtained a 25-year-long exclusive patent on production from the Hapsburgian Empress. Once this first company had set the pace, multiple similar initiatives within different sectors of textile production grew in the city. The period between 1770 and 1795 witnessed important growth, with new companies hiring hundreds of people every year in Antwerp alone [12].

Despite being a large port city, the main outputs of Antwerp's production were inland, towards the central cities of the empire. This was mainly due to the blockade of the estuary of the Schelde River, which had been imposed since 1578 by the forces of the northern Netherlands [13].

The era of growth in the southern Netherlands came to abrupt end in the late years of the century with the entry of French revolutionary armies into the region. The ensuing battles and eventual integration into the French Empire in 1796 marked a period of socio-political instability, leading to the return of economic challenges for local enterprises [14]. Despite the removal of the blockade of the Schelde River, which in the first instance seemed to re-open possibilities for the city's exports, assimilation to France introduced unfamiliar contexts and limited the established trade towards the Hapsburg Empire. Unable to rapidly adapt to the new context and competition, local enterprises again faced economic struggles throughout the first half of the 19th century [15].

The manuscript discussed in this research serves as a business-related report and lacks explicit details about the impact of the political situation on everyday operations. The sole visible related detail is the use of the French revolutionary month name 'Le Floréal' (20th or 21st of April to the 19th or 20th of May) in one of the French-written delivery notes (Figure 6) [16]. The manuscript's last dated page is in 1802, with a few blank pages preceding the closing cover. The absence of a clear ending and the organic structure of the book's contents, including recipes, accounts, and letters, make it challenging to establish if the manuscript was concluded due to historical events or spatial constraints. Nevertheless, through this socio-economic analysis, we were able to better understand the conditions in which this business developed, and most likely came to an end.

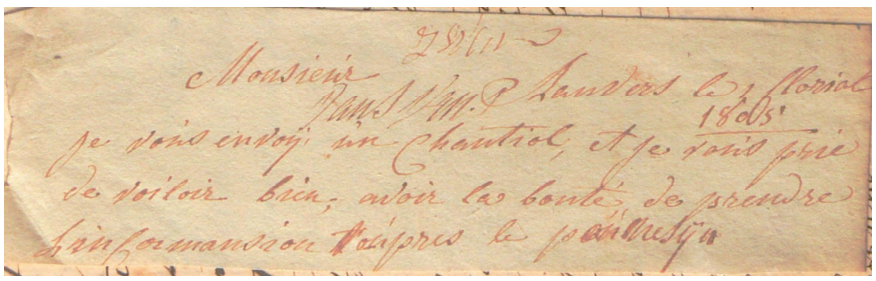

Figure 6. Delivery note, 'Monsieur, Anvers le Florial 1800, Je vous envoy mon chantiol et je vous prie de vouloir bien avoir la bonte de prendre. . .' ('Antwerp, Floréal 1800, with this I send you my chantiol and I kindly ask you to accept. . .').

2.4. Contents of the Manuscript

To fully grasp the relevance of the manuscript in its complexity, we opted for a broad approach. Rather than exclusively focus on the dyeing practices, our analysis extended also to social and historical contexts. This approach led us to interesting hypotheses and conclusions, which will be presented in the subsequent section.

The manuscript, featuring its original binding, is the work of a single main author. Of the 160 pages, about 110 are physically part of the book and exhibit the same regular, vertical indentations due to the mold used to produce them. The remaining 50 are loose pages with irregular patterns, written on different papers and then added to the manuscript [17]. This second group of pages also appears to be written mostly by the same hand and forms the main cluster composing the accounting section of the manuscript.

Content-wise, the manuscript can be broadly categorized into three groups, although these are not strictly delineated:

1. Recipes and dyeing tips exemplified by dyed fabric;
2. Accounting notes related to the acquisition and sale of goods;
3. Correspondences of different sorts.

Distributed across 160 pages, the main and predominant section of the manuscript comprises the 132 recipes and dyeing tips. Additionally, we find about 25 notes forming the accounting section related to the business operations (Figure 7). As mentioned, these notes are often external additions, either pinned or inserted within the pages. Most likely, they represent only a fraction of the total accounting documents produced by the dyer and were also likely added to the manuscript as reminders (of materials and quantities thereof) concerning the described recipe.

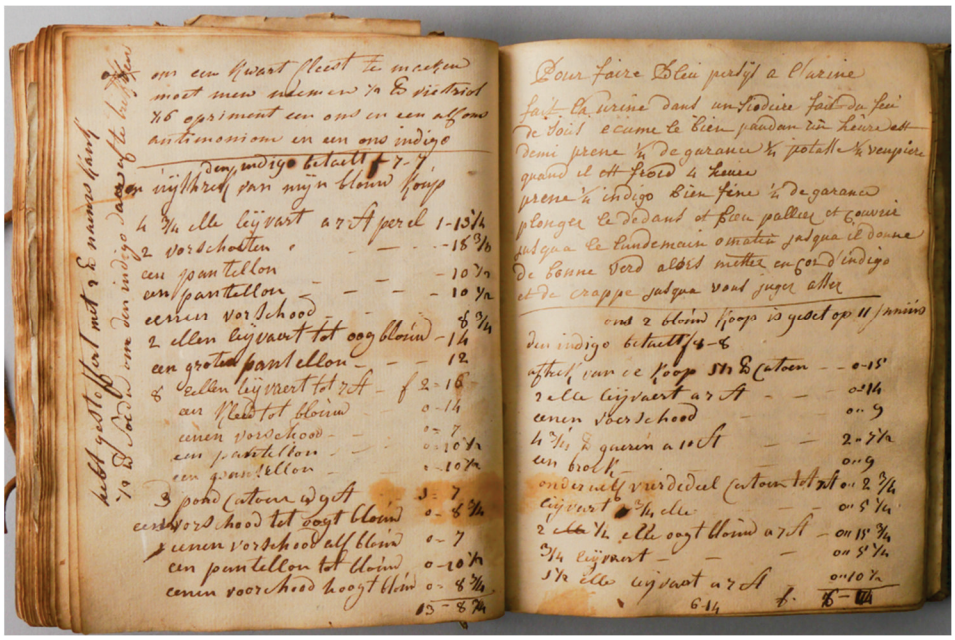

Figure 7. Summary of wares dyed with an indigo vat with an associated value, pp. 101–102.

The third section consists of six examples of correspondence between the dyer and the customers (Figure 8). Despite this being the smallest section of the manuscript, these letters offer us interesting and relevant insights into daily matters such as payment requests, deliveries, and legal matters. Finally, it is important to mention the 104 colored fabric samples, which are included in the manuscript and pinned to the recipe they were supposedly produced with. This addition even further increases the rarity and the value of the manuscript, as these well-preserved samples are a direct testament to the practices of the dyer and are a precious reference with which to further study the recipes.

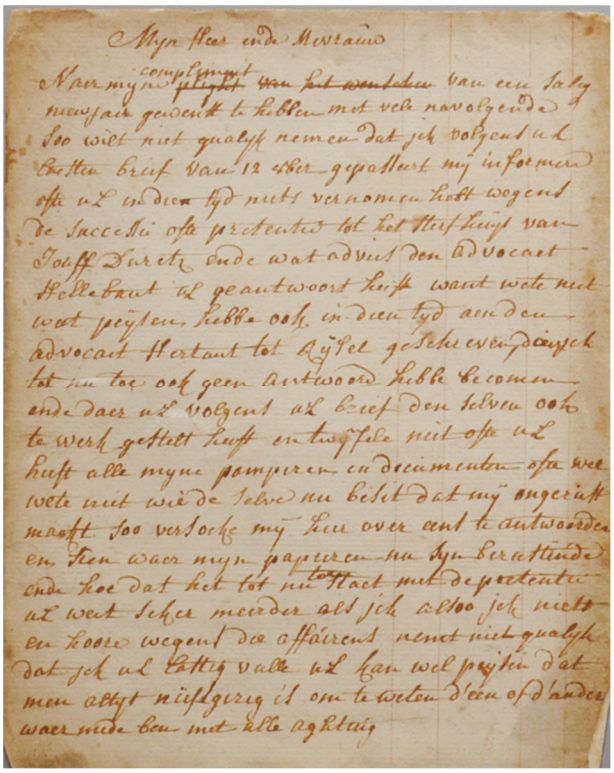

Figure 8. Example of correspondence related to legal matters.

2.5. Wool and Cotton Substrates, a Middle-Class Dyer

Examining the Antwerp Manuscript, it is possible to hypothesize that the dyer's production was destined for a broad middle-class public, offering recipes suitable for 'the poor' as well as expensive ones for a wealthier range of customers. The manuscript concentrates on wool dyeing, with exceptions made for three recipes specifically destined for cotton. Confirming this, nearly all the available fabric swatches are woolen, with some exceptions being cotton.

Historical sources indicate that the finest quality of wool was used to produce long and fine broadcloth. Especially proficient in this field were some of the dyers of the Languedoc, located in the south of France, of which a collection of documents has remained preserved and analyzed [18]. Additionally, the South of England also historically served as a significant hub for the production and trade of high-quality wool in Europe [19], but not much is known about the Low Countries.

The manuscript also provides indications regarding the type and quality of cloth being dyed. While the general term used is 'goet' ('wares'), specific textile-related terminology such as 'bayes' (a plain, woven, napped woolen fabric, generally coarse depending on quality) and 'sayes' (a light, twilled form of wool) [20] is mentioned in about 30 between recipes and accounting notes. Other references to dyed textiles include 'garens' (yarns), cited six times, and 'kerseys', (a coarser, thinner, woolen product with a distinct, visible weave pattern) [20,21] cited eight times. Bayes and sayes (Figure 9) are consistently mentioned together, reflecting their similarities and frequent production by the same clothiers [19]. These types of cloth were primarily intended for the middle class, sold as products of medium quality, and were less refined than broadcloth [22].

Figure 9. Recipe to dye madder red on bayes or other wares pp. 41–42.

Historical sources attest to the widespread production of these fabrics across multiple European hubs. Venice, renowned for its high-quality textile production, excelled in the production of sayes. This form of textile was then exported, especially to markets in the East, where demand was high [23]. Notably, Venetian sayes and bayes were so popular that they were not only bought and sold, but also imitated by producers in other regions, who hoped to pick up a share of this profitable market. Some of the locations we have information about include the Languedoc in France and the Low Countires [23].

The production of sayes and bayes in Flanders and Brabant predates the 16th century, but with time, knowledge from there and Italy traveled to England, especially to the Colchester area, where sayes and bayes were termed 'The new Draperies' [24]. Proximity to the sources of raw materials and important trading hubs facilitated the rapid establishment of a sizeable production there, leading to a growth in exports toward the continent [19]. These practices are examples of intense competition within the cloth market, which, by the 17th century, had turned into an immense theater of economic operations. This included the borrowing or sometimes the smuggling of technologies, patterns, and designs, as well as materials. The entire production process, from raw materials to finished products, developed on a massive scale, exemplifying the complexity and the interconnectedness of European cloth trading [21]. Knowledge in textile production spread across Europe through the hands of different actors, determining a diversification of the quality of the same product. These variations then depended on the quality of raw materials and the skill, infrastructure, and effort invested in the production process. Sayes and bayes, being versatile products, presented an ample spectrum of qualities and ranged from semi-luxurious products, especially high-end Venetian ones [18], to more affordable ones, such as those used in the clothing of monks and nuns and produced, for instance, in the northern Netherlands and England [19].

The quality and price of the product were then also determined by the choice of the dyestuff. Cheaper dyes were used for more economical products [25]. In this case, for sayes and bayes, dyestuffs like sappan and brazilwood fell into this category. In contrast, expensive dyes like cochineal, were mostly reserved for the production of high-end products, reflecting the correlation between the choice of dyestuff and the value of the finished product [22].

As the microscopical and technical analysis (HPLC, XRF, and color measurement) of the textile samples within the Antwerp manuscript is currently pending, it is premature to

provide a definitive statement regarding the overall quality of the production. However, based on the translated text and the range of employed dyes, it can be reasonably stated that the dyer worked with a range of different qualities of textiles.

Within the recipes, the prevalence of brazilwood and redwood, is potentially indicative of lower-quality products. On the other sid, the abundant presence of cochineal points towards a more refined range of goods (Figure 10) [18].

Figure 10. Recipe and samples of Cramoise and Fire color, dyed with cochineal pp. 55–56.

Moreover, the inclusion of colored yarn production in the manuscript, along with the mention of kersey, adds another layer to the diversity of the dyer's production. Kerseys, being cheaper than sayes and bayes, likely supplied less wealthy markets. Notably, these were dyed exclusively with lesser-quality dyes or recycled color baths from previous dyeing processes. Historical sources mention the practice of dyeing kerseys and yarns in Antwerp already during the 16th century. Despite this, this specific kind of production did not gain significant importance in the city [4].

Dyeing yarns before weaving ensures a better color penetration within the fibers and results in more vibrant hues afterward. This process was mainly applied when brilliant hues were necessary, for example, in the production of expensive multi-colored fabrics such as tapestries. However, despite this, it was rarely done, and Antwerp was not an exception in this regard. Dyeing the finished piece, or after the weaving process, remained the more prevalent practice. One key advantage of dyeing with this method was the minimization of waste, as both the dye and textile were used efficiently in the coloring stage [4]. The result is that, even though dyeing yarn yielded the best result, dyers still retained the habit of first coloring the finished pieces, and only after that, the yarns. Consequently, the latter were always dyed in partially exhausted dyeing vats, rendering the results less appealing [4].

The manuscript also documents this practice of recycling dye vats, with a noteworthy illustration found in the recipe (Figure 11). This particular recipe refers to the brown dyeing process applied to three kerseys directly addressed to be 'For the poor'. In this instance, the dyer utilized a vat containing residual dyes from prior black and red coloring procedures. These residual dyes were mixed and reheated, resulting in deep, dark brown hues on the fabric.

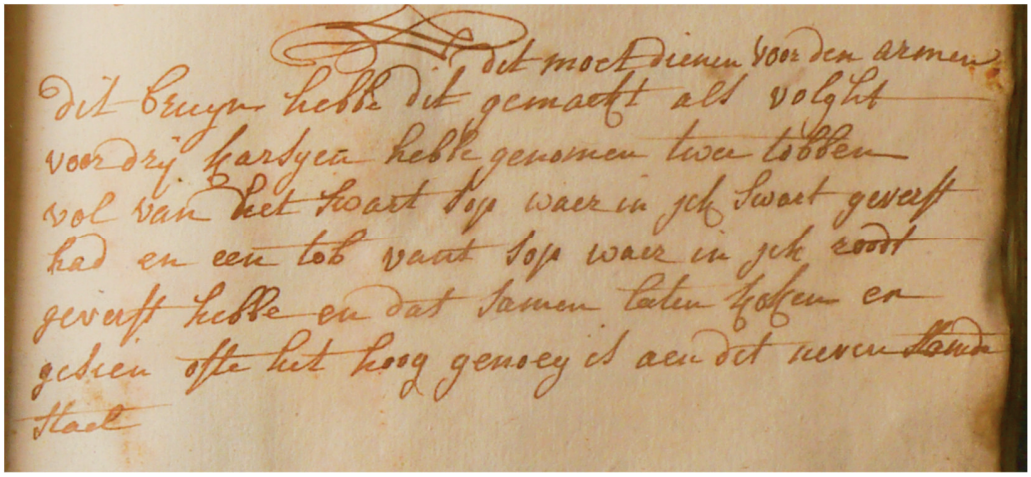

Figure 11. 'Dit moet dienen voor den armen' (this is to be used for the poor)—a recipe recycling a red and a black vat to dye three kerseys brown. p. 90.

From this analysis, it can be concluded that the dyer opted for a versatile production approach, supplying a diverse clientele. The selection of textile and dye qualities was tied to the audience for whom the final product was intended. This audience spanned from the lower middle class, as seen in the aforementioned recipe (Figure 11), to the higher middle class, as shown in the recipe that presents a meticulous procedure for dyeing intense scarlet through a double cochineal bath (Figure 10).

Wool emerged as the central focus of production, with cotton playing a secondary role, mentioned in the manuscript on three occasions. The primary emphasis on sayes and bayes suggests that these forms of textiles were the core of the production within the enterprise, as well as the highest-quality products within the capabilities of the dyer. Utilizing leftovers from these higher-end products and employing less stable and economical dyes, the dyer then produced mainly kerseys, a more affordable form of wool. Furthermore, hybrid recipes, blending both inexpensive and premium dyes, were likely aimed at creating an intermediate range of products to accommodate varying consumer preferences.

2.6. Small-Sized Enterprise

Closely tied to the previous paragraph is a hypothesis about the possible size of the enterprise that generated this document. The central deduction that led us to this consideration is mostly found in the accounting notes and in some of the recipes, more specifically, the ones carrying references to specific orders that included the quantity of material that was dyed.

One example (Figure 12) describes the most sizeable order in the document and reports on the production of 12 woolen kerseys. On page 133 of the document, (Figure 13) a single kersey is reported to weigh about 30 pounds (about 13.5 kg), thus 12 kerseys is equivalent to an order of roughly 360 pounds (about 160kg) of dyed goods [26]. To compare the order with other available sources, the industrial-sized production of the dye master Antoine Janot in Saint-Chinian, Languedoc, would export woolen fabric in bales weighing in at about 200 kg each [27]. Consequently, the largest order we have an account of is smaller than the average unit an industrial-sized dyer would export.

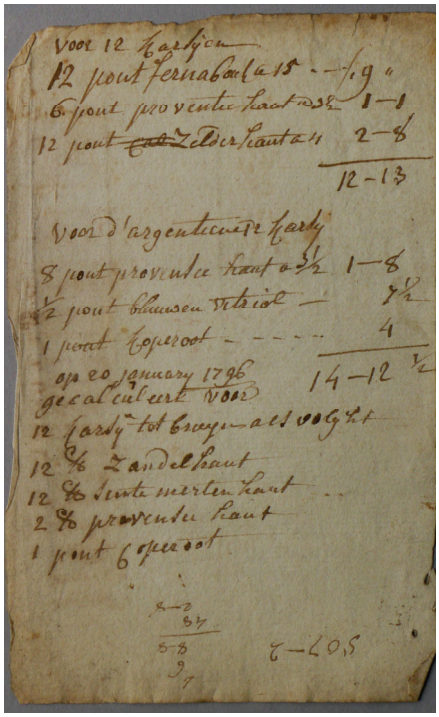

Figure 12. Materials used to dye an order of 12 kerseys p. 158.

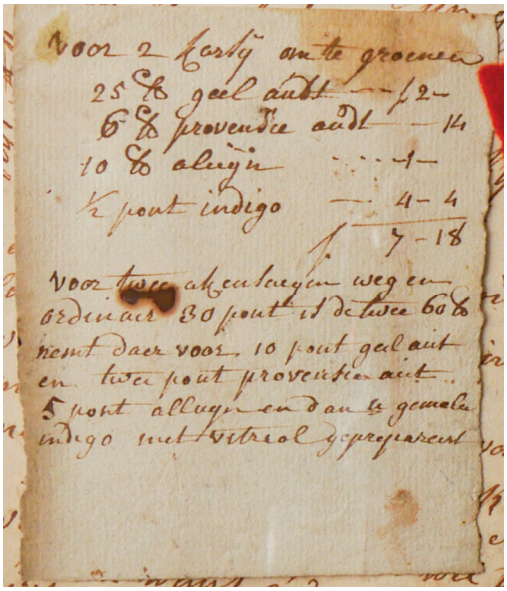

Figure 13. Order with reference to the weight of a saye p. 113. 'Voor twee Akensaeyen wegen ordinair 30 pont is de twee 60 pont, neem daer voor 10 pont geel aut. . .' (For two, as akensaeys weigh usually 30 pounds, the two of them weigh 60 pounds, for that, take 10 pounds of–yellow wood. . .).

Another indicative measure of the scale of the enterprise was deduced through a comparison with the Crutchley Archive's cashbook, which mirrors similar accounts to those found in the Antwerp manuscript, including transactions and tabs. The financial records in the Crutchley Archive extend up to GBP 2586 (equivalent to over EUR 345,000 today) for a single order. In contrast, the Antwerp dyer's accounts (Figure 14) document tabs up to 643 fl. (approximately EUR 5000 based on contemporary currency conversion rates) [28].

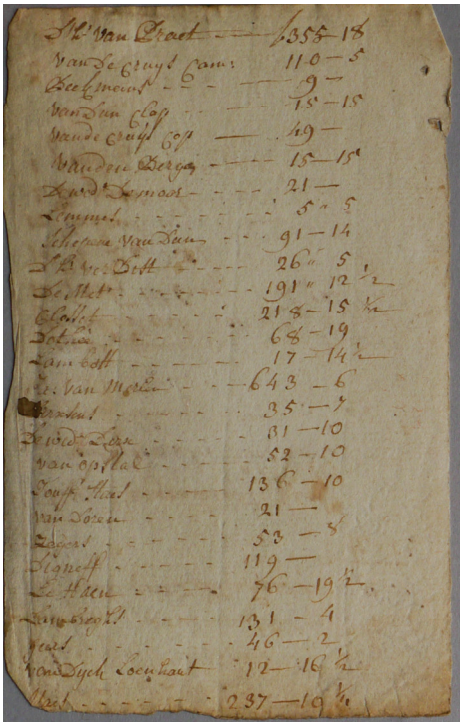

Figure 14. Tabs from the Antwerp manuscript, p. 159.

A similar juxtaposition can be traced between the size and timeframe of the two accounts. the Crutchleys produced a total of 15 books in 28 years [22], whilst we only have one book covering the whole timespan between 23 years (1779–1802) for the Antwerp dyer. The final element contributing to the proposition regarding the scale of the enterprise is the range of cities referenced in the manuscript, including Brussels, Liege, Dendermonde, and Louvain. These cities seem to sketch the boundaries of a network that was limited to the borders of today's Belgium. Within the manuscript, accounts are only given in the Flemish pound and the north-Netherlandic gulden, further indicating the local nature of the business. Lastly, also within the material orders, there are no indications of long-range business activities.

While acknowledging that this comparison may not offer an exhaustive conclusion due to the potential lack of complete accounts of the Antwerp company, which is limited to one single manuscript, it nonetheless provides consistent indicators supporting our hypothesis. Altogether, these clues suggest the profile of a local enterprise, primarily serving regional customers and retailers in line with a market orientation focused on the middle and lower-middle classes.

3. Dyeing Recipes

Given that the manuscript primarily serves as a record of practical instructions for textile dyeing, this initial section comprises about 70% of the totality of the document. The recipes within this section show important diversity, ranging from brief (Figure 15) to very extensive descriptions. This second category is frequently associated with specific orders, wherein the quantities utilized are meticulously outlined, providing a step-by-step breakdown of the dyeing process (Figure 16). A third category of recipes within this section involves extensive and complex dyeing procedures, which different to the previous category, focus uniquely on the sequence of procedures to achieve specific shades of color, without references to quantities (Figure 17).

Example of a short exemplifying recipe:

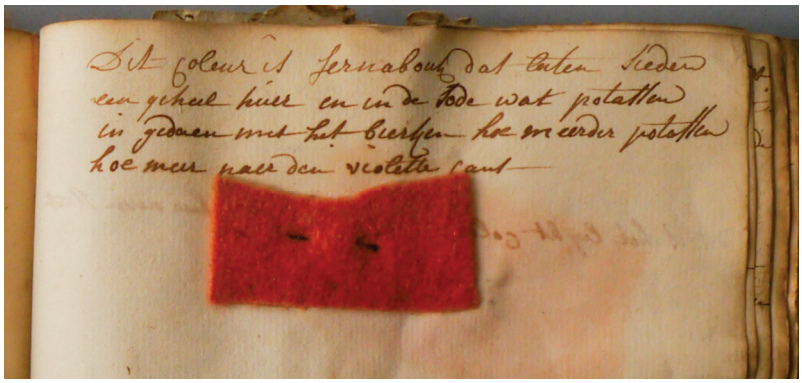

Figure 15. Dyeing red with brazilwood pp. 40. 'Dit coleur is fernanbouk dat laten sieden een geheel huer en in de sode wat potassen in gedaen met het bierken, hoe meerder potassen hoe meer naer de violette kant'. (This color is brazilwood which is cooked for an hour, and in the solution, I put some potash with some of the 'small beer'. The more potash you add the more purple it turns.).

Example of a 'production' recipe:

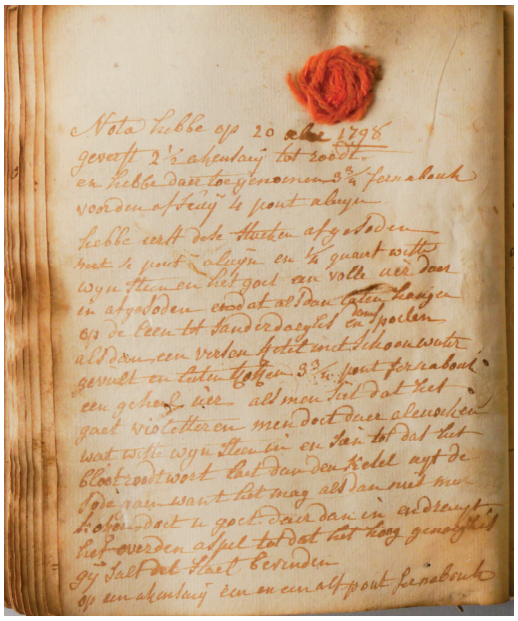

Figure 16. Dyeing of two 'akensaey' in red 1798 pp. 83. 'Nota hebbe op 20 . . . 1798, geverft twee en half akensaey tot rood en hebbe daer toe genomen drie en drie kwart fernanbouk. . . vier pont aluyn. . . een kwart witte wijnsteen. . .' (Nota this was dyed. . . 1798, two and a half akensaey in red. I took three and three-quarters of brazilwood. . . four pounds of alum. . . one-quarter of cream of tartar. . .).

Example of a procedural recipe:

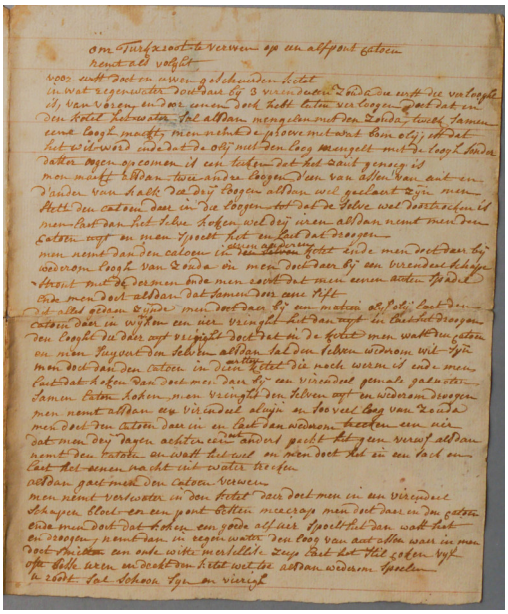

Figure 17. To dye Turkish red P.134. Om Turks root te verwen op en alfpont catoen nemt als volgt. Voor eerst doet in uwen geschuurden ketel in wat regen water, doet dan daer bij drie vierendeelen souda die verloghen is van voren. . .' (To dye Turkish red on half a pound of cotton do as follows. First, fill your clean kettle with rain water, add up to three-quarters of soda which has already been dissolved. . .).

3.1. Dyestuff and Mordants

Within the manuscript, various dye sources are mentioned, exhibiting similarities to those commonly employed in analogous works [22]. The primary focus of the manuscript centers on red hues, with brazilwood (fernanbouk), madder, redwood, and cochineal as prevalent sources of dyestuffs. Additional utilized dyestuffs include indigo, logwood, turmeric, old fustic, weld, sumac, gallnuts, and sandalwood. Selection of the dyestuffs was based on different criteria, including the desired color and its quality, cost considerations, and the intended public for the final product. Accordingly, the mordants with which the textile was prepared were chosen and applied.

The manuscript describes a diverse range of mordants in the fabric preparation for the dyeing process. Within these, we find the most commonly used substances in the 18th-century (wool) dyeing industry [29]. Alum and cream of tartar are the predominant mordants, featured in nearly every red dye recipe, whether involving madder, brazilwood, or cochineal.

An interesting addition, particularly in cochineal dyeing, is the use of the 'Bierken' or 'little beer', twice described in the manual. This mixture consists of a mixture of water, strong water derived from fermenting bran over several days or weeks, combined with ground English tin. Interestingly, the 'bierken' is used differently than conventional mordants as it is not utilized in the initial fabric preparation stage but rather during the coloring process, serving as a 'middle mordant' to enhance color quality [30]. A comparable compound appears in the dyeing instructions of the Crutchley archive, where a 'spirit' is formulated using similar ingredients: water, nitric acid or aqua fortis (sour water) produced through bran fermentation, and tin [22]. Furthermore, the manuscript describes, next to tannins, the use of various other metallic salts, such as iron oxides, 'antimonium', and orpiment, further broadening the spectrum of mordants employed in the dyeing recipes.

The practice of dyeing has given us insights into the essential steps for achieving optimal results in textile coloring. Certain key elements, such as meticulous mordanting, precise temperature control, or the consistent movement of textiles during the procedure, play key roles in assuring even absorption of the dyestuff. Upon analysis of the recipes, it

becomes clear that some of these crucial steps are either briefly summarized, implied or occasionally omitted. For instance, keeping the textile in motion is explicitly mentioned only in a few of the recipes, as illustrated in (Figure 18), the same indication is absent in the majority of the other recipes.

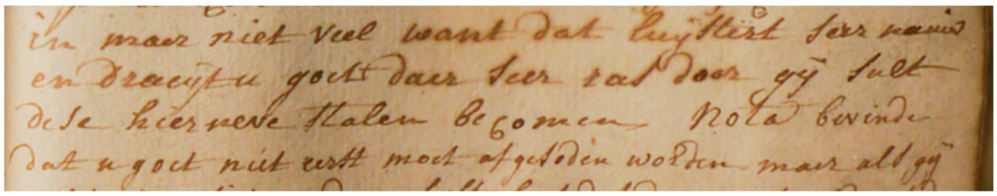

Figure 18. Fragment from (Figure 10), to dye fire red p. 56. 'Doet uw curcuma daer in. . . en draeyt u goed daer seer ras door, gy sult dese hier neve stalen becomen. . .' (Add the turmeric. . . and stir consistently, then you will obtain the same as the sample attached next to this recipe. . .).

Similarly, mordanting is also often implied unless specific additives, like cream of tartar or the previously mentioned 'bierken' were required. Analogous situations can be observed in other manuscripts, such as those in the Crutchley archive, indicating that these recipes were primarily intended for internal use within the company or for transmission to another skilled craftsman. Consequently, certain procedures may not have been explicitly documented as they were considered to be common knowledge.

Additionally, an examination of the recipes also seems to reveal that this manuscript was not only a compendium of practical recipes but rather an instrument for daily use. Many recipes show signs of corrections, adjustments, and in some cases, markings denoting their non-validity (Figure 19). This suggests that the manuscript is not only a replication or a compilation of recipes, but rather a dynamic, developing collection that was regularly updated to document new recipes and underwent regular refinement through time.

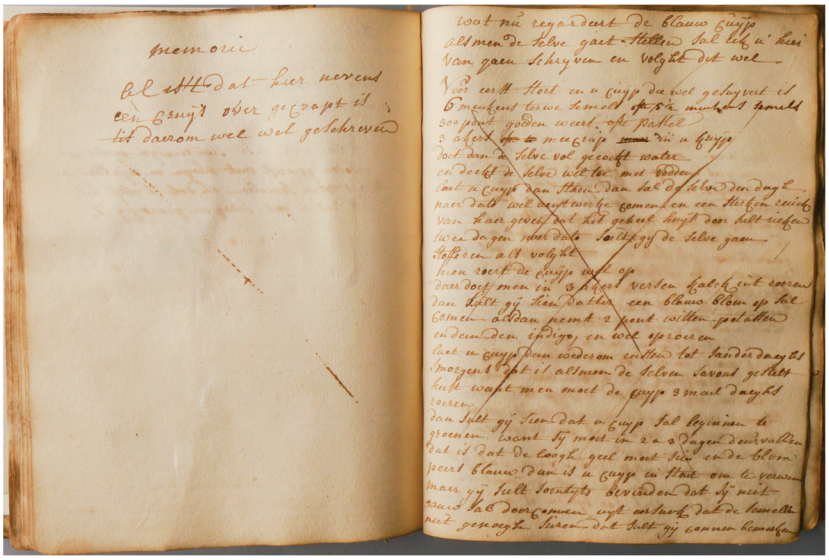

Figure 19. Setting up an indigo vat pp. 23–24. Left page: 'Memoire, Al staat dat hier neven en cruis over gecrapt is t'is daarom wel geschreven' (Reminder, even if there is a stripe on the next recipe, do not mind that as it is still well written).

3.2. Color Terminology

Another topic taken into consideration during our research is the color terminology utilized in the manuscript to specify the different hues derived from the use of the recipes. In dyeing, specific terminology seemed to be of great relevance, as it was used as a means of precise description and communication between dyers. One definition would identify one specific hue of color, and one color could have many hues. This use of terminology

seems to be consistent across hubs all over Europe, and this practice is documented in multiple manuals, like the ones produced by Paul Gout's enterprise and referenced by Dominique Cardon [18,29].

The degree of specificity in the terminology also seems to be dependent on the specialization of the analyzed dyer. The Antwerp dyer, being mostly specialized in the production of red hues, has, in that segment, a higher degree of specificity in terminology, while for other colors, definitions are scanter. Among the sixty recipes for red, twelve different definitions are utilized for a single color, while the remaining seventy recipes in the book utilize eight total definitions to describe green, blue, and gray colors (Table 1). However, to validate this hypothesis, especially concerning the international conformity of definitions, further research is necessary.

Table 1. Chart of all color definitions contained within the manuscript.

Red		**Green**	
Manuscript definition	Translation	Manuscript definition	Translation
Suijver crap rood	Pure madder red	Licht oliyf	Light olive
Formeel crap rood	Formal madder red	Saksisch groen	Saxon green
Crap rood	Madder red	Verdebouteille	Bottle green
Scharlaek	Scarlet	Pissgroen	Piss green
Cramoise	Crimson	**Blue**	
Bloed rood	Blood red	Manuscript definition	Translation
Gloeiend rood	Glowing red	Celadon	Celadon
Vuur kleur	Fire color	Piss blauw	Piss blue
Turks rood	Turkish red	Saksisch blauw	Saxon blue
Carnaet	Flesh color	**Gray**	
Vals rood	Fake red	Manuscript definition	Translation
Carmosyn	Carmine (dark red)	Argentien	Argentine

These color definitions present an interesting avenue for further research in the domain of textile color and trade. Interestingly, distinct definitions (Figure 20) found in the Antwerp Manuscript have been found in other manuals, as exemplified in the analysis conducted by Dominique Cardon. A comparative study could shed light on whether colors produced under the same definition in different hubs aligned, potentially establishing a standard within the market, possibly even on an international scale [31].

Figure 20. How to make pissblue and pissgreen.

We know that samples circulated widely within the Low Countries; many archives still bear traces of this trade [32]. Consequently, some level of standardization is to be expected. Whether these standards were then extended on an international level is at the moment uncertain. Additionally, by studying these definitions throughout time, it could be possible to trace the movement of knowledge between production and trading hubs.

4. Conclusions

To conclude, this 18th-century Flemish dyer's manuscript from Antwerp is a rare and relevant finding in the study of textile-bound practices. This unique artifact contains valuable first-hand insights not only into the dyeing procedures, but also into the accounting practices, and relations with customers. Directly, and indirectly, through our analysis, we were able to develop insights into the socio-historical context and the daily practices of the dyer, and further understand the development of knowledge across the 25 years covered by the manuscript. Lastly, the presence of more than 100 colored samples even further enriches the manuscript, granting tangible proof of the dyer's skill and providing a reference as to how materials like cochineal, madder, brazilwood, redwood, indigo, and other dyestuffs were utilized. These processes were then translated into products for the customers of the enterprise, which, through analysis, we were able to identify as a broad middle class.

Beyond the practical aspects of dyeing, the manuscript also contains a section consisting of accounting notes, detailing transactions and materials orders for and from customers. Correspondences in French and Dutch inform us of the legal and practical matters of the dyer's business in its historical context. Both sections allowed us to better understand the development of the commercial operations and the day-to-day practices of the company.

Tracing of the manuscript within the city of Antwerp and ascertaining its timeframe were achieved through archival research. Even though this task proved arduous due to the apparent lack of sources, we were able to retrieve information, and through the elements described in the previous paragraphs, partially reconstruct its context. The dyer was located within the famous dyer's district of the city, in the key years of the transition from the Austrian–Hapsburgian influence to the French revolutionary and Napoleonic one. These years also correspond with the transition from a period of economic growth to one of economic stagnation and recession. This section of the research could further be developed by delving within the city archives, determining the specific name and owner of the enterprise, and developing that avenue.

The contents of the manuscript also reveal a broad range of textile products, with a general focus on wool and occasional references to cotton. The dyer's customer base seemed to range from the middle class to the middle-low class, producing a range of products varying from the relatively high-end woolen sayes and bayes to the more coarse and cheap kerseys. The choice of dyestuffs also supports this statement, ranging from expensive cochenille to cheaper sappanwood. The use of this range of dyes is also a testament to the skill of the dyer and their adaptability to the needs of the market.

The size of the enterprise is mainly derived from the accounting pages, which include orders and delivery notes. These seem to trace the footprint of a local enterprise, with a network of customers limited to the cities of today's Belgium. Also confirming this hypothesis is a comparison with the similar manuscripts of Antoine Janot in France and Crutchley's in England, which were exporting goods worldwide and had accounts that were almost a hundred times larger than those detailed in this manuscript.

The extensive compound of dyeing recipes grants us a broad insight into the know-how as well as the dyeing-related activities of the dyer. Notably, within the manuscript, recipes are often adjusted, updated, or even invalidated, suggesting the use of the manuscript as a practical working document and not solely a theoretical collection of recipes. Furthermore, the analysis of the color terminology utilized in the manuscript offers us the opportunity for further research on color and practice standardization throughout production and trading hubs.

In summary, through the study of this manuscript, this paper aims to contribute to a more ample understanding of the dyeing practices of the 18th century in Antwerp and Europe, further adding to the pool of existing knowledge. Our approach aims to develop an overall understanding of the manuscript, focusing, in addition to the dyeing practices, on the socio-historical context of the manuscript.

Lastly, avenues for potential future research are also presented. Through microscopical observation, practical reproduction, HPLC, XRF, and color measurement, future research will evaluate the quality of the dyer's finished products, as well as confirm the matching between the samples and the recipes of the book. Different possible avenues include direct comparisons of this manual with the other available ones, in order to trace similarities and common trends between countries and production hubs. By sharing our research, we would like to add a valuable element to the panorama of existing knowledge, hopefully fostering interdisciplinary research.

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Notes

1 Museum of Industry. Entry no. V37828-001. Museum of Industry Collection, Minnemeers 10, Ghent, Belgium

2 Hogeschool Ghent, ex Hoger Rijksinstituut voor Textiel en Kunststoffen collection, Voskenslaan 364, Ghent, Belgium

3 Felix archive–city archive Antwerp, Oudeleeuwenrui 29, 2000 Antwerp

4 Wijk 2, BE SA 209546, inventory N. 12#4263, Felix-Archief Antwerp. Ca. 1800

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Article

Natural Dyes in Embroideries of Byzantine Tradition, the Collection of Embroidered Aëres and Epitaphioi in the National Museum of Art of Romania

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Abstract: The medieval textiles collection of the National Museum of Art of Romania (MNAR) has been in place since 1865 and nowadays preserves about 1000 medieval and pre-modern weavings and embroideries. These extremely valuable objects, dated between the 14th and the 19th centuries, are mainly religious embroidered garments and veils with special significance in the Byzantine li-turgy. Ecclesiastical embroideries of Byzantine tradition are characterized by a complex technique: metallic threads with a silk core, metallic wires and coloured silk threads are couched over padding on layers of silk and cellulosic supports so as to create relief through light reflection. The silk sup-ports and the sewing threads are coloured, mainly in red, blue, green and yellow hues, and analytical investigations of the dyes used in embroideries preserved in the MNAR, in the Putna and Sucevița Monasteries, have been released in previous studies by the corresponding author. The present work continues the approach with research into dyes in about 25 *aëres* and *epitaphioi* from the MNAR collection. Considering their privileged function in the liturgical ritual, these luxurious pieces embroidered with silver, gilded silver or coloured silk threads and decorated with pearls, sequins or semi-precious stones are the most faithful description of the stylistic and technological evolution of the art of post-Byzantine embroidery in the Romanian provinces. The data resulting from the present research will improve the knowledge regarding this topic. Dye analysis was performed by liquid chromatography with diode array detection, while fibres were characterized by infrared spectroscopy (with attenuated total reflectance) and optical microscopy. The biological sources identified—carminic acid-based dyes, redwood, dyer's broom, weld, indigo-based dyes—-will be discussed in correspondence with their use in the embroidery technique: support, lining and embroidery threads, together with other sources previously reported on Byzantine embroideries in Romanian collections, and in similar objects preserved at Holy Mount Athos.

Keywords: natural dyes; liturgical embroideries of Byzantine tradition; *epitaphios*; *aër*; liquid chromatography; identification; Romania

1. Introduction

Public and ecclesiastical museums in Romania preserve valuable medieval and pre-modern textile collections, perfectly integrated within the European luxury textiles, especially the Byzantine and post-Byzantine. Medieval embroideries, and especially the liturgical vestments and veils, are the most representative. These objects belong to the treas-uries of the Orthodox or Catholic churches that have been active over time in the three historical Romanian provinces, Moldavia, Wallachia and Transylvania. Liturgical

embroideries in the Byzantine style particularly enjoyed great appreciation in the Romanian ter-ritories and set up a special chapter in the history of medieval and pre-modern South-eastern European art.

The large number of embroidered liturgical objects in Byzantine or post-Byzantine workshops perfectly document the interest of the Romanian medieval cultural elites in the Byzantine imperial art. The same enthusiasm was equally evident in all the other artistic fields: architecture, painting, sculpture and illuminated manuscripts. The geographical position of the three historical Romanian provinces allowed direct cultural exchanges with Byzantium during the Middle Ages, which is nowadays richly documented by archaeological research. However, towards the end of the Middle Ages, the political history of the provinces took different forms of attachment to the Byzantine artistic heritage. The principality of Transylvania, which had been in the sights of the newly established Hungarian state in the Pannonian Plain since the 10th century, was much more receptive to Western European art, which was intensively promoted through the Catholic Church and the papacy. Moldavia and Wallachia remained constantly within the sphere of influence of the Byzantine Empire, especially after the state organization of the two provinces, which had been under the spiritual authority of the Patriarchate of Constantinople since the mid-14th century [1].

The National Museum of Art of Romania (MNAR) preserves the largest and most representative collection of medieval textiles in Romania. Created in and developed since 1865, it was at that time, the first public collection of Byzantine and post-Byzantine art in the world [1]. Some of these objects, mainly those dated from the 15th and 16th centuries, were studied in terms of materials and techniques in the early 2000s, the years which preceded the re-opening of the Romanian Medieval Art Gallery [2]. Other liturgical embroideries from the same period, or later, preserved in MNAR or in monasteries in the northeastern part of Romania were also subject of research, with reference to the metallic threads and dyes [3–7].

Liturgical textiles of Byzantine tradition have two different supports, with distinct roles: one to provide resistance and another one as a base for building the relief [8]. The former is composed of a cellulosic support (never visible) (Figure 1), which is not coloured, and a silk support with an aesthetic role, which is totally or partially visible [8]. In order to provide a contrast with the precious metallic embroidery, as well as to give it importance, the silk support was coloured according to the Church canons: purple-red in most cases, with blue, yellow and brown also accepted [8]. Embroidery is made with silk threads—visible or wrapped up in precious metallic bands and wires—-or just with metallic threads, to result in the so-called "needle painting" [9]. The scenes and decoration cover most of the silk support, which in some cases becomes almost completely masked [8] (Figure 1).

Natural dyes' identification, together with attribution of the most probable biological sources used, represents an essential output in the studies of historical textiles. Data regarding the dyes' places of origin, information on their first commerce and about trade routes, as well as guild regulations represent valuable instruments to document textile production and place a studied object in time and place [10,11]. The identification of dyes in historical textiles is nowadays possible mainly by liquid chromatography with diode array detection (LC-DAD). Since its first use in 1985, the above-mentioned configuration was considered for many years as the standard method for dye analysis [12–16]. Later on, the development of mass spectrometers (MS), with increased sensitivity and lower detection limits, mainly used in LC-DAD-MS layouts, proved to be extremely useful in biolog-ical sources' detection [17–19]. Results are optimized when these structures are exploited together with dedicated in-house built databases. Moreover, when applied in tandem configurations, mass spectrometers confirmed their efficiency to characterize unknown marker compounds, with consequences in the accurate attribution of the biological sources used, and better contextualization of the studied textiles [20–22]. The interest in optimizing the information acquired from the tiny samples available and discerning between sources

containing the same aglycones but different glycosides also led to the development of mild extraction methods, as alternatives to the classical acid hydrolysis [23–26].

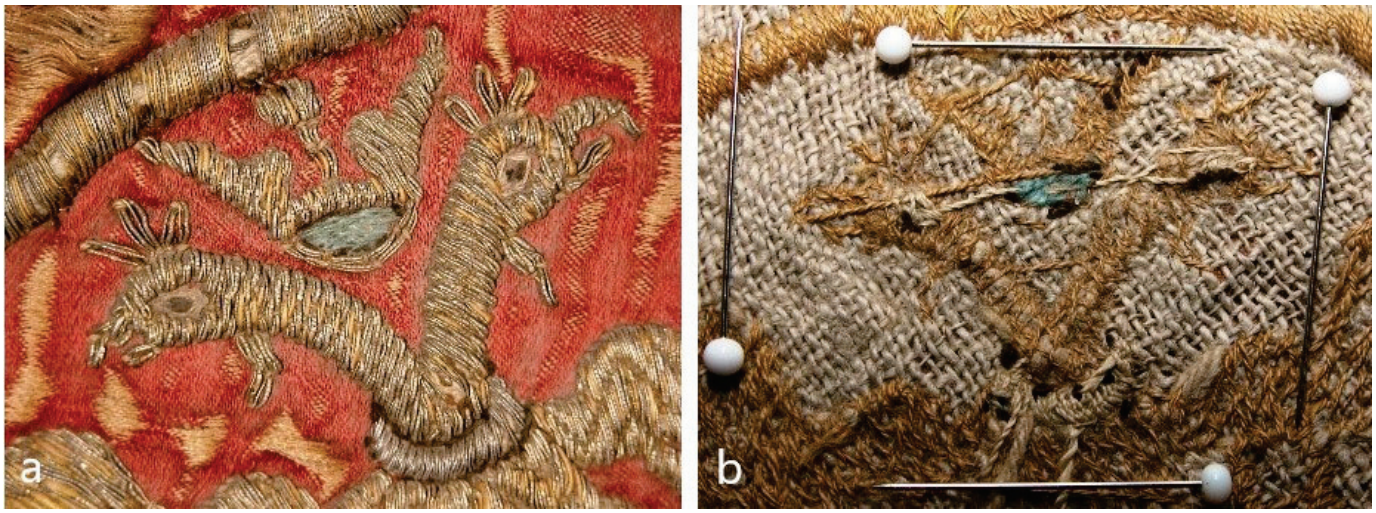


Figure 1. Images to illustrate the technique of liturgical embroideries worked in the Byzantine tradition. (**a**) Left, front side: detail of embroidery on satin where the metallic thread, which runs only on the obverse, is visible. (**b**) Right, reverse side: detail of the embroidery where the cellulosic support and the attachment points of the metal threads are visible.

With all these resources available, a vast amount of knowledge was acquired regarding the dyes used in various textiles from archaeological and historical contexts [27–29]. With reference to liturgical embroideries worked in the Byzantine tradition, the studies performed on textiles in Romanian collections evidenced that for the purple-red silk satin embroidery supports in objects dating from the second half of the 15th century, the combination of lac dye (*Kerria lacca*) and madder (*Rubia tinctorum* L.) was used for the warp, and redwood (*Caesalpinia* species, as, for example, *C. sappan*—now reclassified as *Biancaea sappan* or *C. echinata*—now *Paubrasilia echinata*) for the invisible weft. Kermes (*Kermes vermilio*) was responsible for the colour in the warp in a few samples, which correspond to very precious objects [4]. Starting from the last decades of the 16th century, warps in purple-red silk supports were dyed with Mexican cochineal (*Dactylopius coccus*) [4]. For the rare cases when blue silk satin supports were used in 16th century embroideries, indigo dyes were detected. A larger palette of colours and dyes, used individually or in combination, was identified in the embroidery threads in the studies performed on liturgical textiles in Romanian collections [2–5].

The present study aims to contribute to the existing knowledge on liturgical embroideries illustrating the theme of "Lamentation over Dead Christ" and dated between the 14th and the 19th centuries, using dye research. The objects had an important role in the Eastern Church ritual and this gives them the greatest artistic, historical and material value from the whole collection of liturgical embroideries of Byzantine tradition preserved in Romania. *Epitaphioi* and *aëres* belong to the same group of liturgical textiles but have different functions during the Orthodox religious service. *Epitaphioi* are mainly used on Good Friday when they are brought into the Church to symbolize Descending from the Cross and Lamentation and are then returned to the Altar and laid on the Table until Re-surrection (Figure 2). *Aëres* are used to cover the vessels and are then worn on the priest's shoulders during the ceremony of the presentation of the "holy gifts" [1,30] (Figure 3). The objects studied are dated over a period of about 500 years, with most of them from the 17th to the 19th century and are all conserved in the National Museum of Art of Romania (MNAR).

(**a**)

(**b**)

Figure 2. *Cont.*

(**c**)

(**d**)

Figure 2. *Cont.*

(**e**)

Figure 2. Examples of *epitaphioi* preserved in the National Museum of Art of Romania (MNAR): (**a**) *Epitaphios* dated 1437, Moldavia (inv. 15827_B182); (**b**) *Epitaphios* dated 1661–1662, Constantinople? (inv. 10718_B111); (**c**) *Epitaphios* dated 1679–1680, Wallachia (inv. 10683_B76); (**d**) *Epitaphios* dated 1752, Wien (inv. 15833_B188); (**e**) *Epitaphios* dated 19th century, Russian (inv. 10695_B88).

Figure 3. *Aër* dated ~1700, Greek? (inv. 10668_B61), worked in the Byzantine tradition, preserved in the National Museum of Art of Romania (MNAR).

2. Materials and Methods

2.1. Objects, Samples and Sampling Strategy

Twenty-four liturgical textiles were studied, all defined as *epitaphios* or *aër*. According to the technique, most of the objects (21/24) are embroideries in the Byzantine tradition, while two have the scene painted on a silk support (Figure 4), and in one other, it is represented in the Gobelin needlepoint technique. The textiles are dated between the 14th and the 19th century and are documented as Byzantine, Moldavian, Wallachian, Greek, Russian, of Viennese origin or from Constantinople (present-day Istanbul) (see Table 1). Fifty-seven samples were available for analysis. According to the sampling strategy, the specimens' withdrawal was limited to the degraded areas, as the objects reverse sides were not accessible because they were covered by linings. As a consequence, most of the samples (32/57) are from the textiles' supports, with samples being taken either from the main scene or from the frame, for all but four objects. For the other objects, samples are from embroidery threads (17/57) or from the original linings (8/57). One sample (1/57) comes from an ornamental silk cord frame. The present approach, which aims to document materials in the MNAR collection of liturgical textiles is very different compared with the previous ones performed in the same research group [2–5], where studies were correlated with restoration and more sampling areas were accessible.

Figure 4. *Epitaphios* dated 19th century, Greek (inv. 10869_Ț148), painted on silk support, preserved in the National Museum of Art of Romania (MNAR).

Table 1. Information about the liturgical textiles studied: inventory number, date, technique, brief description and workshop.

Object, Inventory Number	Date	Technique	Brief Description	Workshop
Epitaphios, inv. 15826_B181	1395–1396	embroidery	embroidery on blue satin support, frame with embroided inscription on blue support	Byzantine
Epitaphios, inv. 15827_B182	1437	embroidery	embroidery on red satin support, frame with embroided inscription on blue support	Moldavia
Epitaphios, inv. 15829_B184	1556	embroidery	embroidery on red satin support, frames with embroided inscription and decoration on red silk support	Moldavia
Epitaphios, inv. 15832_B187	1600–1601	embroidery	embroidery on red satin support, frame with embroided medalions on blue satin support	Russian
Epitaphios, inv. 11048_Ț327	1613	painting on silk support	painting on red satin support over a blue satin support, blue cotton lining (observed in the degraded areas), beige satin frame with traces of painting	Moldavia
Epitaphios, inv. 15830_B185	1628	embroidery	embroidery on dark green satin support, frame with embroided inscription on the same support, red lining	Moldavia
Epitaphios, inv. 15831_B186	1638	embroidery	embroidery on red satin support, two frames with embroided inscription and decoration respectively, both on green satin support, and a green velvet frame	Moldavia
Epitaphios, inv. 15845_B200	~1639	embroidery	embroidery on red satin support, frame with embroided decoration on the same red support; blue lining	Moldavia
Epitaphios, inv. 10718_B111	1661–1662	embroidery	embroidery and embroided frames on red satin support, embroided insriptions on green velvet frame (with interventions in some areas)	Constan-tinople?
Epitaphios, inv. 10683_B76	1679–1680	embroidery	embroidery on red satin support, frames with embroided inscription and medallions on the same support, green velvet frame	Wallachia
Epitaphios, inv. 16154_B288	1680–1681	embroidery	embroidery on red satin support, frames with embroided inscription and medallions on the same support, green velvet frame (not embroided); red satin lining	Wallachia
Aër, inv. 10668_B61	~1700	embroidery	embroidery on red—violet velvet, frame with embroided decoration on yellow satin applied on the velvet, pale blue cord frame	Greek?
Aër, inv. 10676_B69	end 17th c.	embroidery	embroidery on yellow satin support	Wallachia
Epitaphios, inv. 15835_B190	1751	embroidery	embroidery on brown satin support, frames with embroided medalions and inscription on the same support; yellow-green silk lining	Wallachia
Epitaphios, inv. 15833_B188	1752	embroidery	embroidery on green velvet support, decorative embroided frame on the same support	Wien
Epitaphios, inv. 15834_B189	1770	embroidery	embroidery and decorative embroided frame on velvet support	Wien

Table 1. *Cont.*

Object, Inventory Number	Date	Technique	Brief Description	Workshop
Epitaphios, inv. 10686_B79	1791	embroidery	embroidery on red velvet support, frames with embroided decoration, frame with tassels in the corners on the same velvet support; red lining (new?)	Wien
Epitaphios, inv. 15837_B192	end 18th c.	embroidery	embroidery on red satin support, frames with decoration and embroided inscription on the same red support and one more frame, everything mounted on a new blue satin support; red cotton intervention on the silk support	Moldavia?
Epitaphios, inv. 15836_B191	1823	embroidery	embroidery on pale blue support, frame with embroided inscription on pale blue support, red velvet decorated frame; fringes frame with tassels in the corners	Wien
Fragment of embroidery with "Lamentation", inv. 10673_B66	19th c.	embroidery	embroidery on satin support	Wien
Epitaphios, inv. 10695_B88	19th c.	embroidery	embroidery on red—violet velvet support, frames with inscription and decorations on the same support, yellow fringes frame	Russian
Epitaphios, inv. 10869_Ţ148	19th c.	painting on silk support	painting on red satin support centered to leave a (red satin) frame, yellow fringes frame	Greek
Epitaphios, inv. 11047_Ţ326	19th c.	gobelin needle-point technique	gobelin, frame with embroided inscription on ochre cotton support, yellow fringes frame	Romanian
Epitaphios, inv. 15825_B80	19th c.	embroidery and painting	painted central scene with embroided decorations on red—violet velvet support in the corners, frame with inscription on velvet support, yellow fringes frame	Russian

2.2. Sample Documentation and Preparation for Dye Analysis

Samples about 0.5–1 cm long were first observed under the digital microscope at ~50× magnification and non-destructively analysed by attenuated total reflectance infrared spectroscopy (FTIR-ATR) for fiber identification. Yarns of about 0.5 cm (~3 mg) were cut from the original samples, when larger specimens were available, and placed in Eppendorf vials for sample preparation.

Dyes were extracted from the yarns by acid hydrolysis. This was an assumed decision although the limits of this method, caused by the decomposition of glycosides to their parent aglycones, in the case of flavonoid dyes, were known [23–26]. The reason for choosing acid hydrolysis was the existing database, which contains information about natural dyes, used as standards or extracted from standard dyed yarns by acid hydrolysis. An amount of 200 µL of a mixture containing 37% HCl, CH_3OH and H_2O in a ratio of 2:1:1 ($v/v/v$) was added to each yarn, followed by incubation at 100 °C for 10 min. Samples were then evaporated to dryness in a vacuum desiccator. Each sample was re-dissolved in a 100 µL solution of CH_3OH/H_2O 1:1 (v/v) and centrifuged at 12,000 rpm for 10 min. The supernatants were transferred to chromatography vials and injected into the LC system. When the presence of indigo-based dyes was suspected, as in the cases of visually blue, green and black samples, a second extraction in 100 µL dimethyl sulfoxide (DMSO) was made, with the samples kept at 80 °C for 10 min. The two solutions were analysed separately.

2.3. Fiber Identification

Fiber documentation and image collection were made with a DinoLite digital microscope, model AM4113ZT. Further fiber investigation was made by infrared spectroscopy (FTIR-ATR), where a Bruker Optics Alpha spectrometer equipped with a Platinum ATR single reflection diamond ATR module was used. Spectra were acquired in the 4000–400 cm^{-1} domain, with a resolution of 4 cm^{-1}. Spectra collection and data processing were made with a dedicated software, Opus 7.0. Where FTIR indicated that cellulosic fibers were used, samples were also observed by optical microscopy for the clear identification of cotton.

2.4. Dye Analysis by Liquid Chromatography. Instrumentation and Parameters

All the samples were analysed by liquid chromatography with UV–Vis (diode array) detection (LC-DAD) on System 1. Some of the samples where carminic acid was identified were also examined on a similar configuration, further referred to as System 2, at the Royal Institute for Cultural Heritage (KIK/IRPA), in Brussels. These analyses were aimed at the attribution of the carminic acid-based insects down to the species level. More information about this will be given in Section 3.1., Supports, Red.

2.4.1. System 1 (LC-DAD)

An Agilent 1260 Infinity II series liquid chromatograph (Agilent Technology, USA) consisting of a quaternary pump (G7129A), a standard autosampler (G7111B), a column thermostat (G7116A) and a multi-channel diode array detector (G7115A) was used for dye analysis. OpenLAB CDS software was used for the chromatographic system control, data acquisition and processing. A Zorbax C18 column, of 150 mm length, 4.6 mm i.d. and 5 µm particle size, thermostated at 40 °C, was used. The mobile phase consisted of a mixture of aqueous 0.2% (*v*/*v*) formic acid (solvent A) and methanol/acetonitrile (1:1, *v*/*v* as solvent B). Gradient elution was applied by using the following profile: at 0 min, 15% solvent B; from min 0 to 5, linear increase to 25% solvent B; from min 5 to 10, constant at 55% solvent B; from min 10 to 16, linear increase to 100% solvent B; from min 16 to 18, constant at 100% solvent B; and step jump at 15% solvent B, with 5 min re-equilibration period between runs (post-time). The flow rate was set at 0.8 mL/min and the injected volume of the sample was 10 µL. The UV–Vis spectra were acquired in the range from 200 to 900 nm, with a simultaneous monitoring at five wavelengths (255, 275, 295, 420 and 490 nm), having a frequency of 0.03 min and a resolution of 2 nm.

2.4.2. System 2 (LC-DAD, with a Specific Method Constructed for Species Attribution of Carminic Acid-Based Insects)

High-performance liquid chromatography with diode array detection (DAD) was performed with an ACQUITY Arc HPLC system (Waters Chromatography n.v.), with a column heater/cooler and a quaternary solvent manager, a 2998 PDA with a low-dispersion flowcell detection system and Empower3 data handling software. The solvents used were (A) methanol (for HPLC > 99.8%), (B) a mixture of 1/9 (*v*/*v*) methanol/Milli-Q water and (C) 0.5% phosphoric acid (85 wt% p.a.). The analysis was performed at a flow rate of 1.2 mL/min with the following gradient: isocratic state 23A/67B/10C for 0–3 min, linear gradient to 90A/0B/10C between 3 and 29 min and isocratic 23A/67B/10C from 30 to 35 min. For the stationary phase, a temperature-controlled column of LiChrosorb RP-18 with a 125 mm x 4 mm diameter end cap with 5 µm particle size and 100 Å pore diameter was used. Calculation of the relative percentage of anthraquinone dyes was made after integration of the areas in the chromatograms registered at 255, 275, 290, 420 and 500 nm. More information regarding the methodology used is given below (see Section 3.1. Supports, Red) and an in-depth description of the method can be read in an earlier publication [31].

2.4.3. Dye Attribution—Databases

Dyes were attributed based on their retention and UV–Vis data, according to information collected on standards, dyes and dyed yarns. MS data were also considered for

identification when the samples were investigated by LC-DAD-MS. As described in previous publications [32,33], biological source attribution was based on data collected on yarns dyed in the laboratory, by following traditional dyeing recipes. Analytical data (retention and UV–Vis spectra) and the corresponding biological sources of the natural dyes discussed in the present study are given in Table 2.

Table 2. Dyes identified in the present study, their biological sources and identification criteria: retention and UV–Vis maximum.

Dye	Abb.	Biological Source Common and Latin Name(s)	Retention (min.)	UV-Vis Data (nm)
Alizarin	al	Madder (*Rubia tinctorum* L.) Synthetic alizarin (1869)	15.4	202; 248; 278; 430
Anthrapurpurin (1,2,7-trihydroxyanthraquinone)	anthra	Synthetic alizarin (1869)	13.6	274; 338; 428
Apigenin	ap	Dyer's broom (*Genista tinctoria* L.) Weld (*Reseda luteola* L.)	13.9	210; 268; 336
Dehydro-brazilein product (also called Type B)	bra'	Redwood based dye (*Caesalpinia* species, see text)	9.2	238; 260; 322; 384; 452
Carminic acid	ca	Carminic acid-based dye Mexican cochineal (*Dactylopius coccus* C.) Armenian carmine scale insect (*Porphyrophora hameli*) Polish carmine scale insect (*Porphyrophora polonica*) (see text)	8.5	226; 276; 310; 494
Chrysoeriol	chry	Weld (*Reseda luteola* L.)	14.2	206; 268; 348
Ellagic acid	ea	Tannins	10.3	254; 366
Flavopurpurin (1,2,6-trihydroxyanthraquinone)	flavo	Synthetic alizarin (1869)	13.8	272; 406
Genistein	ge	Dyer's broom (*Genista tinctoria* L.)	13.5	208; 260
Haematein derivative (also called Type H)	hae'	Logwood (*Haematoxylun campechianum* L.)	7.9	244; 276; 330; 456
Indigotin	ind	Indigo-based dye (see text) Woad (*Isatis tinctoria)* or Indigo (*Indigofera* sp.)	16.2	238; 285; 330; 610
Luteolin	lu	Dyer's broom (*Genista tinctoria* L.) Sawwort (*Serratula tinctoria* L.) Weld (*Reseda luteola* L.)	13.0	208; 254; 266; 348
Urolithin C	srw	Redwood based dye (*Caesalpinia* species, see text)	10.8	238; 306; 336

2.5. Elemental Analysis

In two cases, when the presence of iron needed to be confirmed, the samples were investigated by X-ray fluorescence spectrometry (XRF). Elemental analysis was performed with a portable XRF spectrometer Bruker S1 TITAN Model 600, with the following specifications: rhodium (Rh) tube, silicon drift chamber detector (SDD) and 5 mm spot size. The system used was air-path, with an elemental range Z > 12 (Mg). Energy was set at 40 keV.

3. Results

Results will be discussed according to the visual colours of the yarns (Table 3) and the function of the fibers (support, lining, embroidery thread (Table 4)) and will be correlated with similar data obtained in previous studies of liturgical embroideries in the Byzantine tradition, in Romanian collections and beyond.

Table 3. Samples (textile, colour and description of the type of thread), dyes identified and their biological sources. Objects are listed in chronological order. For more information regarding the objects, see Table 1.

Epitaphios, inv. 15826_B181 (1395–1396)						
1.	15826_P1	blue	silk	support, warp	ind	Indigo based dye
2.	15826_P2	blue	silk	support, weft	ind	indigo based dye
Epitaphios, inv. 15827_B182 (1437)						
3.	15827_P1	blue	silk	embroidery thread	ind	indigo based dye
4.	15827_P3	red	silk	embroidery thread	ca	carminic acid based dye
Epitaphios, inv. 15829_B184 (1556)						
5.	15829_P1	red	silk	support, warp	ca	carminic acid based dye
Epitaphios inv. 15832_B187 (1600–1601)						
6.	15832_P2	blue	silk	support (frame)	ind	indigo based dye
Epitaphios, inv. 11048_Ț327 (1613)						
7.	11048_P1	yellow	silk	red support, weft	urolithin C, ea	redwood based dye and tannins
8.	11048_P2	red	silk	red support, warp	ca	carminic acid based dye
9.	11048_P3	pale blue	silk	blue support, weft (frame)	ind	indigo based dye
10.	11048_P5	blue	cotton	lining, weft	ind	indigo based dye
Epitaphios, inv. 15830_B185 (1628)						
11.	15830_P1	brown-green	silk	support, weft	ind	Indigo based dye (in a dyeing combination with a yellow dye (under detection limit)
12.	15830_P2	red	silk	lining	ca	carminic acid based dye
13.	15830_P3	dark blue	silk	support, warp	ind	indigo based dye
Epitaphios, inv. 15831_B186 (1638)						
14.	15831_P1	red	silk	red support, warp	ca,	carminic acid based dye
15.	15831_P2	green	silk	green satin support, weft	lu, ge, ap, ind	dyer's broom and indigo based dye
Epitaphios, inv. 15845_B200 (~1639)						
16.	15845_P1	yellow	silk	support, weft	urolithin C	redwood based dye
17.	15845_P2	blue	silk	lining	ind	indigo based dye

Table 3. *Cont.*

Epitaphios, inv. 10718_B111 (1661–1662)						
18.	10718_P1	yellow	silk	red support, weft	urolithin C	redwood type
19.	10718_P2	red	silk	red support, warp	ca, ea	carminic acid based dye and tannins
Epitaphios from Cotroceni, inv. 10683_B76 (1679–1680)						
20.	10683_P1	yellow	silk	red support, weft	urolithin C	redwood based dye
21.	10683_P2	red	silk	red support, warp	ca	carminic acid based dye
Epitaphios from Tismana, inv. 16154_B288 (1680–1681)						
22.	16154_P2	yellow	silk	red support, weft	urolithin C	redwood based dye
23.	16154_P3	yellow	silk	lining, weft	urolithin C	redwood based dye
24.	16154_P4	red	silk	lining, warp	ca	carminic acid based dye
25.	16154_P5	green	silk	green velvet plush (frame)	lu, ge, ap, ind	dyer's broom and indigoid based dye
Aër, inv. 10668_B61 (~1700)						
26.	10668_P1	yellow-pink	silk	yellow satin support (frame)	urolithin C and bra' (type B)	redwood based dye
27.	10668_P3	pale blue	silk	blue cord	ind	indigo based dye
Aër, inv. 10676_B69 (end 17th c.)						
28.	10676_P1	yellow	silk	support	lu, ge, ap	dyer's broom
Epitaphios, inv. 15835_B190 (1751)						
29.	15835_P1	yellow-green	silk	embroidery thread (silk core in metallic thread)	lu, ge, ap	dyer's broom
30.	15835_P2	brown	silk	support, warp	ea	tannins
31.	15835_P3	yellow-green	silk	lining	lu, ap, chry	weld
Epitaphios, inv. 15833_B188 (1752)						
32.	15833_P1	green	silk	velvet	lu, ap, chry, ea ind	weld and tannins indigo based dye
33.	15833_P2	yellow	silk	embroidery thread (silk core in metallic thread)	lu, ge, ap	dyer's broom
Epitaphios, inv. 15834_B189 (1770)						
34.	15834_P1 galben	yellow	silk	embroidery thread (silk core in metallic thread)	lu, ge, ap,	dyer's broom
35.	15834_P2	red	silk	velvet, warp	Bra' (type B) urolithin C	redwood type
36.	15834_P3	red	silk	velvet, plush	urolithin C, bra' (type B)	redwood type
37.	15834_P5	green	silk	embroidery thread	lu, ge, ap, ind	dyer's broom and indigo based dye
38.	15834_P6	green	silk	embroidery thread	lu, ge, ap, ind	dyer's broom and indigo based dye

Table 3. *Cont.*

Epitaphios, inv. 10686_B79 (1791)						
39.	10686_P2	pale yellow	silk	embroidery thread (silk core in metallic thread)	lu, ge, ap	dyer's broom
40.	10686_P4	green	silk	embroidery thread	lu, ind	luteolin based dye and indigo based dye
41.	10686_P5	red	silk	velvet lining (new?)	ca, ea	carminic acid based dye and tannins KIK/ IRPA: Mexican Cochineal and tannins
Epitaphios, inv. 15837_B192 (end 18th c.)						
42.	15837_P2	red	silk	support (frame with inscription), warp	ca	carminic acid based dye
43.	15837_P3	red	cotton	support (new?) (central area)	al, anthra, flavo	synthetic alizarin (1869)
Epitaphios, inv. 15836_B191 (1823)						
44.	15836_P1	black	silk	embroidery thread (with metallic thread)	ea	tannins
45.	15836_P2	green	silk	embroidery thread	lu, ge, ap, ea	dyer's broom
46.	15836_P4	yellow-pink	silk	velvet, plush (support, frame)	urolithin C, bra' (type B)	redwood based dye
Fragment of embroidery with " Lamentation ", inv. 10673_B66 (19th c.)						
47.	10673_P1	green	silk	embroidery thread	lu, ge, ap	dyer's broom
Epitaphios, inv. 10695_B88 (19th c.)						
48.	10695_P1	red	silk	velvet, warp	ca, ea	carminic acid based dye and tannins KIK/ IRPA: Mexican Cochineal and tannins
49.	10695_P2	red	silk	velvet, plush	ca, ea	carminic acid based dye and tannins
50.	10695_P3	blue	cotton	lining, warp	Prussian Blue *	Prussian Blue * (1704)
Epitaphios, inv. 10869_Ţ148 (19th c.)						
51.	10869_P1	yellow	silk	support, weft	urolithin C	redwood based dye
52.	10869_P2	red	silk	support, warp	ca, ea	carminic acid based dye and tannins
Epitaphios, inv. 11047_Ţ326 (19th c.)						
53.	11047_P2	red	silk	embroidery thread	ca, ea	carminic acid based dye and tannins
54.	11047_P4	green	silk	embroidery thread	lu, ap, chry, ind	weld and indigo based dye

Table 3. *Cont.*

55.	11047_P5	pale violet	silk	embroidery thread	hae' (type H) bra' (type B) urolithin C	redwood based dye logwood based dye
56.	11047_P6	grey	silk	embroidery thread	ind	indigo based dye
Epitaphios, inv. 15825_B80 (19th c.)						
57.	15825_P1	red	silk	velvet	ca	carminic acid based dye

* Note: Prussian blue was revealed by FTIR-ATR (specific CN signal at 2083 cm^{-1}) and confirmed by the presence of Fe in the XRF spectrum.

Table 4. Objects (listed in chronological order) and summary of results, presented separately for the three fibre functions: support, lining, embroidery thread.

Object, Inventory Number/ Technique	Date	Workshop	Results		
			Support	Lining	Embroidery Threads
Epitaphios, inv. 15826_B181, embroidery	**1395–1396**	Byzantine	Indigo based dye (satin)		
Epitaphios, inv. 15827_B182, embroidery	**1437**	Moldavia			Indigo based dye Carminic acid dye
Epitaphios, inv. 15829_B184, embroidery	**1556**	Moldavia	Carminic acid based dye (satin)		
Epitaphios, inv. 15832_B187, embroidery	**1600–1601**	Russian	Indigo based dye blue (satin) (frame)		
Epitaphios, inv. 11048_Ţ327, painting on silk support	**1613**	Moldavia	Carminic acid based dye (satin) Indigo based dye (satin)	Indigo based dye (silk)	
Epitaphios, inv. 15830_B185, embroidery	**1628**	Moldavia	Indigo based dye (satin)	Carminic acid based dye (silk)	
Epitaphios, inv. 15831_B186, embroidery	**1638**	Moldavia	Carminic acid based dye (satin) Indigo based dye and dyer's broom (satin) (frame)		
Epitaphios, inv. 15845_B200, embroidery	**~1639**	Moldavia	Redwood based dye (weft) (satin)	Indigo based dye (silk)	
Epitaphios, inv. 10718_B111, embroidery	**1661–1662**	Constan-tinople?	Carminic acid based dye (satin)		
Epitaphios, inv. 10683_B76, embroidery	**1679–1680**	Wallachia	Carminic acid based dye (satin)		
Epitaphios, inv. 16154_B288, embroidery	**1680–1681**	Wallachia	Redwood based dye (weft) (satin) Indigo based dye and dyers broom (satin) (frame)	Carminic acid based dye (silk)	
Aër, inv. 10668_B61, embroidery	**~1700**	Greek?	redwood based dye (satin) (frame) Indigo based dye blue cord		
Aër, inv. 10676_B69, embroidery	**end 17th c.**	Wallachia	dyers broom (satin)		

Table 4. *Cont.*

Object, Inventory Number/ Technique	Date	Workshop	Results		
			Support	Lining	Embroidery Threads
Epitaphios, inv. 15835_B190, embroidery	**1751**	Wallachia	tannins (satin)	weld (silk)	dyers broom
Epitaphios, inv. 15833_B188, embroidery	**1752**	Wien	Indigo based dye (velvet)		dyers broom
Epitaphios, inv. 15834_B189, embroidery	**1770**	Wien	redwood type (velvet)		dyers broom dyers broom and indigo based dyers broom and indigo based
Epitaphios, inv. 10686_B79, embroidery	**1791**	Wien		Mexican cochineal silk and tannins (silk)	dyers broom luteolin based dye and indigo based
Epitaphios, inv. 15837_B192, embroidery	**end 18th c.**	Moldavia?	Carminic acid based dye (satin) Synthetic alizarin support central area (intervention)		
Epitaphios, inv. 15836_B191, embroidery	**1823**	Wien	Redwood based (velvet)		tannins dyers broom
Fragment of embroidery "Lamentation", inv. 10673_B66, embroidery	**19th c.**	Wien			dyers broom
Epitaphios, inv. 10695_B88, embroidery	**19th c.**	Russian	Carminic acid based dye (velvet)	Prussian blue (cotton)	
Epitaphios, inv. 10869_Ț148, painting on silk support	**19th c.**	Greek	Carminic acid based dye red		
Epitaphios, inv. 11047_Ț326, gobelin	**19th c.**	Romanian			Carminic acid based and tannins weld and indigo based Redwood based and logwood based dyes indigo based
Epitaphios, inv. 15825_B80, embroidery and painting	**19th c.**	Russian	Carminic acid based dye red (velvet) (frame)		

3.1. Supports

In total, 32 samples from the supports in 20 liturgical textiles were available, which means they were from all but four of the textiles under discussion. In the present publication, the term "support" is used in a larger sense to include un-embroidered frames.

3.1.1. Red

Due to the high liturgical symbolism, red is the most common support in Christian Medieval Europe, regardless of the production area. About half of the supports in the *epitaphioi* and aëres studied (14/20) are red and the material was characterized as satin in most cases (10/14) and velvet in the remaining cases (4/14). With reference to textiles in the present study, red satin support corresponds to liturgical textiles worked in the Byz-antine technique dated from 1556 to the end of the 18th century and red velvet supports are correlated with similar objects from 1770 to the 19th century. This perfectly aligns with the scientific literature which states that in the embroideries of Byzantine tradition, satin supports are replaced by velvet starting from the 16th–17th centuries [8]. Red satin was also used as the support in two painted *epitaphioi*, dated 1613 and the 19th century, respectively. The poor conservation status of *epitaphios* inv. 11048 (dated 1613, painted), enabled a detailed investigation of the support. Microscopic observation of both sides of the red satin

revealed that it was woven with a red warp and a yellow, or more correctly yellow-pink, weft (Figure 5). Carminic acid was the main dye component identified for the red warp, according to retention and the UV–Vis spectrum (λmax = 226; 276; 310; 494 nm). Carminic acid is the main dye component in several species of insects, with *Porphyrophora* species from the Old World and *Dactylopius coccus* (Mexican cochineal) from the New World as the main representatives. Identification down to the species level is sometimes possible based on the calculation of the relative amount between the minor compounds, dcII (the 2-C-glucoside of flavokermesic acid), kermesic and flavokermesic acids, with re-ference to carminic acid [34–37]. For the seven samples in this study where carminic acid was identified in red satin warps, no minor components were detected, which made any precise attribution of the species impossible.

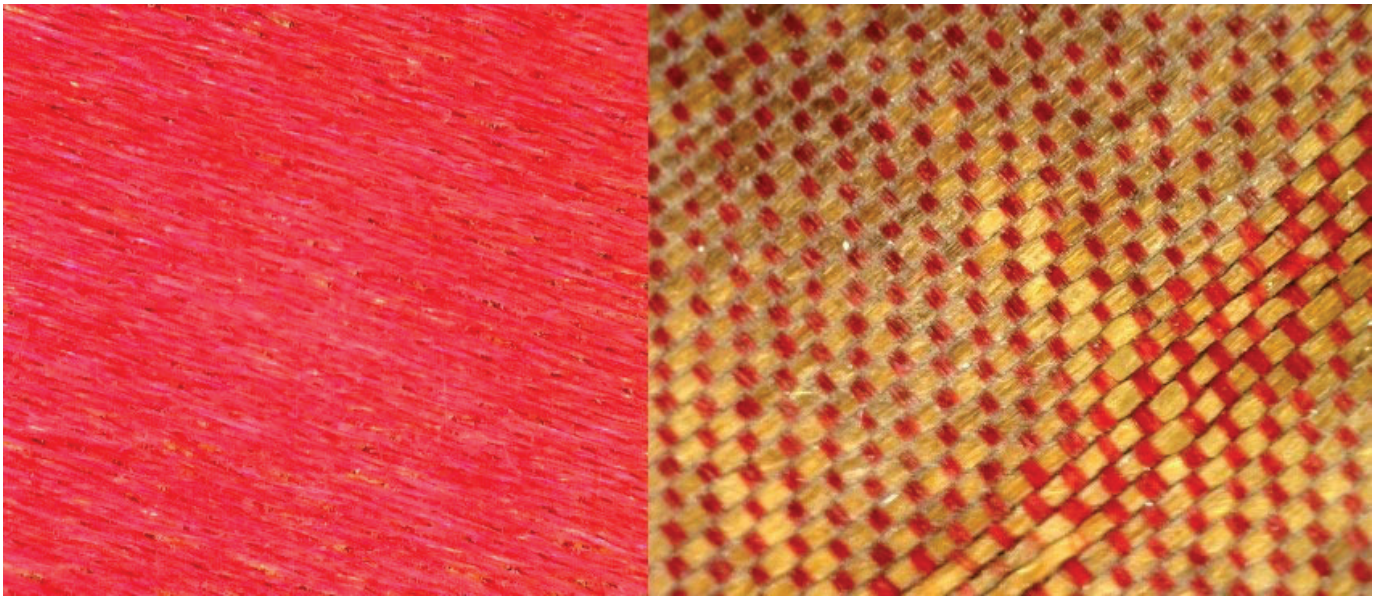


Figure 5. Image (~50x) to illustrate the weaving structure in the red satin support in *Epitaphios* inv. 11048. (**Left**) Front side where only the red warp dyed with carminic acid-based dye is visible. (**Right**) Back side where both the red warp and the redwood dyed yellow weft could be observed.

Urolithin C, whose structure was only recently elucidated [38], was identified in the corresponding yellow-pink wefts, as well as in wefts from satin supports where no sample was available from the warp (inv. 15845). Its presence was revealed by retention and the UV–Vis spectrum (λmax = 238; 306; 336 nm) and suggests a soluble redwood species was used for dyeing. The above-mentioned dye component, also called "srw" or "type C" [39,40], was considered by the dye expert community as representative of the recognition of the soluble redwood dyeings for many years before its structure was decoded. Soluble redwoods contain brazilin as the main dye component, which oxidizes to brazilein, and transforms through acid hydrolysis to a brazilein derivative, coded "bra' (bra prime)" or "type B" (λmax = 238; 260; 322; 384; 452 nm) [38], characterized as a dehydro-brazilein product [17]. Analysis performed on historical objects may not reveal the brazilein deri-vative due to its severe degradation, and attributions of redwood dyeings are in many cases based on the detection of urolithin C, thus a marker compound, which remains vis-ible in historical samples, even if the dehydro-brazilein product is gone [40]. It should be supposed that the original colour of the yellow-pink redwood dyed yarns was red.

In contrast to the samples discussed above when only urolithin C was present in yellow or yellow-pink yarns, in others described as red, the brazilein derivative bra' (also called type B) was detected. These samples come from the warp and plush in velvet supports in *epitaphios* inv. 15834 (dated 1770). Brazilein derivative was also evidenced together with

urolithin C in a yellow-pink sample from the satin in *epitaphios* inv. 10668 (dated ~1700) and from the velvet plush in *epitaphios* inv. 15836 (dated 1823). Figure 6 illustrates the difference in the analytical results of redwood dyed red and yellow yarns. While urolithin C (238; 306; 336 nm) is present in both cases, detection of the dehydro-brazilein product (bra') (238; 260; 322; 384; 452) is associated with the red colour of the sample.

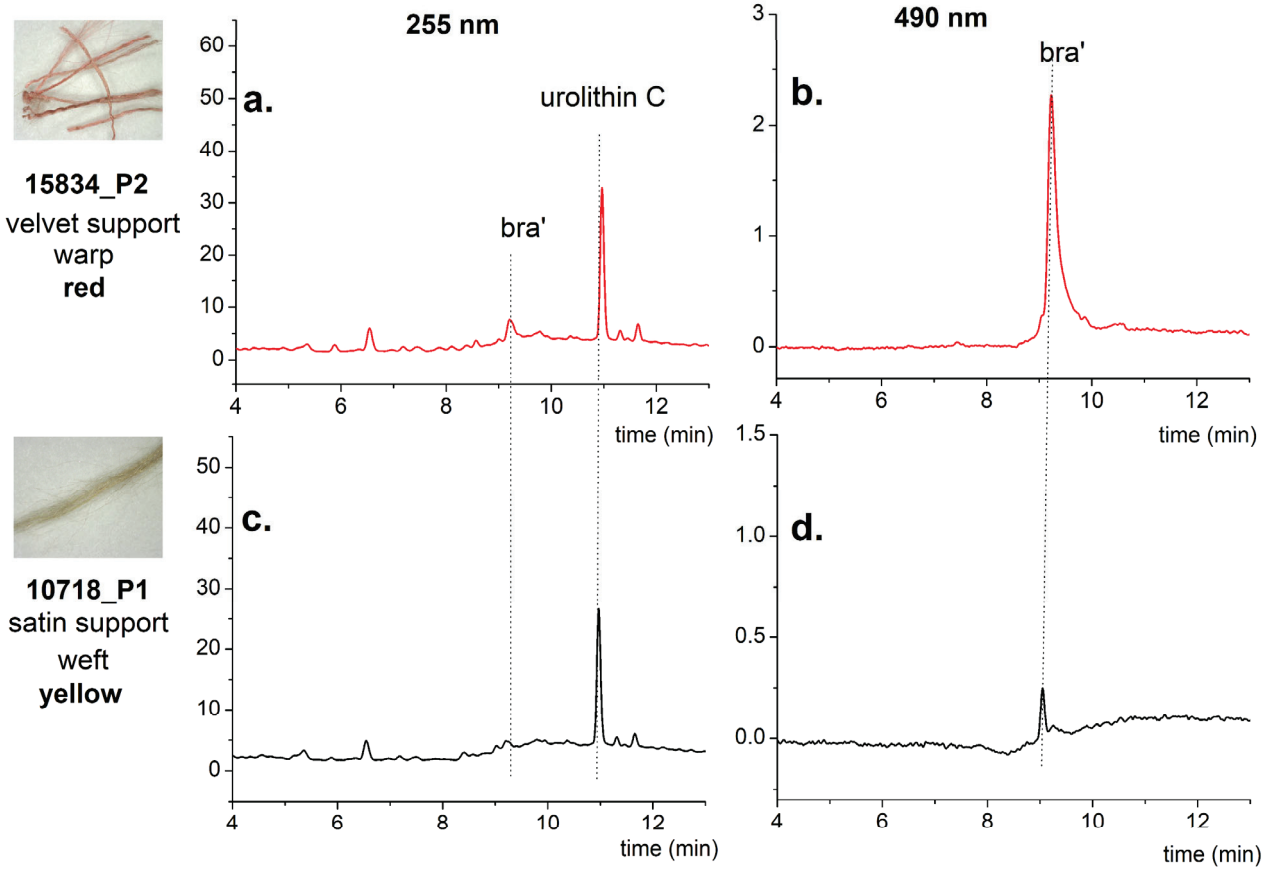


Figure 6. Comparative chromatograms of samples 15834_P2 (velvet support, warp), red ((**a**,**b**) top images) and 10718_P1 (satin support, weft) yellow ((**c**,**d**) bottom images). While in both samples urolithin C (238; 306; 336 nm) is present, detection of the dehydro-brazilein product (bra') (238; 260; 322; 384; 452) in 15834_P2 should be associated with the red colour of the sample. Details of the region between 4 and 13 min. Left: 255 nm; right: 490 nm.

Three samples from red velvet supports in two 19th century *epitaphioi* were available, and carminic acid was identified in all cases, for warp and plush (10695_P1 and P2; 15825_P1). Analysis performed on sample 10695_P1 (warp) at the Royal Institute for Cultural Heritage in Brussels (KIK/IRPA), where a procedure to discriminate between the carminic acid insect dyes was set up [37], revealed the presence of minor components dcII (the 2-C-glucoside of flavokermesic acid), and kermesic and flavokermesic acids. Furthermore, based on calculation of the ratio between the amounts of flavokermesic acid C glycoside and the total percentage of flavokermesic and kermesic acids, relative to carminic acid, it was proved that *Dactylopius coccus* (Mexican cochineal) was used for dyeing (Figure 7). More details regarding the procedure used was given in an earlier publication [37].

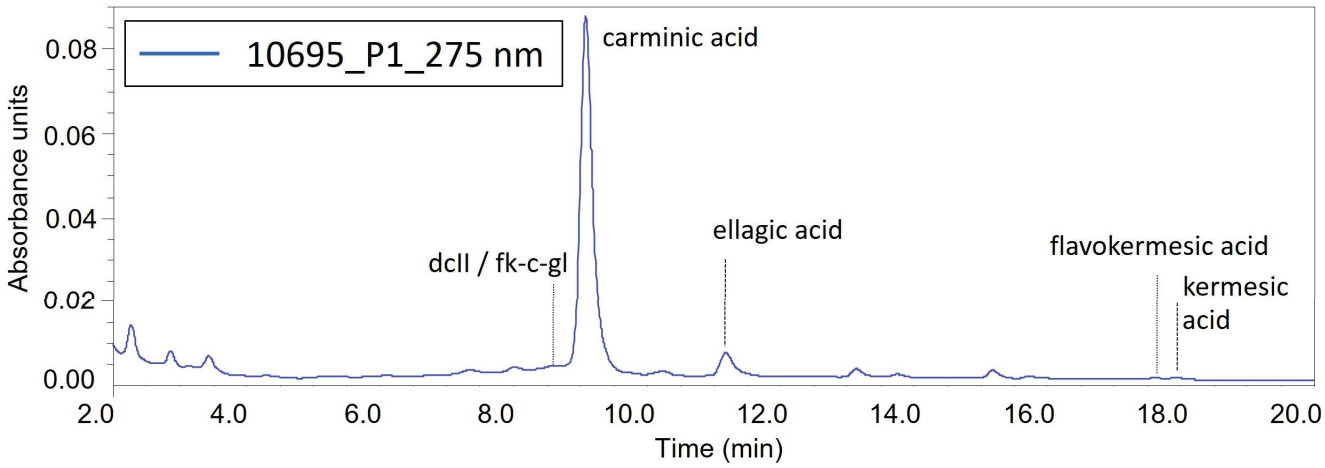


Figure 7. Chromatogram (registered at 275 nm) to support identification of Mexican cochineal in sample 10695_P1 based on the detection of carminic acid and the minor components dcII (flavokermesic acid C glycoside), flavokermesic and kermesic acids.

As already mentioned, red satin was the most common support for *epitaphioi* worked in the Byzantine tradition. In the present study, it was observed in embroidered liturgical textiles dated from the 15th to the 18th century, from various workshops: Moldavian, Wallachian, Russian and from Constantinople as well as in painted *epitaphios* from Moldavian (17th century) and Greek workshops (19th century). In previous studies which referred to Byzantine liturgical embroideries from the Romanian provinces Moldavia and Wallachia, the combination of lac dye and madder was revealed for the weft in the 15th and the 16th century satin supports, while the preference for carminic acid-based dyes was observed from the late 16th century onwards. The small amounts of samples in the present approach made any attribution down to the species level impossible. However, it may be supposed that Mexican cochineal was used in these textiles, as it has been described as having replaced all the other insect dyes in European textiles from about 1570 [36]. This hypothesis is also supported by analysis performed on the support (warp) in a Byzantine liturgical embroidery preserved in Putna Monastery, dated to the late 16th century, where Mexican cochineal was identified in the presence of tannins [3].

One sample, visually red in colour, was available from the central area of *epitaphios* inv. 15837 (dated end 18th century), from a zone which according to visual and microscopic observations represents a later intervention. Analysis performed on the cotton red yarn evidenced the presence of alizarin (λmax = 202; 248; 278; 430 nm), anthrapurpurin (1,2,7-trihydroxyanthraquinone) (λmax = 274; 338; 428) and flavopurpurin (1,2,6-trihydroxyanthraquinone) (λmax = 272; 406), which suggests the use of synthetic alizarin. As the synthetic dye became available only in 1869, it becomes clear that the *epitaphios* was repaired and the intervention took place after the date mentioned.

3.1.2. Blue and Green

Samples were available from five blue or green silk satin and velvet supports, including frames in the respective colours. As in the case of red, satin was observed in objects dated from 1395-96 to 1638 and velvet in those dated later, more exactly, 1680 and 1752. For the blue satin supports, when samples from both weft and warp were analysed, indigotin was identified in both, as, for example, in *epitaphios* inv. 15826 from Cozia Monastery (dated 1395-96). Indigotin was detected based on retention associated with the UV–Vis spectrum (λmax = 238; 285; 330; 610 nm) and suggests that indigo-based dyes were used for dyeing. There are several species of plants which contain precursors of indigotin. *Isatis tinctoria* (woad), which was cultivated in Europe for a long time, and *Indigofera* species (indigo), which have a long history of use in Europe [10], would be the most probable candidates. However, with the analytical instrumentation and existing knowledge, it is not possible

to distinguish between the various indigo-containing plants, nor between natural and synthetic indigo [41,42]. From the theoretical perspective, both woad and indigo could have been used.

When embroidery satin supports with green hues were intended, a combination of indigo-based and yellow flavonoid dyes was used for the weft, as for *epitaphios* inv. 15831 (dated 1638). Luteolin, genistein and apigenin were evidenced based on retention and UV-Vis spectra (λmax = 208; 254; 266; 348 nm, λmax = 208; 260 nm and λmax = 210; 268; 336 nm) in the acid hydrolysed extract of 15831_P2, and indigotin in the di-methyl-sulfoxide extracted solution, which suggests that *Genista tinctoria* (dyer's broom) was used for dyeing. The same biological source was evidenced in the green velvet frame and pile threads (plush) in *epitaphios* inv. 16154 (dated 1680–1681). The yellow dye source was combined with indigo dyes to achieve green. For the green velvet support in *epitaphios* inv. 15833 (dated 1752), luteolin and apigenin were identified in the presence of chrysoeriol (λmax = 206; 268; 348 nm), which suggests the use of *Reseda luteola* (weld) (Figure 8).

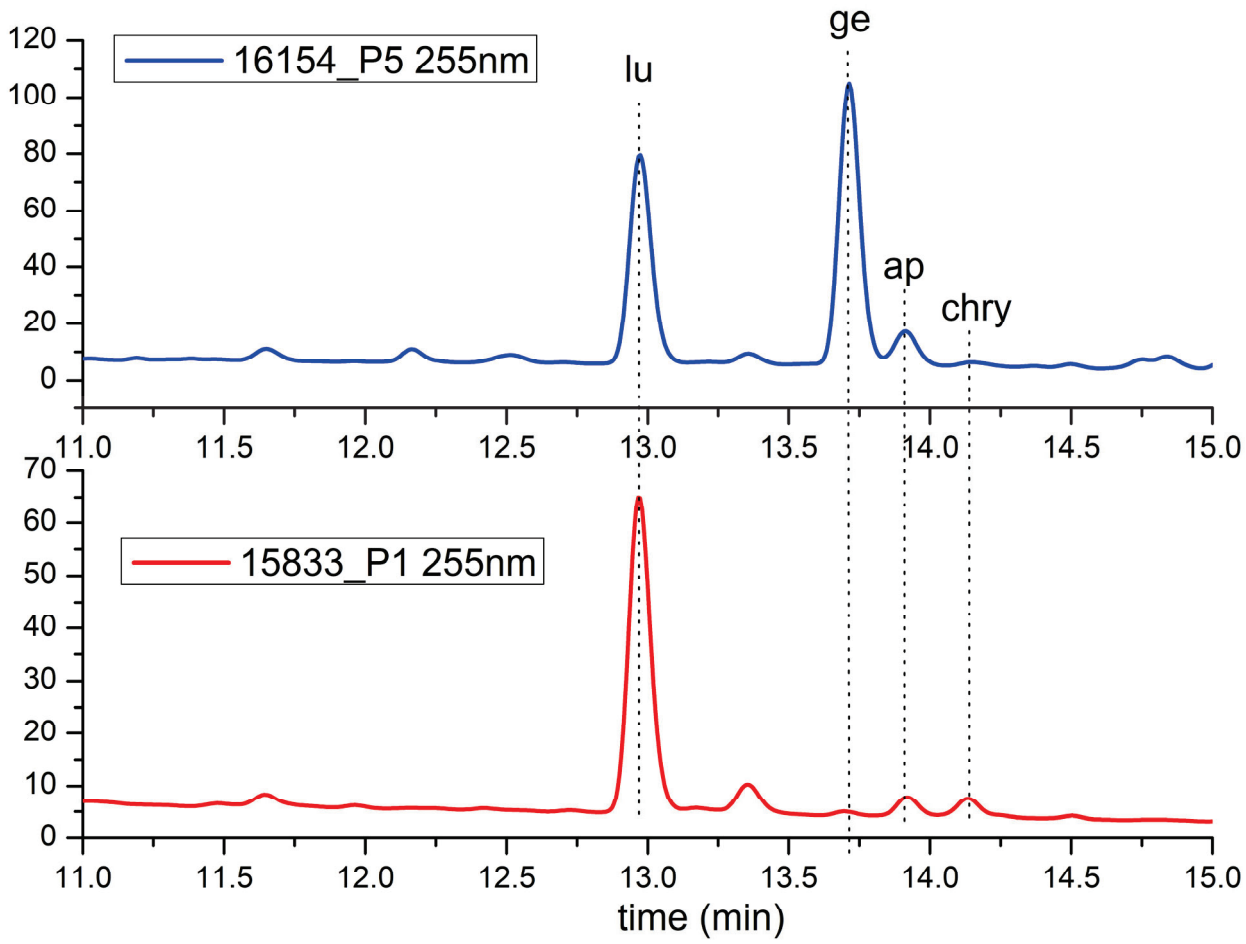


Figure 8. Comparative chromatograms (registered at 255 nm) of samples 16154_P5 (velvet plush) and 15833_P1 (velvet) to suggest identification of dyer's broom (luteolin, genistein, apigenin) and weld (luteolin, apigenin, chrysoeriol). Detail from 11 to 15 min.

3.1.3. Yellow

The three dyes representative of dyer's broom were identified in a yellow satin support used as a decorative frame in *aër* inv. 10676 (dated to the 17th century), the only support in this colour in the actual group of objects.

3.1.4. Brown

A brown silk sample from the warp in the embroidery satin support in *epitaphios* inv. 15835, dated 1751, was selected for analysis. The presence of ellagic acid (λmax = 254; 366 nm) suggested that tannins were used for dyeing. Tannins are substances of vegetal origin, very common in the plant world, which give a brown-black hue in the presence of iron salts. The use of iron was confirmed by elemental analysis performed non-destructively by XRF (see Section 2.5.). Although very colourfast dyes are produced by tannin dyeing in the presence of iron, the mordant gradually corrodes and degrades the fibers [10]. This process was also observed for *epitaphios* inv. 15835.

3.2. Linings

Eight samples from linings in seven objects were available for analysis, with all but two characterized as silk.

3.2.1. Red

Carminic acid was detected in the red satin in two linings, from *epitaphios* inv. 15830 (dated 1628) and inv. 16154 (dated 1680–1681) (weft), as well as in the red velvet in *epitaphios* inv. 10686 (dated 1791). Analysis performed on the latter, at the Royal Institute for Cultural Heritage in Brussels, evidenced the presence of minor components dcII (the 2-C-glucoside of flavokermesic acid), and kermesic and flavokermesic acids, and proved that Mexican cochineal was used for dyeing.

Urolithin C was identified in a yellow silk sample from the weft in the lining of *epitaphios* inv. 16154 (dated 1680–1681), which suggests the use of soluble redwood. As carminic acid-based dyes were identified for the warp (see text above) in the same weaving, it is clear that the satin lining is similar to that used in the red embroidery supports discussed in Section 3.1. Furthermore, it should be noted that the satin lining is similar to the support in *epitaphios* inv. 10683, documented in the museum archives as donated by the same prince to a different monastery, and dated 1679–1680.

3.2.2. Blue

Indigo-based dyes were detected in a blue silk lining in *epitaphios* inv. 15845 (dated ~ 1639). As explained earlier, when blue embroidery supports were discussed, either woad or indigo could have been used for dyeing.

Two samples from blue cotton linings were available for analysis. Indigo-based dyes were detected in the painted *epitaphios* inv. 11048 (dated 1613) and the Prussian blue pigment in *epitaphios* inv. 10695 (dated 19th century). Prussian blue was identified based on the specific carbon–nitrogen bond at 2083 cm^{-1} in the attenuated total reflectance infrared spectroscopy (FTIR-ATR) and confirmed by the detection of iron in the elemental analysis by X-ray fluorescence spectrometry (XRF) (Figure 9). Prussian Blue, a pigment with the chemical formula $Fe_4[Fe(CN)_6]_3$, was discovered in the early 18th century; although mainly used as pigment, it became a popular alternative to indigo in textile dyeing in the 18th and 19th centuries [43]. With reference to textiles in Romanian collections, this statement was proved by its identification, in dyeing combinations with Mexican cochineal or yellow dye sources, in black wool threads used in the decoration of 19th century traditional shirts or sheepskin coats from Sibiu, Transylvania [44,45].

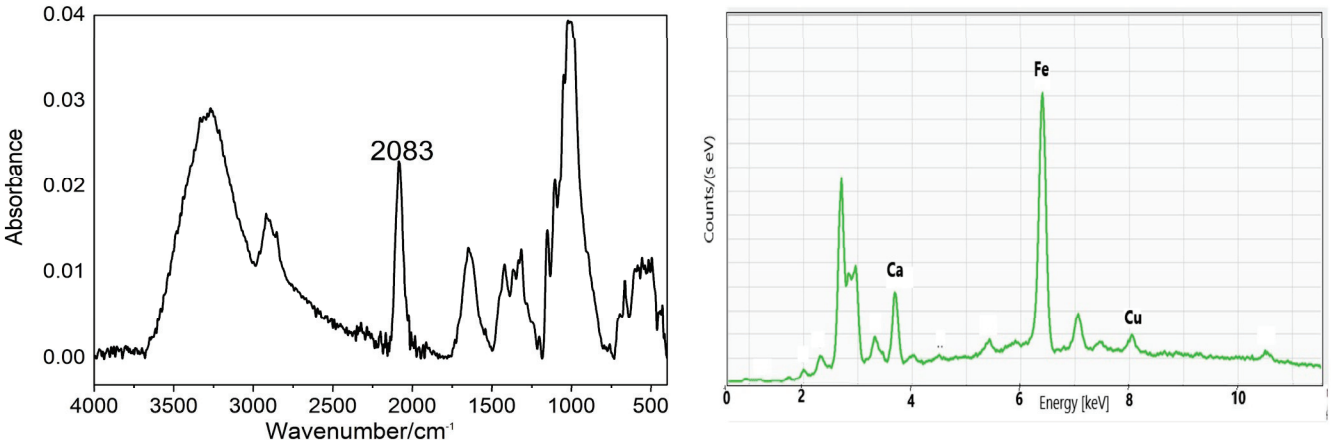


Figure 9. Image to support identification of Prussian Blue ($Fe_4[Fe(CN)_6]_3$) on cotton, in *Epitaphios* inv. 10695 (19th century). (**Left**) FTIR-ATR image where the specific carbon–nitrogen bond at 2083 cm^{-1} could be observed. (**Right**) XRF image where the presence of iron is confirmed.

3.2.3. Yellow

For the only yellow-green silk lining in *epitaphios* inv. 15835 (dated 1751), luteolin, apigenin and chrysoeriol were identified, which suggests the use of weld.

3.3. Embroidery Threads

Sixteen samples of embroidery threads were available from eight *epitaphioi*, one dated 1437 and the others from the 18th and 19th century.

3.3.1. Red and Violet

Two red samples representing embroidery threads in two different *epitaphioi* were studied. Carminic acid-based dyes were detected in both cases, the first dated 1437 (*epitaphios* inv. 15827) and the other 19th century (*epitaphios* inv. 15825). In none of the cases was it possible to establish the species of the insect used. However, it may be supposed that for the object dated 1437, a date which is before the arrival of the Mexican insects in Europe, either the Armenian or the Polish carmine scale insects were used.

In one case only were the dye components in redwood (urolithin C and brazilein derivative) and the hematein derivative coded hae' (also called Type H) detected. For the latter, identification was made based on retention time and UV–Vis data (λmax = 244; 276; 330; 456 nm), which were compared with information available in the literature [17,46]. The compounds were evidenced in a visually pale violet embroidery thread from the only *epitaphios* in the present study, which is worked in the Gobelin needlepoint technique (inv. 11047, dated 19th century). Logwood was identified in previous studies in liturgical embroideries in the Byzantine tradition from Romanian collections, dated to the 18th and 19th centuries [47], as well as in similar 19th century textiles preserved at the Holy Mount Athos [17]. In some of these detections, logwood was also determined in dyeing combination with redwood type. The identification of logwood in 18th and 19th century European textiles is not surprising considering that the biological source is native from South America [10].

3.3.2. Blue, Green and Yellow

Indigo-based dyes were identified in five cases, twice in blue and three times in green samples. In all the cases when a green hue was intended, indigoid dyes were detected together with dyer's broom. The flavonoid dye source was also responsible for the colour in four embroidery threads with a yellow colour. When these samples represented silk core in metallic threads, the objects were all dated to the 18th century, more specifically, between

1751 and 1791. While the earliest of these objects, *epitaphios* inv. 15835, is from Wallachia, all the others are attributed, for stylistic reasons, to Viennese workshops.

4. Discussion and Chronology

Carminic acid-based dyes represent the most frequent source of red. They were identified in the warp, which gives the colour, in the red satin, in objects dated from 1556 to the end of the 18th century. Satin was used as a support for embroidery or painting, and as a lining. Carminic acid was also detected in velvet supports in 19th century *epitaphioi* and in a red velvet lining in an embroidery dated 1791. Carminic acid-based dyes were also the source of red in embroidery threads in *epitaphioi* which are dated 1437, and from the 18th and 19th centuries. In just two cases, both from velvets, one used as a support in a 19th century *epitaphios* and the other the lining of an embroidery dated 1791, was it possible to establish that Mexican cochineal was used as a dye source (see Section 3.1. Supports, Red and Section 3.2. Lining, Red). In the case of the latter, the identification of Mexican cochineal indicates that it is more likely that the velvet is the original lining and not a later addition, as suggested by visual observations.

The identification of expensive insect dyes in the liturgical objects perfectly corresponds to the high value of the objects. The hypotheses stated earlier, about the use of Mexican cochineal in the red satin supports (Section 3.1. Supports, Red) in objects dated after ~1570, could be extended for the velvet, for linings and embroidery threads. The two successful identifications of Mexican cochineal tend to support these hypotheses. Moreover, the Mexican insect was also attested in previous studies on liturgical embroideries in Romanian collections [4,47]. The insect was also recognized in similar liturgical objects worked in the Byzantine tradition, from the same period, conserved in monasteries of the Holy Mount Athos [17]. As Mexican cochineal was a frequently used dye source, available everywhere in Europe, it becomes impossible to draw any conclusions regarding the origin of the materials in the *epitaphioi* studied.

Redwood dyes, known for their poor lightfastness, were detected in the (invisible) warps of the satin used in the *epitaphioi* supports and linings, as well as in velvets. The colour of the threads varies from yellow-pink to red, depending on the amount of dehydrobrazilein product present, and a perfect correlation was observed between the colour of the thread and the relative amounts of the two components in the chromatograms. While most of the detections are in the materials used as supports, redwood dyes were also identified, in a dyeing combination with logwood, in a pale violet embroidery thread in the 19th century *epitaphios* worked in the Gobelin needlepoint technique. The presence of logwood explains the violet colour of the fiber. Redwood and logwood dyes were also present in similar liturgical objects from the Holy Mount Athos, but in the cited work, no mention regarding the function of the samples was given [17].

Indigo-based dyes were identified in the blue satin embroidery supports, in silk and cotton linings and in embroidery threads. They were also present in green satin and velvet supports and in embroidery threads, where they were used together with weld and dyer's broom. Either woad or indigo could have been used as dye sources. Indigo-based dyes were also present in liturgical objects from the Holy Mount Athos [17] and were the main source of blue on protein and cellulosic fibers in all the categories of textiles in Europe.

Prussian Blue, a pigment which was introduced in the early 1700s, was identified in a blue cotton lining in a 19th century *epitaphios* attributed as Russian. It was never identified in liturgical textiles from Romanian collections before, nor in similar objects from other regions within the Orthodox space, to the best of our knowledge. However, as already mentioned in Section 3.2. Linings, Blue, it was evidenced in 19th to 20th century traditional textiles from Romanian collections [44].

Weld and dyer's broom are the two flavonoid dye sources identified in the present study. Weld was present in three cases only, in a silk satin lining and in a velvet support—both in *epitaphioi* dated to the 18th century, of Wallachian and Viennese origin, respectively, and in a green embroidery thread in a 19th century *epitaphios* worked in the Gobelin

needlepoint technique. Dyer's broom was the most frequently used source of yellow in the present study. It was identified in the satin and velvet supports, one time each in 17th century *epitaphioi* from Moldavia and Wallachia, and in embroidery threads in a large number of objects, also from the 17th century onwards. It was also present in an embroidery from Wallachia and in several samples in *epitaphioi* of Viennese origin, mostly as an individual dye source but also in combination with indigo-based dyes. The two yellow dye sources were also detected in liturgical embroideries in Romanian collections previously studied, as well as in similar objects preserved in monasteries from the Holy Mount Athos [17]. It should be noted that in the above-mentioned studies, another flavonoid-based source of yellow, young fustic, was also equally detected as a dye source in textiles dated between the 16th and the 20th centuries. Other yellow dye sources were also detected in liturgical textiles from Romanian collections [4].

Tannins may be used as dye sources, either to achieve black in the presence of iron salts [11], or for ochre yellow when combined with alum. They may also be used for silk weighting, a treatment applied to degummed silk in order to increase its weight. In the present study, tannins were used as a dye, in the presence of iron salts, in a brown velvet support and an embroidery thread in the same colour. The first detection was in a Wallachian *epitaphios*, dated 1752, while the latter was in a liturgical textile, dated 1823, of Viennese origin. The use of tannins in liturgical embroideries was also evidenced in previous studies, both for textiles in Romanian collections and from the Holy Mount Athos [2–4,6,17].

Chronology on the use of dyes in liturgical embroideries worked in the Byzantine tradition

The results of the present study, where most of the objects were dated from the 17th to the 19th centuries, are complementary with previous information achieved in the same research group for liturgical embroideries in Romanian collections, mainly dated to the 15th and 16th centuries [2–6]. Table 5 presents an overview of the dyes detected for each of the fibers and their function discussed in the present study: supports (satin and velvet), lining and embroidery threads.

Red is the main colour for supports, and lac dye, madder, Polish carmine and kermes were used in the 15th and 16th centuries, while carminic acid-based dyes (sometimes identified as Mexican cochineal) came from the 16th century onwards. As far as the American insect is concerned, the earliest date of use may be around 1570. It should be noted that the above-mentioned sources are used for the visible warp, while redwood dyes are mainly used for the wefts. Velvets are used as embroidery supports after the 18th century, and red is always achieved with carminic acid insect dyes. Earlier velvets dyed with lac dye and madder (or yellow and blue sources dyer's broom and indigo-based dyes) were also observed in liturgical embroideries but they were not really used as supports, but as frames or base for embroidered inscriptions on satin. Blue is the second most frequently used colour for supports after red, and it is always based on indigo dyes. Yellow and brown satin supports are less common and they are dyed with dyer's broom, safflower yellow (occasionally) and, rarely, tannins. Redwood velvet supports were also observed from the 18th century onwards (Table 5a).

The earliest surviving linings date from the 16th century, and are mainly in blue, silk or cotton, dyed with indigo. Red, yellow and green linings, dated from the 17th century onwards, were also preserved and the same dye sources discussed for the supports were observed. Weld was also detected in yellow 18th century satin linings, while a Prussian blue cotton one was noticed in a 19th century embroidery (Table 5b).

A larger palette of colour sources, as compared with supports and linings, was observed for the embroidery threads. Madder, lac dye, redwood, carminic acid-based (*Porhyrophora* species) and safflower were used for red in the 15th century, while carminic acid-based dye (probably Mexican cochineal) remains the only choice from the 17th century onwards. Several yellow dye sources, which were not detected in the present study, were revealed with different frequencies for yellow and green embroidery threads: young fustic,

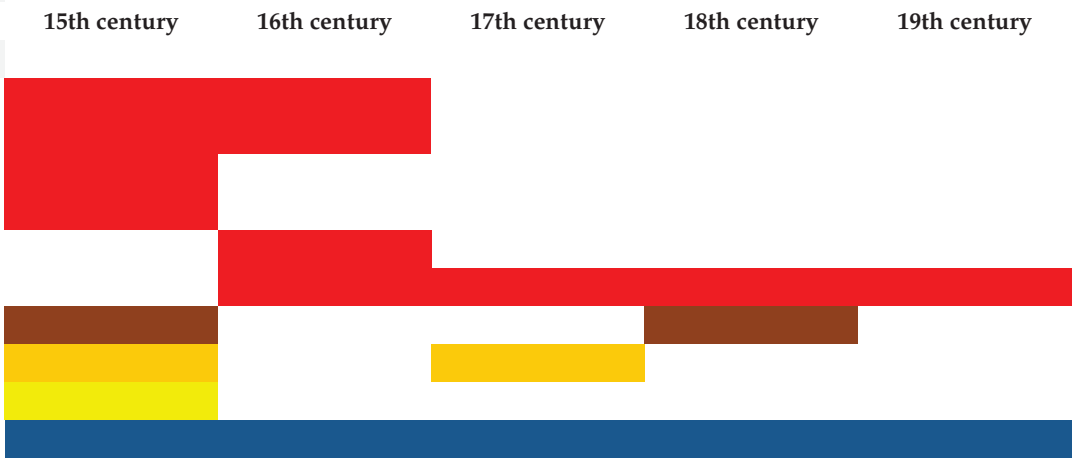
bastard hemp, emodin-based dyes and berries. Indigo-based dyes were used for blue and green embroidery threads (Table 5c).

Table 5. Chronology on the use of dyes in liturgical embroideries worked in Byzantine tradition: (**a**) supports (satin and velvet); (**b**) lining; (**a**,**c**) embroidery threads.

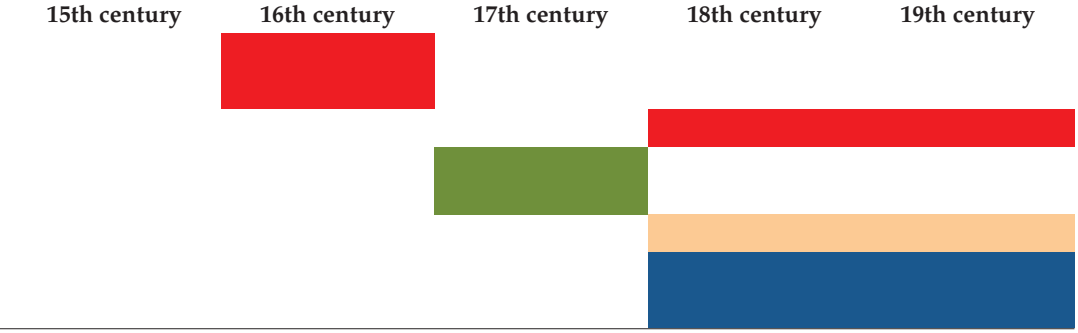
a.

SUPPORTS

SATIN



VELVET



b.

LINING

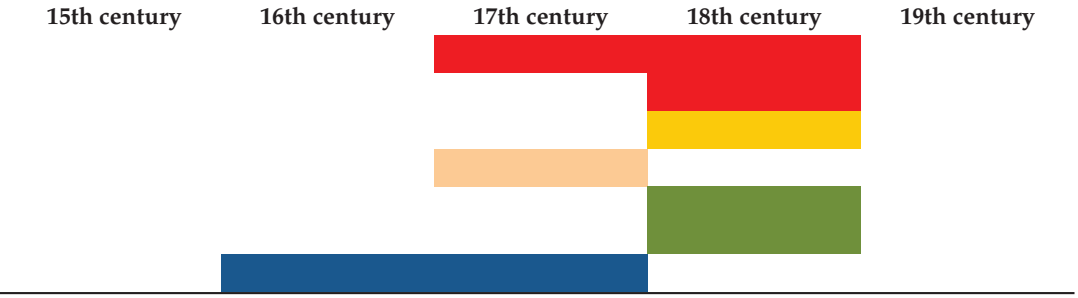
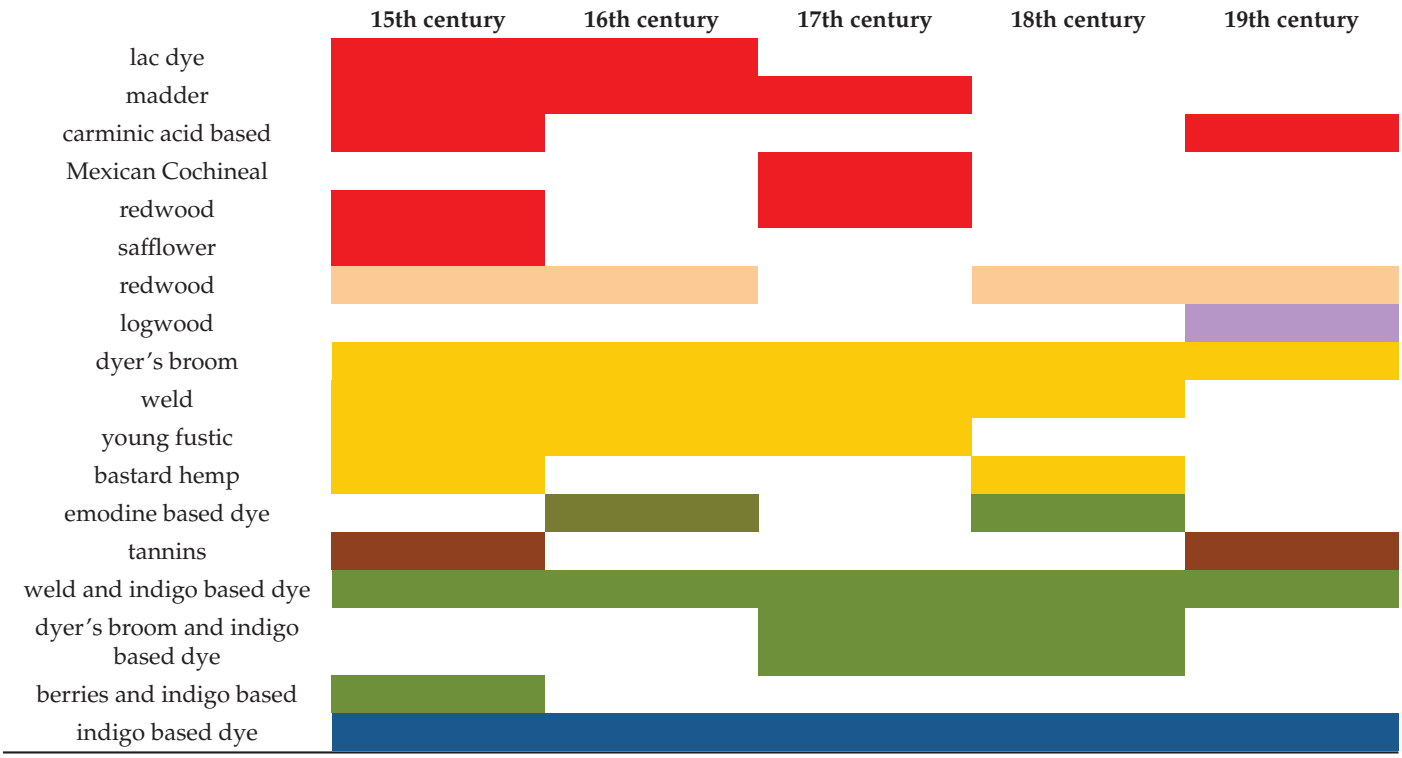


Table 5. *Cont.*

c.

EMBROIDERY THREADS



5. Conclusions

A large number of objects with similar liturgical function, dated over a period of 500 years, were studied in terms of dye analysis, for the first time with reference to Romanian collections. The objects are attributed to Byzantine, Moldavian, Wallachian, Greek, Russian, Constantinople and Viennese workshops.

Most of the samples are from the supports and, of these, the most common were red satin, with a warp dyed with a carminic acid containing dye and a soluble redwood weft. The material was also used as lining. The above-mentioned sources, as well as the others identified in the supports, lining and as embroidery threads were discussed together with those identified in previous studies, and chronologies on the use of dyes were proposed for each of the three functions of the fibres.

The biological sources identified in the few samples accessible for each object do not differ with the geographical areas of provenance of the objects studied. Consequently, it became impossible to establish any criteria to be used for attribution purposes. However, it was observed that Moldavian supports are always red, redwood-type dyed velvet was common for the supports in *epitaphioi* of Viennese origin and all the embroidery threads from Viennese liturgical textiles studied are dyed with dyer's broom.

The results obtained are extremely promising and valuable information was acquired, despite the limited number of samples available for each object. With reference to the whole Orthodox jurisdiction, liturgical embroideries of Byzantine tradition are little studied, and even less with reference to the materials and techniques used, which includes the dye sources. In-depth studies of liturgical embroideries in Romanian collections and beyond, correlated with conservation and a well-defined sampling strategy, would be worthwhile in order to better comprehend and appreciate these extremely valuable testimonies of world heritage.

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Conflicts of Interest: The authors declare no conflicts of interest.

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A Royal Mystery: A Multianalytical Approach for Dyestuff Identification in Seventeenth Century Waistcoats

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Abstract: Early modern materials are not well represented in dye and mordant analyses despite extensive documentary evidence suggesting the enormous demand for coloured fabrics, even among those below the elite. Non-wovens likewise receive less attention than woven textiles despite their ubiquity in the early modern historical record. Knitted garments, in particular, have rarely been subjected to dye analysis. One garment is noteworthy for its colourfulness, despite not being visible in formal wear. Men throughout society wore knitted undergarments known as waistcoats from the late sixteenth century. The waistcoats under investigation here are from the collections at the London Museum and the Grimsthorpe and Drummond Castle Trust, Scotland. They are made of silk and are now a pale blue-green colour. Small samples were taken from each and subjected to a series of analytical techniques: micro-Raman spectroscopy, UV-Vis microspectrofluorimetry, and high-performance liquid chromatography (HPLC) coupled with a mass spectrometer. Using this protocol, it was possible to characterise the dyes in the waistcoats by ensuring that maximum information was gleaned from a sample before it was exhausted.

Keywords: knit; silk; dye analysis; indigo; yellow dyes; early modern

1. Introduction

A knitted silk waistcoat (inventory number A27050) associated with Charles I was bought for the London Museum in 1924, and arrived with a note suggesting that it was worn at the king's execution on 30 January 1649. Soon after its acquisition, it was referred to as "a rather grim relic" and described as being of "faded blue silk" [1]. Its colour has not been the focus of study before. This paper reports a multi-analytical approach to identifying the dyestuff(s) used to colour it and another garment of a similar type.

The seventeenth century term for a garment worn for warmth over a shirt and under a doublet or as informal wear was "waistcoat", although the example at the London Museum has often been described as "the vest worn by Charles I on the scaffold" [1]. The king was reported to have worn a "Sky-colour satten Wastecoat" by an eyewitness to his preparations for death [2]. A satin garment would have been tailored from a woven silk fabric, not knitted, but that the king owned blue waistcoats is supported by other contemporary accounts. An account dated 1632 to 1633 kept by George Kirke, Gentleman of the Robes, confirms the purchase of "a skieculler satin waistcoat, with two silver bone laces in a seame with linings, coller, buttons and buttonholes lined with skie-culler taffetei" [3], and a portrait by Goddard Dunning from 1649 shows Charles I in a light blue woven fabric waistcoat or doublet [4]. Waistcoats also appear in the wardrobe accounts for Charles I among garments known to be knitted, such as hose and "tennis sockes", which were supplied by haberdasher Thomas Robinson [3]. Some were simply described as silk and

may therefore have been undyed, but at least one was a "fine Carnacion [pink] silke wastcoate" purchased in 1635 [5].

Previous analysis undertaken in the 1950s, the 1980s, and the 2010s focused on the stains on the front of the garment, which had been reported to be royal blood [1]. The first test took place in 1959 (on the 310th anniversary of Charles I's death) at the London Hospital Medical College. The anti-human globulin test was used to detect human protein. Some of the stains gave positive reactions, but these were weak [6]. The stains were analysed a second time in 1988 in preparation for a display in 1989 (the 340th anniversary). The waistcoat was tested for blood using the Kastle Meyer Test. This was negative, but it was noted that "blood could have degraded" and that the waistcoat could have been washed. The report stated that "blood, urine, sweat, semen, vomit, food, drink and cosmetic preparations are all possible sources of the staining, but since non-destructive tests for those substances would almost certainly give negative or misleading results after 340 years, their true nature remains a matter of conjecture" [7]. Further analytical methods were explored in 2010 (following the 360th anniversary) with the Forensic Science Service, but it was deemed unlikely that contemporary tests would lead to any clear results. Chemical tests for blood had not changed since 1989 and were, therefore, of limited value. The waistcoat was most recently shown in an exhibition in 2023, just before it reached 100 years in the collection. This made 2024 another suitable anniversary to report investigations into it again. This time around, its colour was a focus of study.

Approximately 60 knitted silk waistcoats are in collections worldwide, usually dated to between 1590 and 1700. Two-thirds were of more than one colour and were often knitted and/or decorated with metallic thread. These have been described as "brocade-knitted" [8]. A red and gold example is in the collection of the National Museums Scotland, Edinburgh (inventory number A.1973.28). The other third of the knitted silk waistcoats are described as "damask-knitted". These are monochrome and have motifs in patterns created by the use of different stitch types. Most of the brocade-knitted waistcoats were brightly coloured (coral, green, blue, or yellow). The damask-knitted examples are red, green or pale blue [8]. There are examples of seventeenth century silk garments that preserve their bright colours, such as a red waistcoat worn by William III (Historic Royal Palaces, inventory number 3503038), but none have been subjected to dye analysis that has been published.

The London Museum waistcoat is damask-knitted in a pale blue-green colour on the outside with a brighter blue inside and on the back of the garment (Figure 1). Some of the raised surfaces of the knitted loops are notably yellow even to the naked eye, suggesting either that the blue colour has been rubbed away, exposing the natural silk colour, or that both blue and yellow dyes were used to colour it. The hypotheses under investigation were whether the waistcoat was dyed with indigo, suggesting that it had originally been a bright blue, or that it was also dyed with a yellow dye, which would make its original colour more likely to have been green.

Previous work on seventeenth century silk garments from grave contexts has shown that a multi-technique approach is fruitful for analysing dyes [9]. High-performance liquid chromatography coupled with diode array detection (HPLC-DAD) has been used to characterise dyes in seventeenth century beige, green, and light blue silk brocade [10]. Thus far, these techniques have not been applied to any knitted silk fabrics from this period.

Information that came to light during this study provided clear evidence that the London Museum waistcoat was washed during the twentieth century. The student intern who washed it on the instructions of the then head of conservation, remembers that it changed colour slightly, becoming "a little paler" [11]. One of the limitations of this study is not knowing how likely it is that dyestuffs were washed away entirely either during this event or previously in the garment's history.

Figure 1. A knitted silk waistcoat (inventory number A27050) associated with Charles I. Image: © London Museum.

The initial research on the London Museum's waistcoat used microfadeometry to aid decisions about lighting for its future display. Five small areas (0.3 mm each) were subjected to a probe of bright light to induce accelerated colour change by specialists at the National Archives at Kew (UK). This demonstrates the rate at which the colour is likely to fade according to the international standard for assessing lightfastness (ISO 105 B02). It showed that the waistcoat had already faded considerably and indicated the presence of indigo and the possibility of a yellow dye.

A similar example to the waistcoat in the London Museum is in the collection of the Grimsthorpe and Drummond Castle Trust, Scotland (inventory number DCT0032) in the same pale blue-green colour with yellow raised areas (Figure 2). It is said to have been worn by the Earl of Perth in the seventeenth century, but precisely which of the earls is not clear. Two other similar waistcoats are at the National Museum, Oslo (inventory numbers OK-dep-01162 and OK-08800), although they are embellished with silver thread over the pale blue-green knitted fabric.

The opportunity for the collection of samples from these two waistcoats allowed for the characterization of the dyes present, shedding light on their manufacture. A multi-analytical approach was used: micro-Raman spectroscopy, molecular fluorescence in the visible, and high-performance liquid chromatography (HPLC) coupled with mass spectrometry (MS).

The original colours are poorly preserved in the samples (the pale blue-green silk waistcoats) (Table 1). HPLC-MS analysis was able to identify the dye sources present. However, to provide a database of techniques that do not require sample pre-treatment, Raman and molecular fluorescence data were presented. This will allow these dyes to be identified in textiles which cannot be sampled in the future.

Table 1. The two early modern waistcoats studied.

Location	Fibre	Inventory Number	Colour (by Visual Observation)
London Museum	Silk	A27050	Pale blue-green
Drummond Castle	Silk	DCT0032	Pale blue-green

Figure 2. A knitted silk waistcoat (inventory number DCT0032) in the collection of the Grimsthorpe and Drummond Castle Trust, Scotland. Image: © Jane Malcolm-Davies.

The use of these techniques permitted a thorough characterisation of the two waistcoats, leading to a better understanding of the production of such textiles in the seventeenth century. It also initiated the development of a database for further studies of waistcoats from the early modern period.

2. Materials and Methods

2.1. Materials

Spectroscopic or equivalent grade solvents and Millipore-filtered water were used during all the experimental work. Qualitative filter paper from Filter Lab was used. Each chromophore (luteolin, luteolin-7-*O*-glucoside, and quercetin) was complexed with Al^{3+}. Solutions were prepared in methanol/water (70:30, v/v), at 5×10^{-4} M. Complexation of molecules with Al^{3+} (where Al^{3+} is present $\times 100$ in respect to the molecule) was performed with the addition of $AlCl_3$ (0.1 M). Six drops of each solution were then applied on filter paper with a micro-pipette (10 µL). Three replicates for each reference were prepared, and analyses were carried out on the same day as (or the day after) application on filter paper. The filter paper is composed of almost pure cellulose without any additives, providing a support for the analysis of these chromophores. Data acquired in these reference materials composed a database, which was compared with the case studies.

2.2. Sampling

Permission for sampling the waistcoat was granted for dye analysis according to the London Museum's strict criteria. The process of taking samples followed advice from relevant literature, although it proved contradictory. It is often preferable to remove a sample from a part of the object that is already damaged to avoid further injury to its integrity. In such cases, taking a fragment that is still attached by at least one thread ensures it is part of the original [12]. However, other advice suggests avoiding deteriorated parts of the textiles altogether, as these are more likely to be compromised and yield misleading results [13]. A previous protocol for sampling knitted garments at the museum devised during the *Knitting in Early Modern Europe* project, which looked at sixteenth century knitted caps, was also consulted (Table 2) [14,15].

Table 2. Sampling strategy for knitted caps at the London Museum.

No sampling will be considered where previous conservation treatments have distorted the item's original shape.
Items must have existing damage. Caps in pristine or good condition, without any existing areas of loss, will not be sampled.
Areas for sampling are to be hidden from regular view. Sampling from the interior will be preferable to the exterior. External decorative features will not be sampled.
Samples will be taken from areas away from key features.
Multiple sampling of one item will be considered if the item has multiple parts, such as a separate lining, decoration or a strap.
No sampling will be considered in or around a hole where most or all of the material exists around the area of loss (if the hole could be completely closed through conservation).
Sampling items which have not undergone obvious conservation interventions is preferred.
No sampling will be undertaken where a proper assessment of the item is currently impossible (for example, if it has been stitched to a mount).
The maximum sample shape and size is square (0.5 cm × 0.5 cm) or rectangular (1 cm × 2 cm).
Loose dust or hairs in the item's storage box (which would otherwise be discarded) may be collected as samples.

A comprehensive survey of the garment identified two potential locations from which to take samples: fragments from the damaged front and silk thread ends from inside the garment. The damaged section was badly stained, whereas the thread ends were in very good condition. Samples were taken from each to comply with the conflicting sampling advice mentioned above. Similar samples were collected from the Drummond Castle waistcoat.

2.3. Confocal Micro-Raman Spectroscopy

Confocal micro-Raman analysis (micro-Raman or benchtop Raman) was carried out using a Horiba Jobin-Yvon LabRAM 300 benchtop spectrometer, equipped with a diode laser providing excitation at 785 nm and a maximum laser power of 37 mW at the sample. The laser beam was focused through a 50× Olympus objective lens, resulting in a spot size of 4 μm. The laser power at the sample surface was kept between 9.5 and 0.37 mW. No evidence of fibre degradation was observed during or after spectra acquisition. This system enables data acquisition in the 100–4000 cm^{-1} spectral range, with a 3 cm^{-1} spectral resolution, and a grating 1800 gr/mm. Spectra were acquired as a sum of 10–15 scans, with a 15–25 s integration time. A minimum of three measurements were collected from the same sample to ensure data reproducibility, and a silicon reference was used for calibration.

2.4. Molecular Fluorescence in the Visible

Fluorescence excitation and emission spectra were recorded with a Jobin–Yvon/Horiba SPEX Fluorog 3-2.2 spectrofluorometer coupled to an Olympus BX51M confocal microscope, with spatial resolution controlled by a multiple-pinhole turret, corresponding to a minimum 2 μm and maximum 60 μm spot, equipped with a 50× objective. Beam-splitting is obtained with standard dichroic filters mounted at a 45° angle in a two-place filter holder. For a dichroic filter of 500 nm, excitation may be undertaken up to about 490 nm, and emission collected after 510 nm. The signal was optimised daily for all pinhole apertures through mirror alignment, following the manufacturer's instructions and using a rhodamine standard (or other adequate references). For this study, one set of dichroic filters was employed: 430 nm and 500 nm, exciting at 420 nm and reading the emission signal at 510 nm, respectively.

Emission from a continuous 450-W xenon lamp, providing an intense broad spectrum from the UV to near-IR, was directed into a double-grating monochromator, and spectra were acquired after focusing on the sample (eye view) followed by signal intensity optimisation (detector reading). The pinhole aperture that controls the measurement area was selected based on the signal-to-noise ratio. In this work, due to very weak signals, a 30 μm

spot was used (pinhole 8) with the following slit set: emission slits = 3/3/3 mm (6 nm bandpass) and excitation slits = 5/3/0.8 mm (final bandpass of 2 nm). Emission and excitation spectra were acquired on the same spot. When needed, the spectra were normalised by area. When comparing spectra acquired from different samples, four different signals must be considered: the maxima of excitation and emission, the signal-to-noise ratio, the intensity of the signals, and the shape (see [15–18]).

2.5. High-Performance Liquid Chromatography (HPLC) Coupled with Mass Spectrometry (MS)

The dyes from the samples were extracted using a soft-extraction method in order to prevent any molecule degradation [19]. The textile microsamples were placed in a microtube with 400 µL of oxalic acid (0.2 M)/methanol/acetone/water (0.1:3:3:4, *v*:*v*) at 60 °C for 30 min. The solution was left to evaporate under vacuum, and the residues were then dissolved in 400 µL of methanol/water, 7:3 (*v*/*v*); the tubes were centrifuged, and the upper 25 µL of the solution was removed for analysis.

HPLC-ESI-Q-Orbitrap-MS analyses were performed in a HPLC Vanquish (Thermo Fischer Scientific, Bremen, Germany) coupled to an Orbitrap Exploris 120 mass spectrometer (Thermo Fischer Scientific, Bremen, Germany) controlled by Orbitrap Exploris Tune Application 2.0.185.35 and Xcalibur 4.4.16.14. The MS was operated in the ESI positive and negative ion modes, with the following optimised parameters: ion spray voltage, ±4.5 kV; capillary voltage, 16/−18 V; tube lens offset, −70/58 V; sheath gas (N_2), 40 arbitrary units; auxiliary gas (N_2), 20 arbitrary units; capillary temperature, 270 °C. The spectra typically corresponded to an average of 20–35 scans, and were recorded in a range between 100 and 1000 Da. The stationary phase was an Agilent Poroshell 120 CS-C18 column (150 × 4.6 mm i.d., 2.7 µm) at 35 °C. The mobile phases were composed by solvent A, 0.1% (*v*/*v*) formic acid, and solvent B, 100% (*v*/*v*) acetonitrile. The flow rate was 0.30 mL/min, the injection volume was 15 µL, and the gradient method started with a 2 min isocratic 7% B gradient, followed by a linear gradient ranging from 7% B to 80% B in 20 min, and then reaching 100% B in 1 min followed by a linear isocratic four minute 100% gradient; then, the column was re-equilibrated with 7% B for seven minutes [20].

3. Results and Discussion

The complementarity of the analytical techniques permitted a general overview of the materials used and their conservation conditions. While HPLC-MS identified the main molecules present and the degradation products, other techniques that do not require sample pre-treatment, such as Raman spectroscopy and molecular fluorescence in the visible, were also used. These techniques allow for the characterisation of artworks in situ or using microsamples, which are afterwards available for further analysis. By combining these techniques, it has been possible to start building a database of information that will facilitate future studies of comparable material using only Raman and/or molecular fluorescence.

3.1. HPLC-MS Analysis

The HPLC-Orbitrap-MS analysis (Table S1) allowed the identification of indigotin (Figure 3) in both of the blue-green London Museum and the Drummond Castle silk waistcoat samples ($[M + H]^+$ *m*/*z* 263.08).

No yellow dyes were identified in the London Museum's waistcoat samples, but one was found in both Drummond Castle samples. A correspondence with daphnetin ($[M + H]^+$ *m*/*z* 179.01) with MS^2 133.05 suggested that it may have been dyed with flax-leaved daphne (*Daphne gnidium*), a plant native to the Mediterranean used for dyeing yellows and greens (Figure 4). It appears in Arabic texts in the twelfth century and in a regulation published in France in 1671 warning of its health hazards. Nevertheless, it was recorded as achieving green colours from Seville in the eleventh century to Morocco in the twentieth century [21].

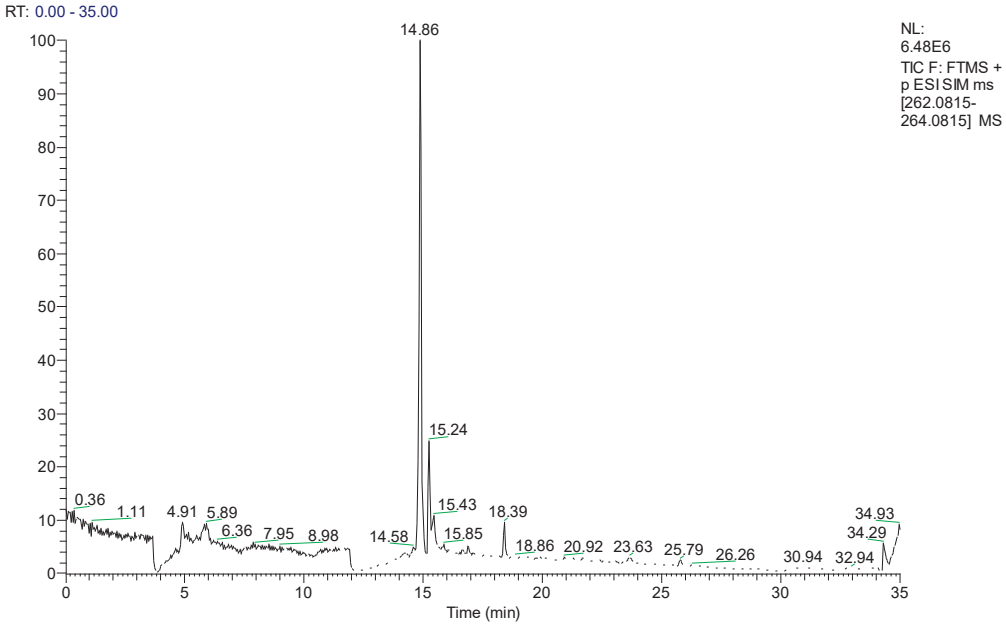

Figure 3. Single ion monitorization LC-MS chromatogram for $[M + H]^+$ m/z 263.08 signal, identified as indigotin.

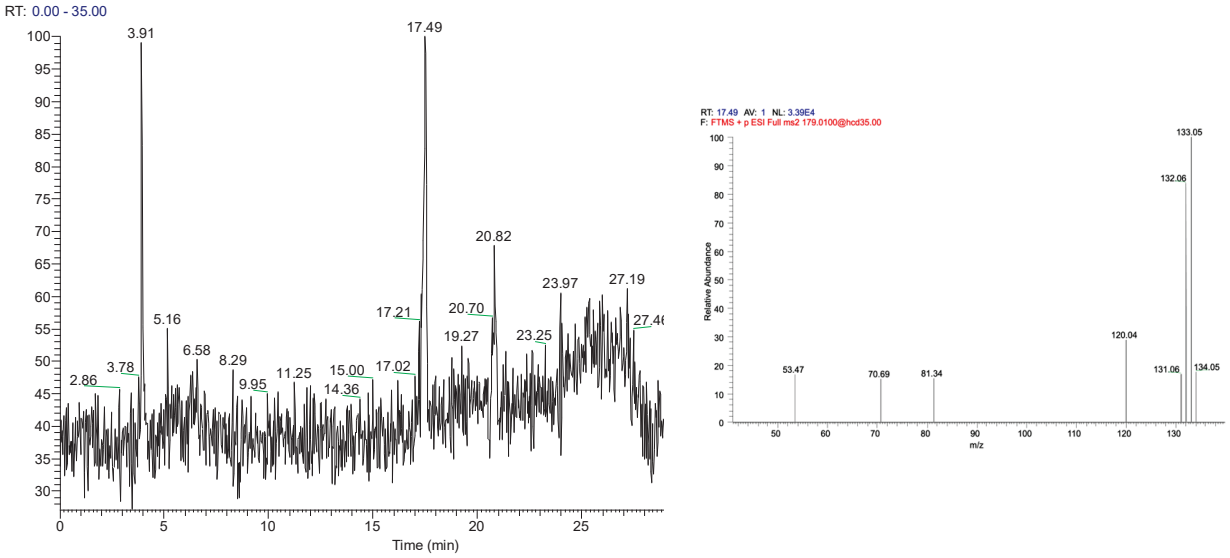

Figure 4. Single-ion monitorization LC-MS chromatogram for $[M + H]^+$ m/z 179.01 signal, identified as daphnetin, with MS2 spectrum fragmentation signal m/z 133.05.

The MS signals suggested potential animal and/or microbial contamination including D-glucosamine (D-GlcN), which is an amino sugar and a prominent precursor in the biochemical synthesis of glycosylated proteins and lipids [21]; or acetylglucosamine (GlcNAc), which is an amide derivative of the glucose and part of a biopolymer in the bacterial cell wall. GlcNAc is the monomeric unit of the polymer chitin, which forms the exoskeletons of arthropods such as insects and crustaceans [22].

HPLC-Orbitrap-MS analysis (Table S1) determined whether the materials had suffered degradation [23]. The London Museum silk sample (A27050) did not show any correspondence to 4-hydroxybenzoic acid ($[M\text{-}H]^-$ m/z 137.03) and had not, therefore, degraded to any significant degree. The Drummond Castle silk samples (DC001 and DC004) corresponded with 4-hydroxybenzoic acid ($[M\text{-}H]^-$ m/z 137.03) with MS^2 93.05, suggesting that the silk had degraded.

3.2. In-Situ Analysis: Raman and Molecular Fluorescence

Raman spectroscopy allowed the identification of indigo in the London Museum and the Drummond Castle samples. The main bands from indigo that were identified were 254 cm^{-1} ($\gamma(C=C)_2$), 545 cm^{-1} ($\delta(C=C–CO–C)$), 599 cm^{-1} ($\delta(C=O)$, $\delta(CNHC)$), and 573 cm^{-1} ($\nu(C=C)$) (Figure 5) [22].

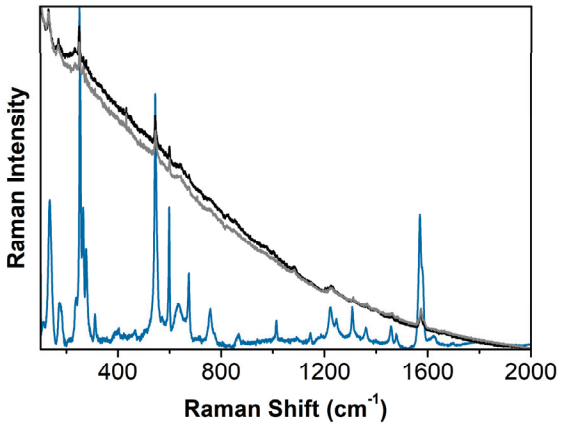

Figure 5. Raman spectra of the London Museum (black) and the Drummond Castle (grey) waistcoats, with an indigo reference in blue.

On the other hand, molecular fluorescence was used to identify the presence of a yellow dye in the Drummond Castle samples. Although microfadeometry indicated the possible use of a yellow dye in the London Museum waistcoat, the analysis using molecular fluorescence in the visible indicated only the presence of yellow silk (Figure 6). This undertone of yellow is possibly due to the degradation of the silk fabric due to its various uses and conservation conditions.

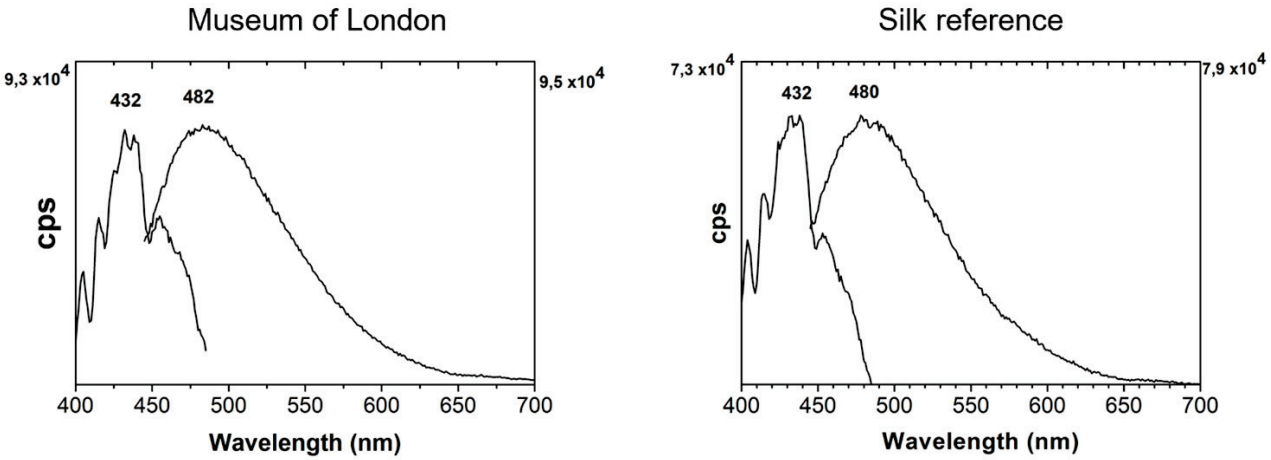

Figure 6. Molecular fluorescence spectra of London Museum waistcoat (**left**) and natural silk (**right**).

In contrast, the Drummond Castle sample indicated the presence of a yellow dye (Figure 7) due to its two excitation bands at 436 and 460 nm and emission maxima at 490 nm. Because these signals do not match those obtained from luteolin-based dyes, namely weld, it is clear that the yellow source used is different. Nevertheless, the flavonoid–aluminium references (Figure 7) have shown that these intervals are standard for benzopyran-based molecules, such as flax-leaved daphne (daphnetin). The lack of thorough references for all yellow dyes used historically throughout Europe has prevented the identification of the exact source. This emphasises the importance of building a reference database.

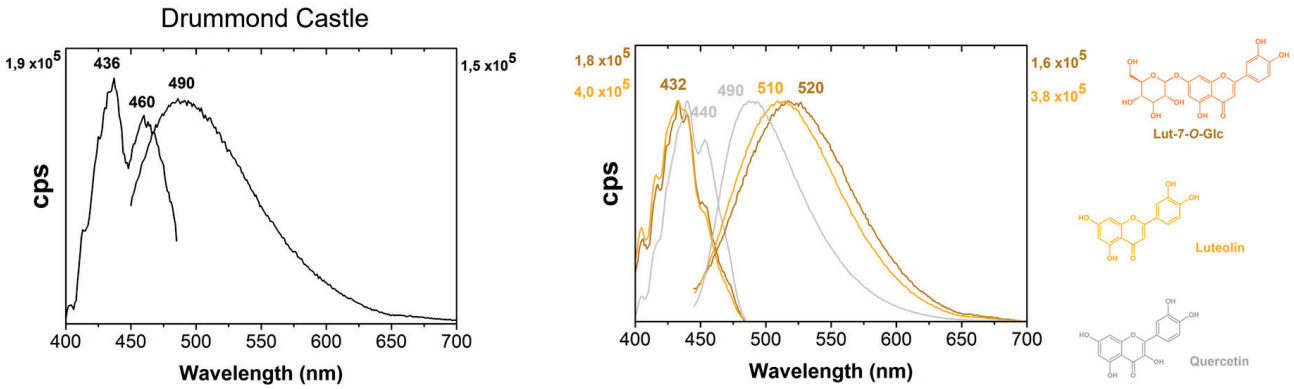

Figure 7. Molecular fluorescence spectra of the Drummond Castle waistcoat (**left**) and luteolin, luteolin-7-*O*-glucoside and quercetin, complexed with Al^{3+} ($\times$100), in filter paper (**right**).

4. Conclusions

The dye analysis undertaken in this study indicates that the hypothesis that a blue dye alone was used to colour the London Museum silk waistcoat is proven. However, the identification of both blue and yellow dyestuffs in the Drummond Castle silk waistcoat makes green a more likely colour for it, proving hypothesis two.

Further dye analysis of knitted waistcoats of similar blue-green colours (all of which are silk with silver thread) is recommended. Examples are held at the Stiftelsen Kunstindustrimuseet, Nasjonalmuseet, Oslo, Norway (inventory numbers OK-dep-01162 and OK-08800); Bergen, Norway (inventory numbers VK4074 and BY03948); and Stålheim, Tønneberg, Norway (no inventory number). Work on green examples is also desirable. These are at Stiftelsen Kunstindustrimuseet, Nasjonalmuseet, Oslo, Norway (inventory number OK 11661) and in Trondheim, Norway (inventory number NK 747).

The development of a comparative set of data from similar garments will permit speculation on the original colour of the London Museum waistcoat and broader conclusions to be drawn about the conventional dyestuffs and colours for early modern waistcoats.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/heritage7080189/s1, Table S1: HPLC-ESI-Q-Orbitrap-MS sample dye analysis.

Author Contributions: Conceptualization, J.M.-D., B.B. and P.N.; methodology, J.M.-D. and P.N.; sample acquisition, J.M.-D. and B.B.; fluorimetry analysis, P.N.; HPLC-MS analysis, N.T.; writing—original draft preparation, J.M.-D.; writing—review and editing, J.M.-D., B.B., N.T. and P.N.; project administration, J.M.-D.; funding acquisition, J.M.-D., B.B., N.T. and P.N. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: All relevant data is available on request.

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Conflicts of Interest: The authors declare no conflicts of interest.

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Ephemeral Orchil in the Lady and the Unicorn Tapestry: Recipe, Experimentation, and Characterisation

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Abstract: Spectroscopic techniques were carried out to identify the dyes used on the famous mediaeval Lady and the Unicorn tapestries kept in the Cluny Museum. Among the six tapestries, *La Vue* shows a colour variation between the front, which appears blue, and the back, which appears violet, on the Lady's skirt. In the Middle Ages, it was common for the violet colour to be made with a blue dye bath (woad or indigo) followed by a red bath, which could be madder, cochineal, kermes, or orchil. Since orchil is known to be very unstable to light, its potential use in the original recipe was investigated and a study on this dye was performed. Contactless analyses (hyperspectral imaging in the visible-near-infrared range and UV fluorescence spectroscopy) were carried out on both the tapestry and mock-ups prepared following various mediaeval recipes. The investigation allowed for the identification of woad and orchil on the back of the tapestry, which was preserved from exposure to light. In addition, an ageing study elucidated colour degradation, revealing not only the different responses to light of different dyes but also the effect of specific dye preparations on light resistance. The experiments showed that the longer the maceration, the higher the light resistance of the dye. Furthermore, the red orchil colour fades faster than the woad.

Keywords: orchil; contactless and portable methods; light degradation; dyes; tapestry

1. Introduction

The 19th century saw a renewed interest in medieval art and craftsmanship, leading to increased study of European tapestry history, especially the 14th and 15th centuries, known as the "Golden Age" of tapestry [1–4]. Numerous documents from this period provide insights into remarkable French tapestries, for instance, the Apocalypse, commissioned by the Duke of Anjou, and the Lady and the Unicorn [5,6]. While these texts focus on the chronology and the involvement of craftsmen and commissioners, they largely overlook the materials, particularly dyes, which are crucial for historical, social, and economic insights and conservation. Consequently, the analysis of these materials is essential for a comprehensive understanding of artwork.

Recent research into tapestries generally favours the use of non-contact methods for material characterisation. Mordants are detected using X-ray fluorescence (XRF) [7], while dyes are determined through fibre optic reflectance spectroscopy (FORS), hyperspectral imaging, and spectrofluorimetry in various ranges such as UV and visible (VIS) [8–12]. Near-infrared (NIR) is used to determine the type of textile [8,9,13]. However, it is sometimes necessary to take samples to validate hypotheses using methods considered invasive. These include SEM-EDS (scanning electron microscopy with energy dispersive X-ray spectroscopy) for fibre analysis [13], high-performance liquid chromatography with diode array

detection (HPLC-DAD), or mass spectrometry detection (HPLC-MS/MS) for dye identification [8,10–12,14,15] and laser-induced breakdown spectroscopy (LIBS) for mordant detection [14].

The study of the Lady and the Unicorn tapestry, using primarily spectroscopic methods, allows us to characterise both the materials used in its creation and those used during the various restoration campaigns it has undergone. These restorations, numbering twelve, span from the late 19th century to the present day [16]. Few of them provide detailed information on the interventions or the materials used; only recent restorations document and provide reports on the analyses and work carried out. For example, during the 2012 restoration campaign, the Laboratoire de Recherche des Monuments Historiques (LRMH) conducted colourimetric measurements of various sections of the tapestry of the Lady and the Unicorn [17]. That study aimed to track changes in dye appearance on both the front and back surfaces after washing the six tapestries carried out by De Wit Manufacture. Upon examination of the *La Vue* tapestry on the Lady's skirt after cleaning treatment on the recto side, a light blue hue was evident. In contrast, a significant colour difference with a Delta E_{2000*} = 15.0 in CIEL*a*b* space was observed on the verso side, which was characterised by a purplish tint. This distinction was already observed and documented between 1941 and 1944 by the Atelier Bregère, who restored the tapestry in that campaign and listed all the changes it had undergone since its creation and before its intervention. In the document, it is possible to read about a colour change in the skirt of the Lady from violet to light blue because of action of air and light: «à l'origine, le coloris de cette partie du vêtement était mauve, soutenu par des ombres noires; ce coloris mauve est devenu bleu clair par l'action de l'air et la lumière» [18]. The following question then arose: what dyes and recipes were used to make the Lady's skirt? What makes up this violet colour that has now faded?

In natural dyeing, there are very few dyes that can be used to dye violet. Only shellfish purple (e.g., *Hexaplex trunculus*) and some lichens can be used to obtain a reddish-purple dye. As the use of shellfish purple is very expensive, other techniques have been developed to obtain similar violet shades [19,20]. One of these techniques involves dyeing blue and then red. All the recipes have in common that the first step is to dye with a plant containing indigoid molecules. In Europe, these plants could be woad in the Middle Ages or indigo after the 17th century [19]. The second step is to make a second bath with a red dye [21]. At the time of the Lady and the Unicorn tapestry's manufacture, plants such as madder (*Rubia tinctorum* L.) or insects such as kermes (*Kermes vermilio)*, Armenian or Polish cochineal (*Porphyrophora hamelii* and *Porphyrophora polonica*), or lichen-like orchil were employed to dye in red colours [19,22]. Orchil is obtained from different families of lichens. There are sea orchils (*Roccella tinctoria*, *fuciformis* or *phycopsis*) and land orchils (*Ochrolechia parella* or *Lasallia pustulata*) [23,24]. Particular interest in this dye has developed because of its use in a large number of heritage items. It has been used since Antiquity and was rediscovered in the Middle Ages in France in the 14th century [24]. Orchil has been identified on parchments [25,26], illuminations [27,28], and textiles [29,30] from various periods. These studies are often conducted using contactless methods (FORS VIS-NIR, UV fluorimetry) and supplemented by micro-invasive analyses (Raman, MALDI, ICPMS). Furthermore, some studies focus on the nature of the lichens used based on their different chemical characteristics using destructive techniques such as Raman SERS (surface-enhanced Raman scattering) or liquid chromatography accompanied by mass spectrometry detectors (HPLC-MS/MS) [31,32]. Furthermore, light degradation experiments were performed to observe and study ageing products possibly responsible for the variation in signals collected on degraded objects under study [27,29,33].

As orchil is known for its low resistance to light compared with other dyes [20], this study aimed to identify its potential use in the original recipe for the violet used in the Lady and the Unicorn tapestry (the Lady's skirt of *La Vue*) and to deepen our understanding of the physico-chemical properties of this dye. For this reason, various mock-ups of orchil were made in the Myrobolan studio using different protocols to complete our database

that comprises different dyes used in tapestry manufacture. Absorbance spectra were then collected using a contactless methodology consisting of hyperspectral imaging in the visible-near-infrared range and UV fluorescence spectroscopy and compared with the tapestry results. Furthermore, HPLC combined with a PDA detector (photodiode array) was used on a sample collected from the tapestry. Finally, a methodology for degrading samples under natural light was set to observe the loss of colours and the influence of the fading on spectra.

2. Materials and Methods

2.1. Creation of the Colour Charts

All the samples were dyed on a canvas fabric made from wool from Belgian and French sheep (Texel and Suffolk breeds 50% + *Est à laine merinos* breeds 50%), washed in Belgium and processed (spinning, weaving, fulling) in Germany.

2.1.1. Orchil

The lichen used in this study was *Lasallia Pustulata*, hand-picked in southeast France by a lichen specialist. The literature on orchil production provides varying information regarding the recipes [22,23,34,35]. The challenge was with the proportions between products, such as the ratio of lichen to ammonia solution, the percentage of ammonia in the solution, maceration time, maceration conditions, the ratio of fibre weight to be dyed to the initial weight of lichen, and the methodologies employed in dyeing.

The orchil preparation initiates with maceration in an ammonia solution. To observe the influence of maceration, the samples were dyed starting from the 17th day of maceration, with a new sample dyed every 3 days thereafter. The last sample was dyed after 87 days of maceration. Twenty-five pots were prepared, each containing 5 g of lichen powder in 100 mL of ammonia solution, composed of 1/3 ammonia at 13% concentration and 2/3 tap water at pH 5.5. The resulting solution was observed to have a pH of 11.5, which was maintained throughout the experimental procedure by adding 13% ammonia from the 38th day of the experiment. The container was opened for approximately 30 min daily to agitate the liquid.

Once the desired maceration was obtained, the contents of the pot were diluted in 500 mL of water and heated to 30 °C. The wool was introduced, and the dye bath was gradually raised to 75 °C. Once this temperature was reached, it was maintained for 1 h and 30 min. Subsequently, the sample was rinsed with clear water and naturally dried. The following day, the process was repeated on the same sample and in the same dye bath to achieve a superposition and intensify the colour. It was repeated a third time on the subsequent day to obtain a third overlay.

2.1.2. Woad Blue

This study employed woad obtained from a supplier in the Tarn region of south-western France, who produced a woad indigo pigment paste. A 5 L vat was established for sampling. The formulation comprised 200 g of woad paste, analysed to contain 12% indigotin, 150 g of fructose as the reducing agent, and approximately 80 g of lime. The vat was prepared 3 days before the dyeing process.

2.1.3. Violets

To obtain the violet-dyed samples with orchil, the previously prepared woad samples were introduced, instead of the natural wool, into the dye bath containing the orchil-based solution described in Section 2.1.1. Similarly, the cochineal-, kermes-, and madder-based violet samples were dyed over the previously dyed woad samples. The ingredients used to prepare the 3 dye baths for these red dyes are listed in Table 1. These three samples were prepared by our research team in collaboration with the Myrobolan studio during a previous study of Aubusson tapestries [7].

Table 1. The ingredients used to prepare the 3 dye baths for cochineal, madder, and kermes on woad (for 100 g of wool).

Sample	1st Bath Dye	Mordant	2nd Bath Dye
Woad and cochineal	Woad	15 g Alum 9 g White tartar	6 g Cochineal
Woad and madder	Woad	31 g Alum 6 g White tartar	50 g Madder
Woad and kermes	Woad	20 g Alum 10 g Red tartar	71.5 g Kermes

2.2. The Lady and the Unicorn Tapestry: La Vue

The tapestry *La Vue* (Figure 1) was chosen for this study because it was the only one cited by Atelier Bregère to contain a violet hue. It features a simple composition in the form of a pyramid. In the centre, a seated Lady contemplates the unicorn on her lap, stroking it with her left hand. Her right hand holds a mirror in which the unicorn is looking. The lion carrying the coat of arms to the Lady's right seems to be watching over the scene to ensure that the Lady is not disturbed [6]. This is the smallest tapestry in the set (314 × 325 cm). The tapestry underwent numerous restorations since its purchase by the Musée de Cluny in 1881 [36]. This research study focused on a specific section of the tapestry—the Lady's skirt (as depicted in Figure 1)—because of its notable fading, making it an intriguing subject for analysis.

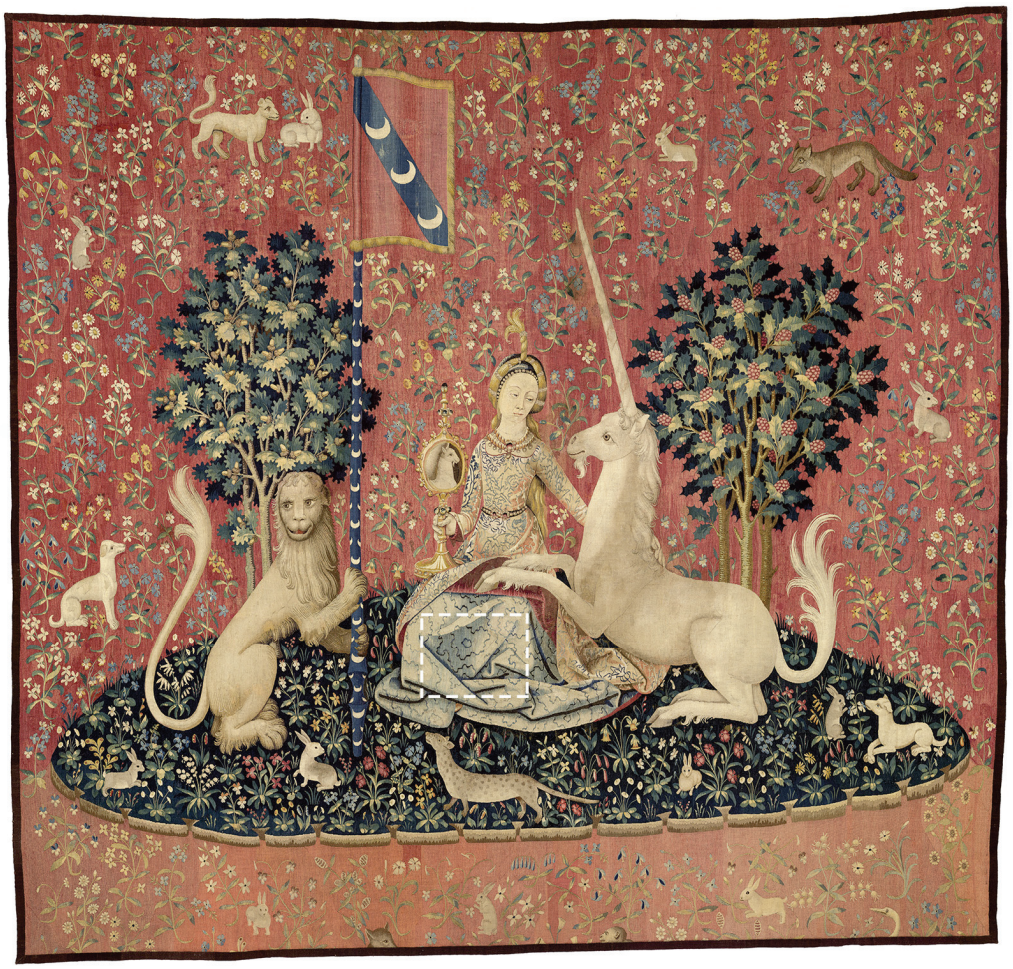


Figure 1. Photograph of *La Vue*—Tapestry the Lady and the Unicorn (314 × 325 cm) © Musée de Cluny. The dotted square indicates the area of interest in this study.

2.3. Spectroscopic Measurements

2.3.1. Hyperspectral Imaging Spectroscopy

Spectral data from the mock-ups and the yarn sample collected on the back of the tapestry (1 cm) were acquired using a hyperspectral camera portable (SPECIM), mounted on a 1.30 m rail and operated as a line scanner to capture data. The visible-near-infrared (VNIR) CCD camera (HS-XX-V10E) employed has a spectral resolution of 2.8 nm (FWHM) and a spectral sampling of 0.7 nm, with a pixel size of 54.7 μm^2. This camera constructed a 3-dimensional data cube (1600 pixels $\times$ X pixels $\times$ 840 bands), where X represents the image width's pixel count, spanning wavelengths from 400 to 1000 nm. Two halogen lamps set at a 45° angle illuminated the samples, and analyses were conducted at a working distance of 70 cm for the mock-ups and 10 cm for the tapestry yarn, with illumination of 2200 lux. A Spectralon fluoropolymer (99% reflectance) covered the detector's entire field of view, serving as a white reference during data acquisition. Additionally, a second acquisition was conducted with the shutter closed to serve as a dark reference, aiding in quantifying electronic noise. These references were pivotal in flattening the field and converting data into reflectance factors.

The front of the tapestry and the spectral data from the degradation study were acquired using a second ultra-portable hyperspectral camera (SPECIM IQ), which covered the visible light and near-infrared (Vis-NIR) spectral range from 400 to 1000 nm, with 204 spectral bands across the entire wavelength range. The spectral resolution (FWHM) was 7 nm. The resolution of the resulting image was 512 $\times$ 512 pixels. The camera was positioned on a photographic tripod, and the analyses were conducted at a working distance of approximately 40 cm under diffuse halogen lightning provided by two single lamps of 1000 W. The integration time for the analysis was 10 ms for the mock-ups and 73 ms for the tapestry analysis. A white Spectralon standard was employed for HSI data calibration. Spectra acquisition, storage, and calibration were executed using IDAQ software v.3.62. All the spectra are collected using Envi software v.5.0 and presented in the form of reflectance spectra as well as second derivatives to highlight absorbance maxima.

2.3.2. LED μ-Spectrofluorimetry (LEDμSF)

Fluorescence emission spectra were captured utilising an LEDμSF, a Thorlabs spectrometer (CCS200/M) equipped with an optical fibre (Ø 400 μm) and boasting a spectral range spanning from 200 to 1000 nm. A low-power LED emitting at 375 nm, filtered at 455 nm, served as the UV excitation source. The analysed area of the sample measured approximately 1–2 mm in diameter. The analysis time ranged between 1 s and 12 s. To enhance the signal-to-noise ratio, a background spectrum was recorded and subtracted from each measurement of the sample spectrum. Subsequently, spectral smoothing was applied. The LEDμSF was operated and controlled via a USB connection to a laptop, featuring a graphical interface developed with Windows Forms using Arduino IDE and MS Visual Studio Express C++ [37]. The instrument was securely mounted on a tripod with micrometric adjustment capabilities, aided by two red lasers to adjust the working distance fixed at 4 cm without any direct contact with the tapestry or the samples. The spectra were collected using Thorlabs software v.2.90.

2.4. High-Performance Liquid Chromatography UV–Visible (HPLC–PDA)

The chromatographic analysis was carried out on a 5 mm yarn taken from the reverse of the tapestry in the Lady's skirt. This sample was taken during the 2012 restoration campaign at the Musée de Cluny. The primary objective of characterising these samples was dual-fold. First, to identify the dyes in both the original sections and the restored areas of the tapestry. This served to document the tapestry's history and anticipate potential risks associated with dye bleeding if subjected to washing. The removal of the lining facilitated the sampling process from the back of the tapestry, focusing on areas less exposed to light. Sample selection targeted regions exhibiting a wide spectrum of colours spanning various historical periods (including medieval and subsequent restorations).

The extraction of the dyestuff was carried out using 5 mm of dyed thread in 20 μL of MeOH (Methanol absolute—HPLC supra gradient from Biosolve)/H_2O/Oxalic acid 0.2 M (99% purity from Sigma Aldrich, St. Louis, MI, USA) (8:2:1) solution, heated for 15 min at 60 °C with sonication and put into Eppendorf PP tubes before being vacuum dried for 12 h. Then, the extracted residue was dissolved in 10 μL of dimethyl sulfoxide (DMSO for spectroscopy 99.9% from Acros organics), for a couple of minutes with sonication at 60 °C. The solution was filtered through 0.2 μm PTFE membrane filters into a glass tube, and 10 μL of this was injected into the chromatographic system [38–40].

The separation was carried out with an HP 1100 system from Agilen Technologies (Walbronn, Germany) consisting of vacuum degasser G1322A, quaternary pump G1311A, autosampler G1329A with thermostat G1330A, thermostated column compartment G1316A, diode array detector G7117C with 10 mm optical path length cell, and ChemStation version C.01.07.SR3 software. The resolution of the diode array detector was less than 1 nm in the range of 190–640 nm. Chromatographic separations were carried out at 30 °C using a Hypersil BDS C-18 3 μm (100 × 2.1 mm) column with guard column 10 × 2.1 mm from Thermo (Runcorn, UK), with an eluent flow rate equal to 0.3 mL·min^{-1}. The mobile phase consisted of A: water (for HPLC gradient from Fisher Scientific), B: acetonitrile (ACN gradient grade for HPLC—99.9% purity from Merck), and C: 1% solution of formic acid (FA—99% purity from Biosolve) in water. They were applied in a gradient mode as follows: A: 85%, B: 5%, C: 10%, linear gradient in 41 min to A: 30%, B: 60%, C: 10%, plus 1 min constant A: 30%, B: 60%, C: 10%, before returning to initial conditions.

2.5. Degradation by Natural Light

Natural degradation was achieved by placing the mock-up samples in a south-facing window for 1 month during March 2024. Temperature, relative humidity, and the number of lux received by the samples were measured twice a week around midnight (22 < T° (C°) < 36, 19 < RH (%) < 47 and 4.5 < Klux < 49, respectively). Colour and spectral measurements were taken before exposure and after 1, 2, 3, and 4 weeks using the SPECIM IQ hyperspectral camera and the UV μ-spectrofluorimeter (described in Sections 2.3.1 and 2.3.2, respectively) and the spectrophotometer Konica Minolta CM 2600d. The spectrophotometer was used to investigate the chromatic variations (in the CIEL*a*b* space) that occurred during ageing. Measurements were conducted with an investigation area of 3 mm in diameter in SCI (specular component included) mode, using a standard illuminant of D65 and a CIE 1964 10° standard observer. The spectrophotometer registered the average of three measurements taken simultaneously. The recorded data were processed using Spectra Magic NX software v.3.31. The Delta E 2000 formula (ΔE_{2000}*) was utilised to calculate the colour differences observed after degradation [41].

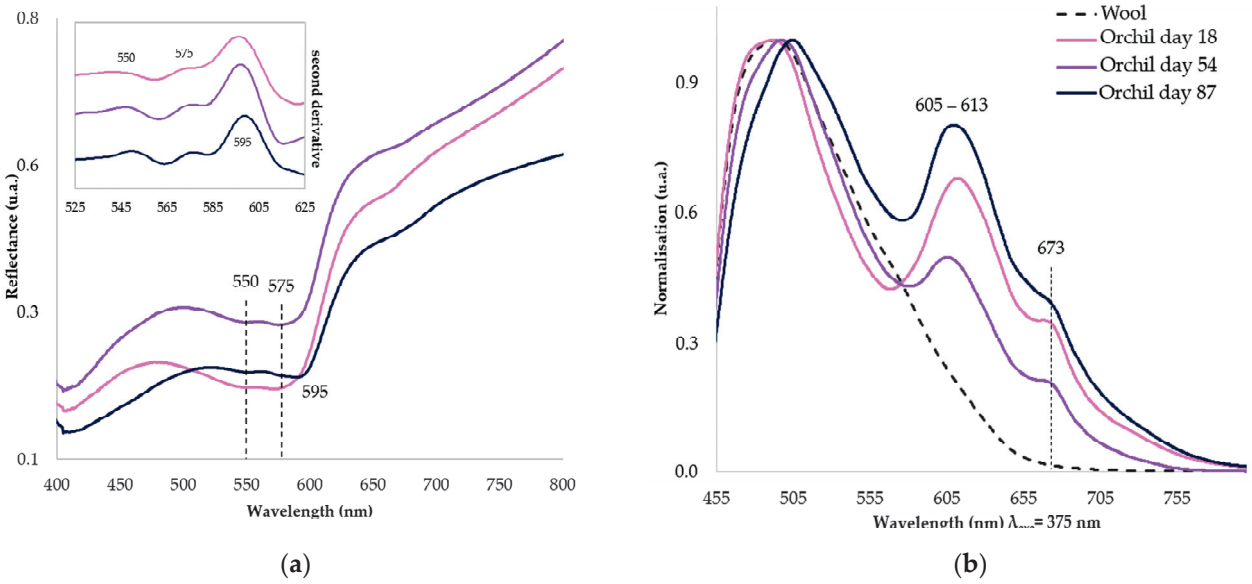
3. Results and Discussion

3.1. Characterisation of the Spectral Features of Orchil

The orchil-based samples, taken after different days of maceration, were analysed with spectroscopic methods. The achieved spectra display significant similarities. For example, Figure 2a shows the reflectance spectra of samples taken on days 18, 54, and 87 of maceration, which were selected to represent the results obtained at the beginning, middle, and end of the experiment. All three spectra show one absorbance band at around 550 nm. Another band at 575 nm is observed in the first and second samples, while it appears slightly shifted towards higher wavelengths (595 nm) on day 87 of maceration.

These absorption bands were further confirmed with a more precise visualisation through the second derivative spectra (graph at top left of Figure 2a). The first band of maxima for all samples corresponds to the value observed in the absorption spectrum (550 nm), while the second band, which is different in the absorption spectrum, appears to be split into two bands (575 and 595 nm for the three spectra). The appearance of these two bands is explained by the presence of a very broad absorption band in the reflectance spectrum. When a sample has a very broad absorption band, as in this case, it is preferable

to refer to the corresponding inflexion point, which, in this case, is at 610 nm for all the samples. These findings agreed with the data in the literature [25,27,28,42] and suggested that the rest period before the dyeing does not influence the spectroscopic signal.



(**a**) (**b**)

Figure 2. (**a**) Reflectance spectra of orchil samples dyed after 18, 54, and 87 days of maceration. The upper left panel shows the second derivative of these samples as a function of wavelength. (**b**) Fluorescence emission spectra of the same three orchil samples normalised to the natural wool signal (dotted line).

The fluorescence emission spectra of the same three samples confirmed the assumption that the maceration time has no effect on the spectroscopic signal of the samples, as shown in Figure 2b, where all spectra are normalised to the textile signal. The main emission band of orchil is observed at around 610 nm, slightly shifting from what is reported in the literature [25,28,42]. This shift towards shorter wavelengths can be explained by the hypsochromic phenomenon, which is related to the concentration of the dye in relation to the textile and the fluorescence of wool [7]. The application of the Kubelka–Munk equation might help correct the fluorescence emission spectra by cancelling the self-absorption of the dye [43,44]. However, this correction is not applicable to textiles as they are neither flat nor opaque, and homogeneity is not verifiable. In the three samples, it is also possible to observe an emission band at 673 nm, corresponding to the presence of chlorophyll, which is part of the composition of lichens [45].

Then, the samples prepared with a blue and a red dye were studied to investigate the colour violet. In the case of orchil, the same experiment as the one with the dye alone was repeated with a first woad bath. As in the first case, all samples were analysed, and the results of the reflectance spectra of 18, 54, and 87 days, shown in Figure 3a, were selected as representatives of the complete dataset. All three absorption spectra of the textiles dyed with woad and orchil show absorption bands characteristic of orchil (545 and 595 nm), together with a wide third absorption band between 660 and 685 nm, indicating the presence of indigotin, the primary colouring molecule in woad [46]. In all samples, the visualisation of the second derivative allowed for a better characterisation of this third band at 700 nm. As seen in the case of orchil, because of the presence of a broad band, it was preferable to consider the inflexion point at 710 nm. The corresponding fluorescence emission spectra (Figure 3b) showed the presence of indigoid molecules characterised by a small band around 720 nm [47–49]. The main band at around 606 nm and the shoulder at 673 nm correspond to the presence of orchil and the detection of chlorophyll, respectively.

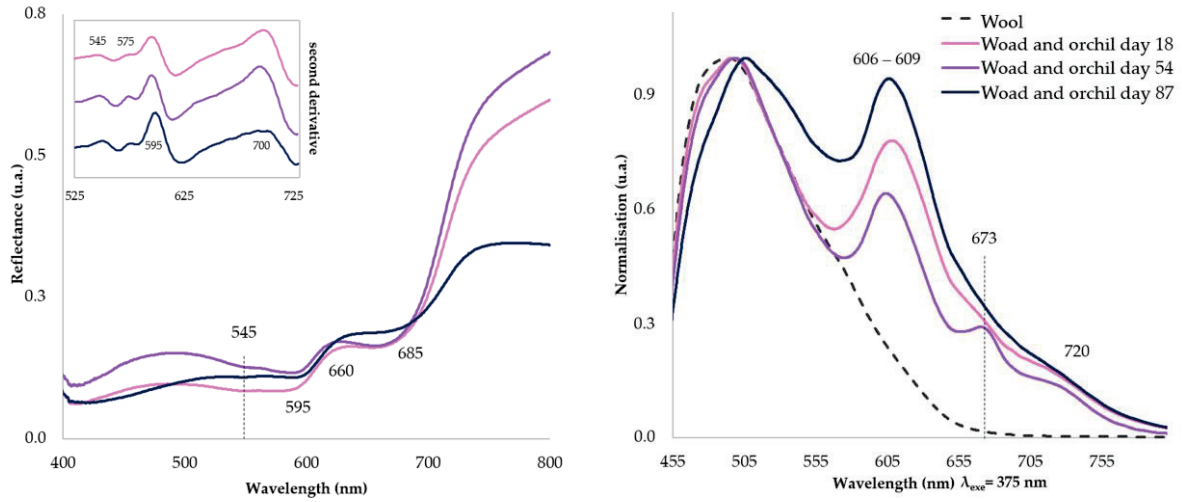


Figure 3. (**a**) Reflectance spectra of woad and orchil samples dyed after 18, 54, and 87 days of maceration. The upper left panel shows the second derivative of these samples as a function of wavelength. (**b**) Fluorescence emission spectra of the same three woad and orchil samples normalised to the natural wool signal (dotted line).

In conclusion, the acquired data from the manufactured samples revealed no significant spectral changes relative to maceration time, either for the orchils alone or when dyed on woad. The 54th day sample, characterised by the two main absorption bands at 545 nm and 595 nm associated with orchil, along with the absorption band at 700 nm characteristic of indigotin, was chosen as the reference for investigating the orchil-based violet in the tapestry.

3.2. Orchil Degradation Study

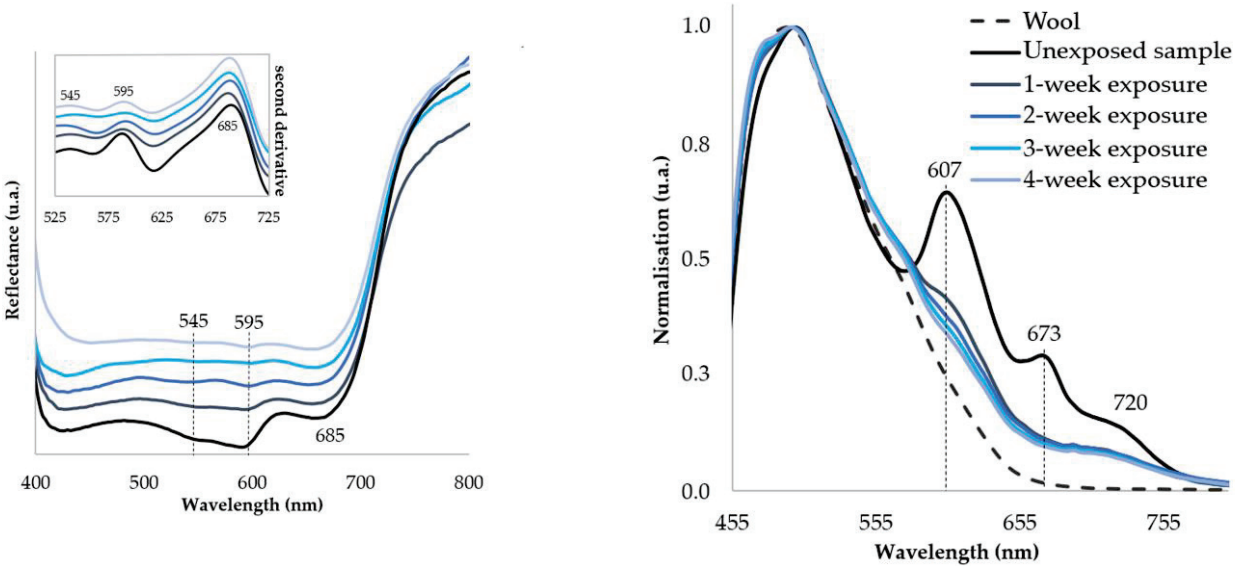
When analysing tapestries, we usually only have access to the front side exposed to light, which is often degraded. Therefore, spectral identification using databases recorded on fresh samples could be biased. The spectra of aged dyes should thus be added to the database. A natural ageing study was performed on the orchil and woad/orchil samples presented above after 18, 54, and 87 days of maceration.

The colourimetric measurements taken after 1, 2, 3, and 4 weeks of exposure for the six samples are presented in Table 2. All the ΔL, Δa, and Δb coordinates are available in Table S1. The orchil sample that macerated for 18 days showed a much more pronounced degradation than the other two samples. Despite the slight superiority of the delta E values of the 54-day sample throughout the exposure, the results were very close to those obtained after 87 days of maceration. This observation can suggest the presence of an optimal maceration threshold to obtain a more durable dye over time and is in agreement with the advice in the dye manuals, which tend to recommend an extended maceration period for orchil [23,34,35]. A similar trend was observed for samples dyed on woad.

Table 2. ΔE_{2000}* obtained after 1, 2, 3, and 4 weeks of exposure to light for samples of orchil dyed on natural wool and woad after 18, 54, and 87 days of maceration.

Sample	First Week	Second Week	Third Week	Fourth Week
Orchil day 18	9.9	12.5	13.5	17.2
Orchil day 54	6.4	8.3	8.6	10.4
Orchil day 87	4.6	7.3	7.6	9.6
Woad and orchil day 18	5.4	7.8	9.2	10.7
Woad and orchil day 54	5.2	8.8	8.3	9.1
Woad and orchil day 87	4.2	5.9	7.8	8.1

Figure 4a shows the absorption spectra of the woad orchil sample dyed after 54 days of maceration following exposure to light for 0, 1, 2, 3, and 4 weeks and their second derivative. A rapid and nearly complete disappearance of the absorbance band associated with orchil was noticeable after 4 weeks of exposure. Conversely, the absorption band for woad remained detectable even after 1 month of exposure. Similar observations were noted in terms of fluorescence emission (Figure 4b). The chlorophyll emission band was the first to vanish after the initial week [50], while the orchil-associated band gradually diminished over time. The woad emission band, already visible, remained unaffected by the accelerated degradation.



(**a**) (**b**)

Figure 4. (**a**) Reflectance spectra of woad and orchil samples dyed after 54 days of maceration unexposed and exposed to the light after 1, 2, 3, and 4 weeks. The upper left panel shows the second derivative of these samples as a function of wavelength. (**b**) Fluorescence emission spectra of the same four samples normalised to the natural wool signal (dotted line).

When the ΔE_{2000}* values of the different shades of violet (Table 3) presented in this study were compared after 1 month of exposure, there was a significant difference between the violet obtained from orchil and those obtained from madder, cochineal, and kermes. These three samples showed a ΔE_{2000}* below the limit of distinction (less than 3) [51], in contrast to what was observed with orchil (Figure S1). The significant difference in the lightfastness of these dyes is essential information for museum curators. Knowing the materials that make up cultural artefacts and their sensitivity to light will enable curators to take better care of them during their exhibitions.

Table 3. ΔE_{2000}* obtained after one month of exposure to light for samples of orchil, cochineal, madder, and kermes dyed on woad.

Sample	1-Month ΔE_{2000}*
Woad and orchil	9.1
Woad and cochineal	1.7
Woad and madder	1.2
Woad and kermes	2.0

3.3. The Identification of the Violet Colour of the Tapestry "La Vue"

As previously mentioned, the *La Vue* tapestry presents an important loss of colour when comparing the area of the Lady's skirt on the obverse and reverse sides (Figure 5).

This difference was also observed spectrally, as the absorbance spectra of the obverse and reverse of the tapestry (Figure 6) exhibited two different signals. In detail, the spectrum of the reverse back of the tapestry seems to indicate the mixing of an indigoid (absorption band at around 690 nm) [46] and a red dye (at around 550 and 595 nm). The absorbance band of the red dye, around 595 nm, seems to have disappeared.

(**a**) (**b**)

Figure 5. (**a**) Detail of the Lady's skirt on the front of the tapestry *La Vue* © Musée de Cluny. (**b**) Detail of the Lady's skirt on the back of the tapestry *La Vue*. The photo is from the restoration report [36].

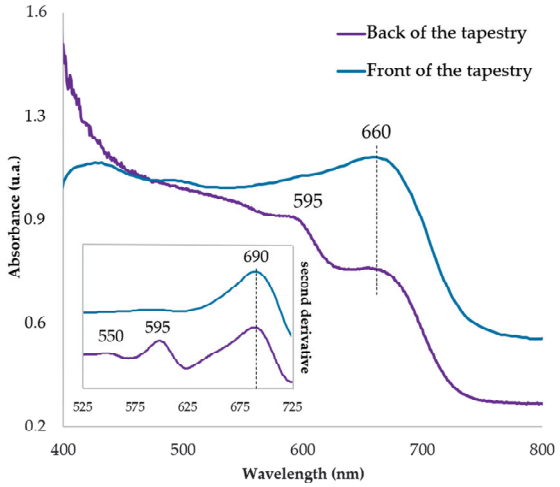


Figure 6. Absorbance spectra of the back and front of the tapestry. The insert panel shows the second derivative of these two zones as a function of wavelength.

The absorbance spectra of all violet dye recipes in our database were compared with the absorbance spectrum from the reverse side of the tapestry (Figure 7a). The characteristic absorption band of woad is discernible across all spectra, typically appearing around 660 nm. The comparison of the bands in the red absorption zone proved challenging because of their broad widths. Therefore, the second derivative of the spectra, shown in Figure 7b, was investigated to facilitate the comparison. This visualisation enabled the distinction among the bands present in mixtures containing cochineal, kermes, and madder, notably located at 570–580 nm and 710 nm, and those of the orchil/woad mixture and tapestry at 550 nm, 598 nm, and 690 nm. Therefore, thanks to the second derivative visualisation of the spectrum, it was possible to attribute the dyes used in the tapestry to a mixture of woad and orchil.

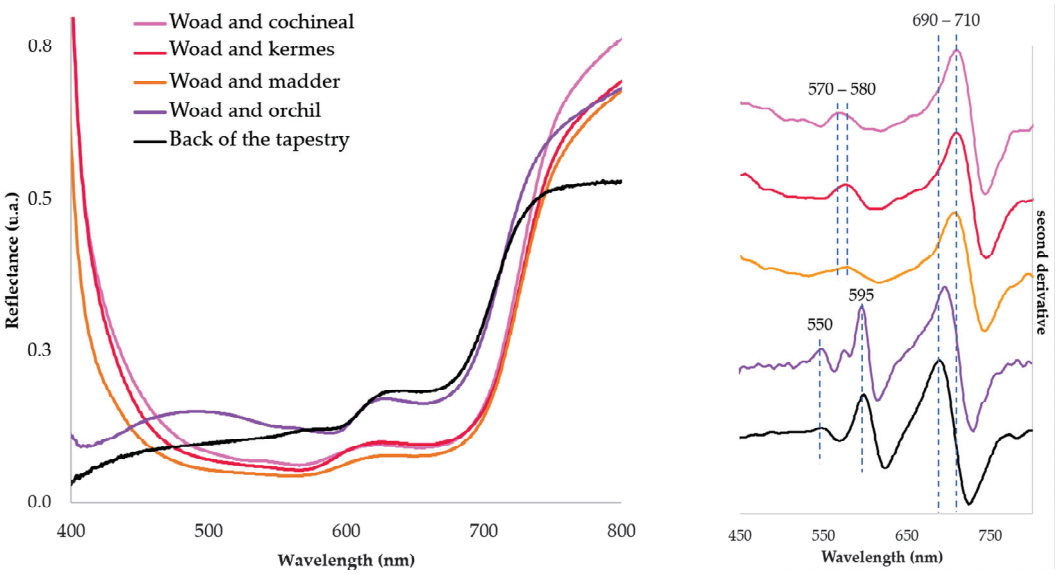


Figure 7. (**a**) Reflectance spectra of all the violet samples and the back of the tapestry. (**b**) The second derivative of the same samples.

Figure 8 compares the degraded spectrum of the orchil/woad sample to the spectrum obtained on the front side of the tapestry to validate this assumption. The spectra of the orchil/woad and those of the front or back of the tapestry appeared almost in perfect agreement. As mentioned in Section 3.2, the absorption bands of orchil tend to disappear when degraded, unlike those of woad, which remain stable. This initial approach to understanding the degradation of woad/orchil dyes provides new information on the Lady of the Unicorn tapestry and confirms the importance of identifying the components and products of degradation in order to assess the current state of conservation of the object [52].

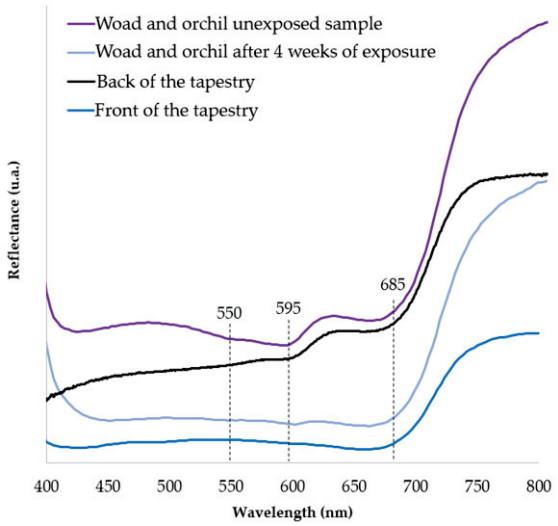


Figure 8. Reflectance spectra of woad and orchil samples dyed after 54 days of maceration, unexposed and exposed to the light after 4 weeks, and reflectance spectra of the front and back of the tapestry.

To complete the results, chromatographic analysis was performed on a thread collected from the back of the tapestry. The chromatogram at 485 nm depicted in Figure 9 illustrates the presence of three indigoid components. The major peak corresponds to indigotin,

observed at 30 min, with its distinctive absorbance band at 615 nm [53]. This is followed by indirubin at 32 min (λmax 545 nm) and isatin at 9 min, identifiable by their absorption maxima at 230 and 280 nm [53,54]. It was not possible to assign the other peaks to any of the known red dye molecules, including alizarin for madder, carminic acid for cochineal, or kermesic acid for kermes [19]. Neither of the main colouring molecules in orchil, namely, hydroxyorceins or aminoorceins [20], were identified on the chromatogram. However, it is interesting to mention that many other previous studies failed to detect orchil in the sample using this technique [20,55], whereas it was identified with spectroscopic techniques, such as that on the *Bible de Théodulfe* (9th century, Puy-en-Velay, France) [56]. Most likely, the difficulty in identifying this dye is related to the advanced state of degradation of the sample studied, which may have led to the loss of the distinct features of orchil, hindering its identification.

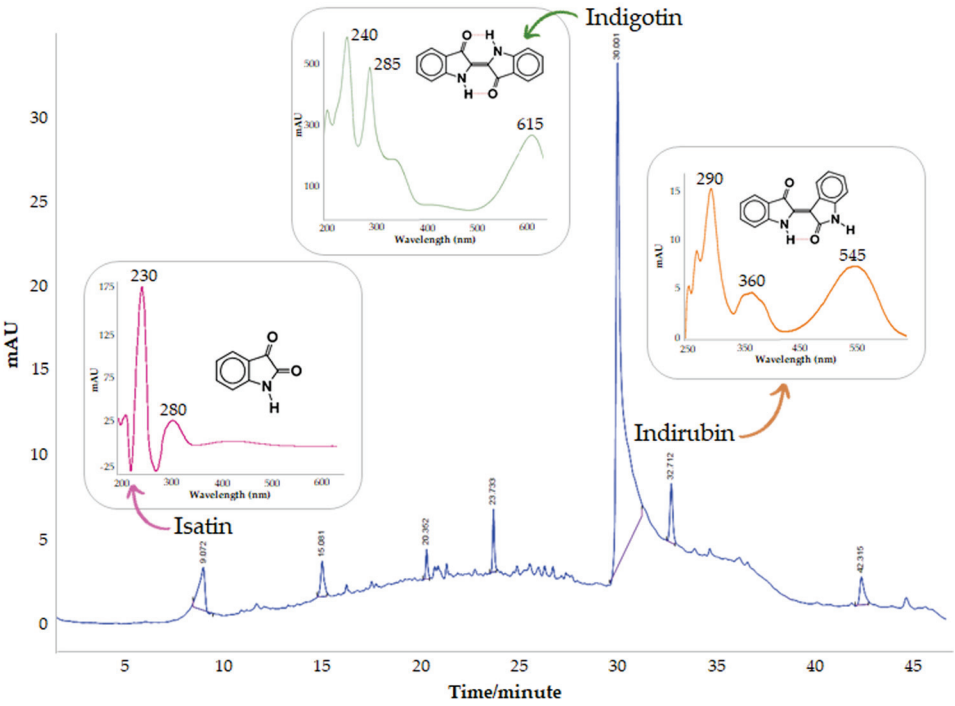


Figure 9. Chromatogram of the yarn sample from the back of the Lady and the Unicorn tapestry at 485 nm.

4. Conclusions

A spectroscopic examination of the Lady and the Unicorn tapestry La Vue provided valuable insights into the dyes used, shedding light on the observed colour variation between the front and back of the Lady's skirt. The method included the integration of a comprehensive set of spectroscopic data of orchil and woad/orchil on wool into the database of different dyes used in tapestry manufacture. This study identified woad and orchil on the violet skirt at the back of the tapestry, which had been preserved from light exposure. The artificial ageing study further clarified the dyes' lightfastness, revealing that longer maceration times enhance the dye's resistance to light. It was confirmed that the orchil sample on the woad exhibited significant light fragility compared with the other violet samples studied, with the red orchil colour degrading faster than the woad. The comparison of spectra from light-aged samples with those from the front of the tapestry strengthened the hypothesis of woad/orchil use. Unlike the spectroscopic methods, the chromatographic analysis of the sample taken from the back of the tapestry only identified blue dye molecules, most likely because of the advanced state of deterioration of the analyses that hindered the presence of orchil. To better understand and characterise the components present in the chromatogram in search of potential orchil degradation products,

chromatographic analyses should be performed on the degraded samples in our database. This should provide a better understanding of the mechanisms involved in the degradation of orchil and allow us to refine our analytical methods for future studies on cultural heritage objects. In this sense, the results of these contactless analyses are of great importance for the historical understanding of the tapestry. By identifying the dyes used at the time the tapestry was made, valuable information was obtained about the dyeing practices of the time and the financial resources of the commissioner, who preferred to use a fugitive dye such as orchil rather than the much more expensive shellfish purple.

This identification sheds new light on the tapestry, as the deterioration of the dyes influences our general perception of the work and can therefore affect its interpretation, as has already been demonstrated in the case of the tapestry *Verdure fine aux armes du comte de Brühl* [7]. Characterisation also provides valuable information for restorers and conservators, facilitating the conservation and restoration of the tapestry. Moreover, identifying the original colours is essential for understanding the artistic aspects, usage, and distribution of colours. It helps us comprehend the degradation phenomenon and explain it, raising awareness among conservators-restorers about this degradation. Now that the methodology has been established to detect this dye, the other five tapestries can benefit from it.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/heritage7070163/s1, Table S1: ΔL, Δa, and Δb coordinates and ΔE_{2000}* obtained before ageing and after 1, 2, 3, and 4 weeks of exposure to light for samples of orchil dyed on natural wool and woad after 18, 54, and 87 days of maceration; Figure S1: Orchil samples and woad/orchil samples dyed after 18, 54, and 87 days of maceration, unexposed and exposed to the light after 4 weeks.

Author Contributions: Conceptualisation, P.C.; methodology, P.C., C.M., F.G., A.M. and M.D.; formal analysis, P.C.; investigation, P.C. and C.M.; resources, C.M.; visualisation, P.C.; writing—original draft preparation, P.C., C.M., F.G. and A.M.; writing—review and editing, P.C., F.G., A.M, M.D. and R.C. All authors have read and agreed to the published version of this manuscript.

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Data Availability Statement: The authors will make the raw data supporting this article's conclusions available upon request.

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Unraveling a Historical Mystery: Identification of a Lichen Dye Source in a Fifteenth Century Medieval Tapestry

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Abstract: As part of a long-term campaign to document, study, and conserve the *Heroes* tapestries from The Cloisters collection at The Metropolitan Museum of Art, organic colorant analysis of *Julius Caesar* (accession number 47.101.3) was performed. Analysis with liquid chromatography–quadrupole time-of-flight mass spectrometry (LC-qToF-MS) revealed the presence of several multiply chlorinated xanthones produced only by certain species of lichen. Various lichen dye sources have been documented in the literature for centuries and are classified as either ammonia fermentation method (AFM) or boiling water method (BWM) dyes based on their method of production. However, none of these known sources produce the distinctive metabolites present in the tapestry. LC-qToF-MS was also used to compare the chemical composition of the dyes in the tapestry with that of several species of crustose lichen. Lichen metabolites, including thiophanic acid and arthothelin, were definitively identified in the tapestry based on comparison with lichen xanthone standards and a reference of *Lecanora sulphurata*, confirming the presence of a lichen source. This finding marks the first time that lichen xanthones have been identified in a historic object and the first evidence that BWM lichen dyes may have been used prior to the eighteenth century.

Keywords: lichen dye; xanthones; medieval art; textiles; LC-qToF-MS; dye analysis

1. Introduction

Prior to 1856, the year Perkin's discovery of mauveine brought about the synthetic dye industry, dyers turned to the natural world to satisfy a deeply human obsession with color. Centuries of demand, trial and error, and global exchange led to a rainbow of hues attainable from a relatively limited range of sources, used both alone and in infinite combinations [1,2].

Natural dyes can be derived from various components of plants, such as the roots of madder (*Rubia tinctorum*), the bark of brazilwood (*Paubrasilia echinata*), or the leaves of weld (*Reseda luteola*). They are also present in insects, such as cochineal (*Dactylopius coccus*) or kermes (*Kermes vermilio*). A limited number of dyes come from animals, such as the famous "Tyrian purple" extracted from mollusks in the *Muricidae* family.

A fourth category of natural dyes is derived from lichens and includes orchil (*Roccella* spp.), cudbear (*Ochrolechia tartarea*), and others. Despite their historical importance in the textile [3–8], culinary [9], and medical [10] industries, lichens are poorly understood by the general population. A lichen is not a single organism but rather a symbiotic partnership between a mycobiont (a fungus, also known as "lichenized fungus") and a photobiont (usually a species of algae, though in some cases cyanobacteria are present

instead or in addition to algae). The photobiont provides nutrients for the fungal partner via photosynthesis. In exchange, the mycobiont provides physical protection for the photobiont and produces secondary metabolites, such as xanthones, depsides, and chromones, with antibiotic, anti-microbial, UV-protective, and herbivore-deterrent properties (Figure 1) [11, 12]. Most of the known lichen metabolites, of which there are currently more than one thousand, are unique to the lichenized fungus and are not produced by other groups of fungi not involved in lichen symbioses [12–14]. Their collaborative relationship allows both partners to occur in extreme environments, such as extreme temperatures, ultraviolet (UV) radiation, or high concentrations of salt [15,16].

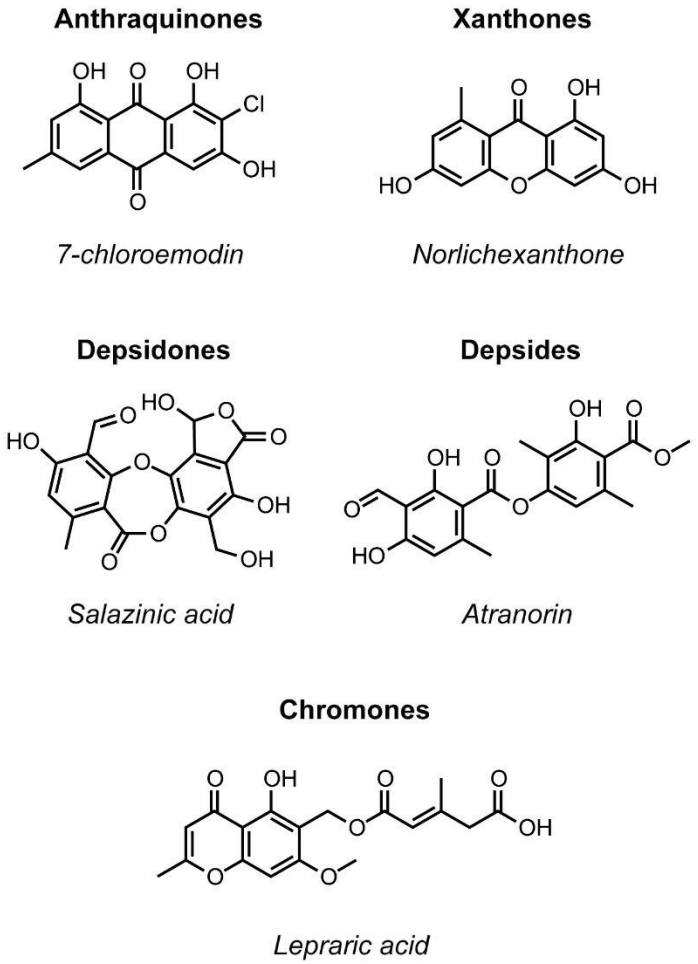

Figure 1. Several classes of secondary metabolites found in lichen.

Depending on their chemical composition and method of preparation, lichen dye preparation can be separated into two categories: the ammonia fermentation method (AFM) or the boiling water method (BWM). With AFM lichen, orsellinic acid depsides (the colorless precursors to orchil dyes) are converted into a bright purple or pink dye through a lengthy fermentation process using ammonia or, historically, urine. In contrast, BWM lichens produce their own colorants, such as atranorin, parietin, or usnic acid, which can be extracted in boiling water [8,17]. To the best of our knowledge, despite centuries of documentation indicating the global importance of lichen dyes, only AFM dyes have been identified in historic objects, using techniques such as Raman or SERS [18,19], fluorimetry [20], FORS [21], and LC-MS [22–24]. The absence of BWM dyes detected in historic objects may be explained by a combination of several factors, including the availability of reference materials, the relative stability of pigments, and a lack of research into the aging and degradation patterns of BWM-dyed materials.

In 2018, The Metropolitan Museum of Art (the Met) initiated a long-term project to study and conserve the *Heroes* tapestries, a series of hangings that depict notable figures from Christian, Jewish, and Classical traditions. The tapestry hangings with the five *Heroes* that survive of the original nine are a highlight of the permanent collection at The Cloisters and have been on display since their acquisition by the Met in the mid-twentieth century [25]. Little is known about the origins of the tapestries; though they were likely made for a wealthy patron connected to the French royal court in the early fifteenth century, it remains unclear exactly where, when, or for whom they were woven. Treatment and dye analysis of *Julius Caesar* ("*Caesar*") commenced in September 2022.

Scientific analysis of tapestries has been used to study a work's historical context [24,26,27], trace the history of intervention and repair [28,29], study degradation of dyes and fibers [30,31], and provide insight into how a work may have originally appeared [32]. Thirty-seven samples of dyed wool of various colors were removed from across the *Caesar* tapestry and analyzed by LC-qToF-MS. The results of the full dye analysis and additional information regarding *Caesar's* conservation and acquisition history are beyond the scope of this article and will be published elsewhere [33]. In the three dark brown samples that were analyzed, chlorinated metabolites deriving from an unknown lichen source were detected. Through a collaboration between researchers at The Metropolitan Museum of Art, The Field Museum of Natural History, and The Rennes Institute of Chemical Sciences, the identities of these compounds were confirmed by comparison to standard lichen metabolites and by analysis of a reference specimen. This study, which highlights the power of an interdisciplinary approach to art history, marks the first time that genuine lichen xanthones have been definitively identified in a historic object.

2. Materials and Methods

2.1. Julius Caesar (from the Heroes Tapestries), Accession Number 47.101.3

Among the oldest surviving medieval tapestries in the world, *Julius Caesar* belongs to the set of *Heroes* tapestries depicting notable figures from Christian, Jewish, and Classical traditions, only five of which have been recovered. Well before their acquisition, these tapestries had been cut apart into fragments and shaped into window curtains [25]. The fragments had to be re-pieced together before they could be displayed at The Cloisters in their current configuration [34]. This work shows Caesar, seated in the center of an elaborate architectural setting with a saber, spear, and crown, identifiable by the double-headed eagle of the Roman empire on his shield (Figure 2). He is flanked by musicians, foot soldiers, and attendants. Likely woven circa 1400–1410 in France or the Southern Netherlands, the tapestry spans 420.4 cm × 238 cm and was woven with wool warps and wefts. The tapestry is composed primarily of bright blues, greens, reds, and yellows, with darker blues, beiges, and browns providing visual contrast and dimensionality.

2.2. Materials

All commercially available reagents and solvents were used as received. All solvents are of analytical or LC-MS grade. High-purity water was provided by a Milli-Q water purification system.

2.3. Reference Material

A specimen of *Lecanora sulphurata* (Ach.) Nyl.: *Lecanoroid Lichens exs. 14* (F) was used for comparison. Reference standards of 3-*O*-methyl-2,4,5-trichloronorlichexanthone (thuringione) and 3-*O*-methyl-2,5,7-trichloronorlichexanthone, as well as acetone extracts of *Lecanora alboflavida* Taylor and *Lecidella asema* var. elaeochromoides (Nyl.) Nimis and Tretiach were provided by Joël Boustie at the Université de Rennes.

2.4. On-Fiber Dye Extraction Methodology

Dye extraction was performed with a process adapted from Mouri and Laursen [35]. Yarn samples of original weaving (approximately 2–5 mm in length) were distinguished

from restoration yarns by a textile conservator. Samples were then extracted with 40 µL of a 0.01 M oxalic acid (aqueous)/pyridine/methanol solution (3:3:4 $v/v/v$) in a 6 × 50 mm glass test tube. The sample was left to extract at room temperature for 30 min and was then heated at 55–60 °C for 30 min. The extract was then transferred to a microcentrifuge tube, and the sample in the test tube was rinsed with 40 µL methanol, which was added to the same microcentrifuge tube. A total of 60 µL of extraction solution was added to the test tube containing the sample, which was heated at 90–100 °C for 10 min, cooled, and transferred to the microcentrifuge tube. Again, the tube was rinsed with 40 µL methanol and the rinsate was transferred to the microcentrifuge tube. The extract in the microcentrifuge tube was dried inside a vacuum desiccator with a water aspirator. Once fully dry, the residue was vortexed with 4 µL DMF, followed by 16 µL of 0.1% formic acid in methanol/acetonitrile (1:1, v/v) and 20 µL 0.1% formic acid in water (for a total of 1:4:5 $v/v/v$ reconstitution solution). The tube was centrifuged at 12,000× g for 10 min, and 20 µL of supernatant was transferred to a 0.2 mL micro-insert autosampler vial (Shimadzu 220-97331-63) for injection (8 µL) onto the LC-MS system. For LC-MS analysis of the other polarity, 10 µL of reconstitution solution was added to the insert and vortexed and then transferred to the original microcentrifuge tube (with the remaining 20 µL of the sample), and the tube was again centrifuged at 12,000× g for 10 min. A total of 20 µL of supernatant was transferred to a new 0.2 mL micro-insert for injection (8 µL) into the LC-MS system.

Figure 2. *Julius Caesar (from the Heroes Tapestries);* wool warp, wool wefts; South Netherlandish, ca. 1400–1410; 165 1/2 × 93 11/16 in. (420.4 × 238 cm); The Metropolitan Museum of Art, New York, Gift of John D. Rockefeller Jr., 1947 (47.101.3). Image © The Metropolitan Museum of Art. The following annotations to the original photograph were added by the author: the individual fragments from which the tapestry was recreated are numbered. White boxes correspond to areas from which the dark brown fibers were sampled.

2.5. Preparation of Lecanora sulphurata for HPLC-ESI-qToF-MS Analysis

A total of 19.4 mg of lichen was removed from the reference sample with a clean razor blade and placed in a clean, 4 mL glass vial. A total of 1 mL acetone (HPLC grade) was added, and the sample was crushed and extracted at room temperature for 1 h. The extract was filtered with an Ultrafree-MC centrifugal filter (0.2 µm pore size, hydrophilic PTFE membrane, Millipore, Burlington, MA, USA), and the solvent was removed with an SP Genevac EZ-2 4.0 centrifugal evaporator (ATS Scientific Products; Warminster, PA, USA. Once fully dry, the residue was vortexed with 4 µL DMF, followed by 16 µL of 0.1% formic acid in MeOH/ACN (1:1, v/v) and 20 µL 0.1% formic acid in water (for a total of 1:4:5 $v/v/v$ reconstitution solution).

2.6. High-Performance Liquid Chromatography Electrospray Ionization, Quadrupole Time-of-Flight Mass Spectrometry (HPLC-ESI-qToF-MS)

The HPLC-ESI-qToF-MS system consists of a Bruker Impact II quadrupole Time-of-Flight mass spectrometer with an electrospray ionization source (Billerica, MA, USA) and a NexeraXR high-performance liquid chromatograph with two LC-20ADxr HPLC pumps, an HPLC gradient mixer, an SPDM30A diode array detector, a CTO-20AC column oven, a DGU-20A5R degassing unit, an SIL-20ACxr autosampler, and a CBS-20A communications bus module (Shimadzu, Columbia, MD, USA).

A Zorbax SB-C18 reversed-phase column (3.5 µm particle size, 2.1 mm I.D. × 150.0 mm, Agilent Technologies, Santa Clara, CA, USA) was used with a Zorbax SB-C18 guard column (3.5 µm particle size, 2.0 mm I.D. × 15.0 mm, Agilent Technologies, Santa Clara, CA, USA). A pre-filter (Upchurch ultra-low Volume pre-column filter with 0.5 µm stainless steel frit, Sigma-Aldrich, St. Louis MO, USA) was attached to the guard column. Chromatography was performed at a flow rate of 0.2 mL/min and a column temperature of 40 °C, with a gradient of 0.1% formic acid in Millli-Q water (mobile phase A) and 0.1% formic acid in methanol/acetonitrile (1:1, v/v) (mobile phase B). The gradient system was as follows: initial conditions of 90% A for 1 min, a linear slope from 90% to 60% A over 6 min, a second linear slope from 60% to 1% A over 23 min, holding at 1% A over 3 min, and then a linear slope to return to 90% A over 1 min and holding at 90% A for 18 min.

Internal calibration of the mass spectrometer was performed daily using 10 mM sodium formate solution. Sodium formate clusters were formed using a mixture of Milli-Q water, 2-propanol, formic acid, and 1 M sodium hydroxide (250:250:5:1, $v/v/v/v$).

ESI operating parameters were as follows: capillary voltage 4500 V, dry gas 8.0 L/min, dry heater 220 °C, nebulizer 1.8 Bar.

Chromatograms were smoothed using a Gaussian algorithm, with a width of 2s.

Operation of the HPLC and MS systems was performed using Compass otofControl Version 6.3.106 and Compass Hystar Version 6.2.1.13. Data analysis was performed using Compass DataAnalysis software Version 6.1.

3. Results

Dyes were extracted from the fiber using mild acid hydrolysis according to the method described in Section 2.4 and analyzed by LC-qToF-MS as described in Section 2.6. Dye analysis was performed to identify the dyes in all colors across all fragments of the tapestry, with a primary focus on the original weaving [33]. In total, thirty-seven samples were analyzed. Whereas most of the colorants used were typical medieval dyes (madder for red and weld or dyer's broom for yellow), three dark brown areas of the tapestry were identified as containing chlorinated norlichexanthone derivatives and subjected to further investigation (Figure 3). Though the dark brown yarns are particularly fragile and much of the original dark brown weft (including nearly all the double-headed eagle on Caesar's shield) has been lost, these samples were determined to be original and likely had a similar dark brown color originally. The chemical components related to the dark brown areas of the tapestry have been identified in Table 1.

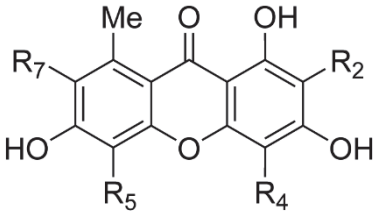

Figure 3. Basic structure of lichen metabolites derived from the norlichexanthone scaffold.

Table 1. Chemical composition of the brown dyes in fragments 3, 4, and 6 and the reference of *Lecanora sulphurata* extracted with acetone. Components are indicated as present (+), present in trace amounts (t), or not detected (-). [a] Is where references were not available and the concentration in the tapestry was too low for absorption measurements and UV data are left blank. [b] Due to the low solubility of indigo and its poor ionization in negative mode, indigotin was identified by the presence of isatin and by matching the retention time and the UV-visible spectrum.

#	Compound Name	RT (min)	$[M-H]^-$, m/z	Product ions, m/z	λ_{max}, nm [a]	Frag. 3	Frag. 4	Frag. 6	*Lecanora sulphurata* Reference
1	isatin	8.4	146.024	118	-	-	-	+	-
2	luteolin 7-*O*-glucoside	9.4	447.093	285	197, 253, 346	-	+	-	-
3	ellagic acid	9.6	300.999	284, 257, 245, 229, 173, 145	252, 366	-	-	+	-
4	*O*-methyl ellagic acid	11.3	315.015	300	-	+	+	+	-
5	luteolin	12.7	285.04	241, 199, 175, 151, 133, 107, 83	204, 253, 346	-	+	-	-
6	$C_{14}H_4Cl_4O_7$	14.8	422.863	381, 346, 318, 307, 289, 279, 251, 224	198, 249, 320, 366	-	-	-	+
7	alizarin	17.5	239.035	211, 195, 183, 167	247, 428	-	+	-	-
8	munjistin	17.6	283.025	239, 211, 195, 167	209, 246, 288, 430	-	+	-	-
9	indigotin [b]	19.5	261.067	260, 233, 217, 156	200, 239, 284, 609	-	-	t	-
10	$C_{14}H_6Cl_4O_6$	20.0	408.885	393, 381, 357, 329	211, 246, 317, 355	+	+	+	+
11	4,5-dichloronolichexanthone	20.6	324.967	290, 261, 233, 183	211, 246, 317, ~366	-	-	-	+
12	2,5-dichloronorlichexanthone	21.1	324.967	290, 261, 233, 183	197, 247, 316	-	-	-	+
13	2,4,5-trichloronorlichexanthone (arthothelin)	22.7	358.929	323, 295, 267, 259, 231	212, 249, 315	+	+	+	+
14	4,5,7-trichloronorlichexanthone (asemone)	23.8	358.929	324, 295, 267.0	248, 314, 352 (sh)	t	t	+	+
15	2,5,7-trichloronorlichexanthone (isoarthothelin)	24.5	358.929	324, 295, 267, 181, 163.0, 137.1	201, 250, 315, 350 (sh)	t	t	t	+
16	2,4,7-trichloronorlichexanthone	25.0	358.929	323, 295, 287, 267, 259, 231, 177, 149	201, 247, 314, 350 (sh)	-	-	-	+
17	2,4,5,7-tetrachloronorlichexanthone (thiophanic acid)	25.8	392.89	360, 329, 321, 301, 293, 264, 303, 265, 149	200, 250, 316, 355 (sh)	+	+	+	+

Table 1. *Cont.*

#	Compound Name	RT (min)	$[M-H]^-$, m/z	Product ions, m/z	λ_{max}, nm [a]	Frag. 3	Frag. 4	Frag. 6	*Lecanora sulphurata* Reference
18	$C_{15}H_9Cl_3O_5$ A	26.4	372.944	358, 330, 294, 266, 97	-	+	+	+	-
19	$C_{15}H_9Cl_3O_5$ B	27.5	372.944	358, 340, 294, 266	-	+	+	+	-
20	atranorin	27.5	373.093	177, 163, 133, 119, 105	208, 250, 319	-	-	-	+
21	chloroatranorin	28.5	407.054	211, 167, 163, 139, 131, 119	211, 248, ~350	-	-	-	+

All three dark brown samples that were sampled from the tapestry included components with isotopic patterns, indicating the presence of multiple chlorine atoms (Figures 4 and 5).

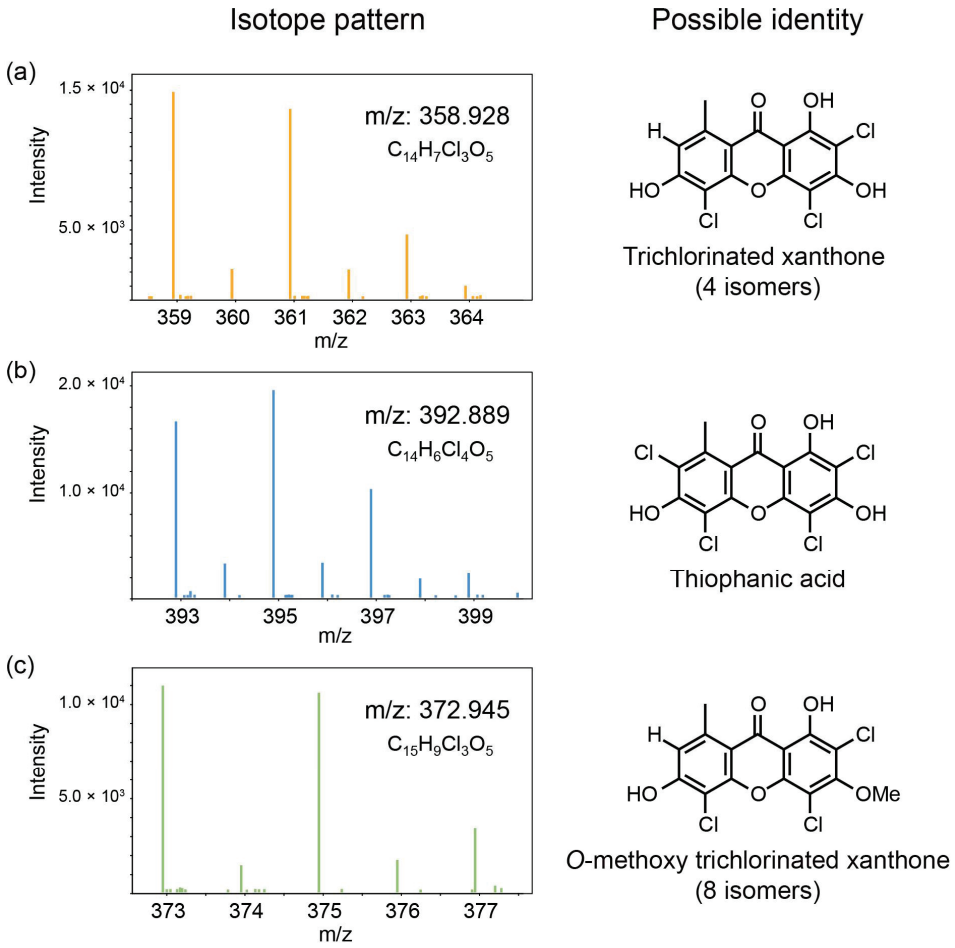

Figure 4. Isotopic pattern, exact mass and $[M-H]^-$ formula, possible chemical structure, and number of possible isomers for the components at 22.7, 23.8, 24.5, and 25.0 min: (**a**), 25.8 min (**b**), and 26.4 and 27.5 min (**c**).

Halogenated metabolites are not uncommon in nature [36,37], but few are present in common sources of natural dyes. Perhaps the best-known exception to this rule is 6,6′-dibromoindigo, a colorant found in shellfish purple and derived from mollusks from the *Muricidae* family [38].

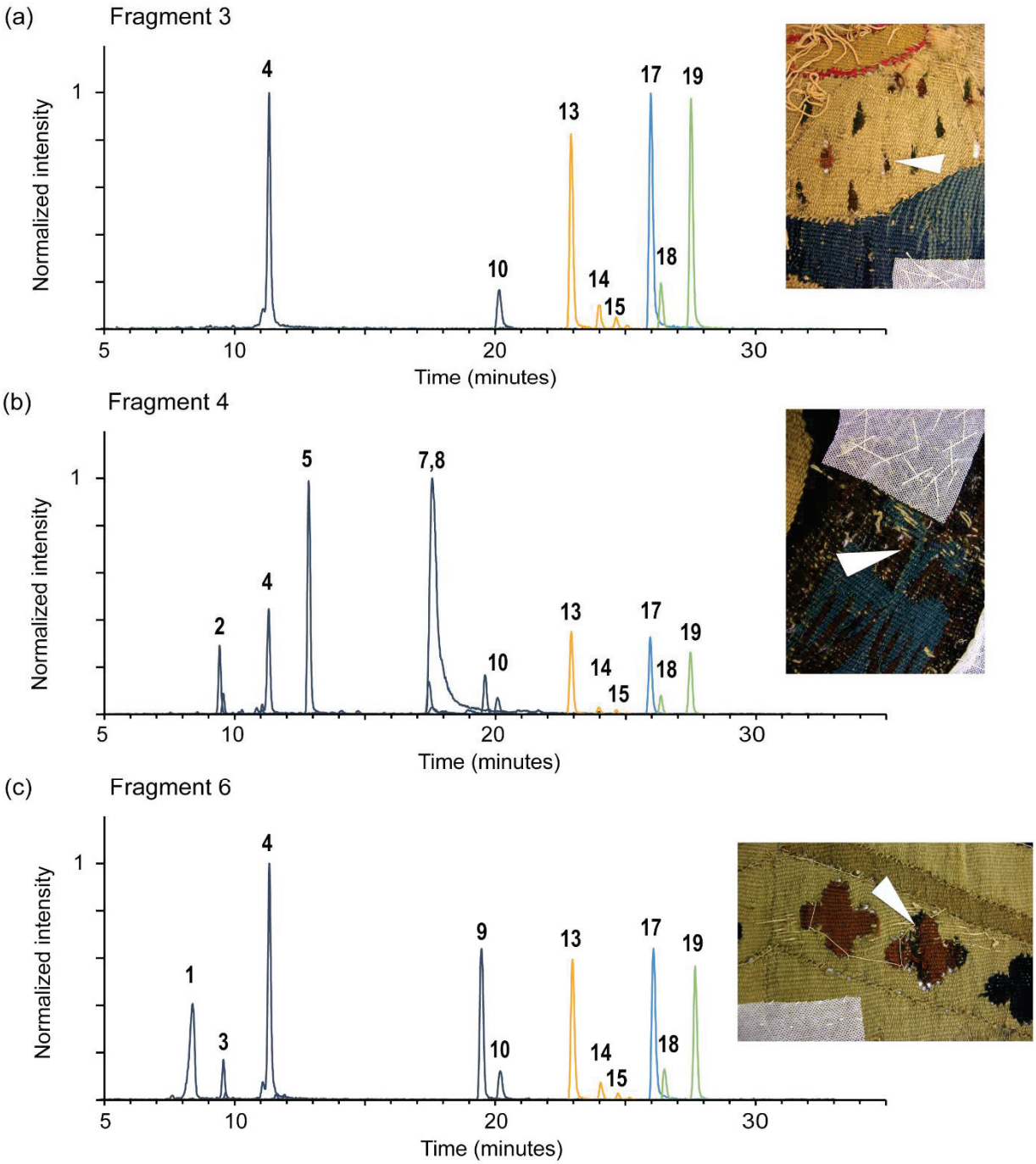

Figure 5. Extracted ion chromatogram (EIC) for colorants and lichen xanthones identified in the dark brown samples from fragments 3 (**a**), 4 (**b**), and 5 (**c**). The components are numbered corresponding to Table 1. The colors for compounds **13–15** and **17–19** correspond to the chlorinated xanthones in Figure 4. The white arrows in the image indicate the location from where the samples were taken (see Figure 2).

Based on accurate mass measurements and the isotopic pattern (Figure 4b), the component at 25.8 min was determined to have a chemical formula of $C_{14}H_6Cl_4O_5$ (error = 0.8 ppm), which corresponds to thiophanic acid (TA) **17**, a tetrachlorinated xanthone that is specific to certain species of crustose lichens, primarily those of the genera *Lecanora* and *Lecidella* [39,40]. In addition to potential fungicidal properties, TA absorbs light in the UVA range (315–400 nm) and is believed to function as a UV-protectant compound (Figure 6) [41]. In lichen, UV protectants often localize in the thallus, or upper portion of the lichen,

and act as chemical filters of UV light without blocking the visible light necessary for photosynthesis [16].

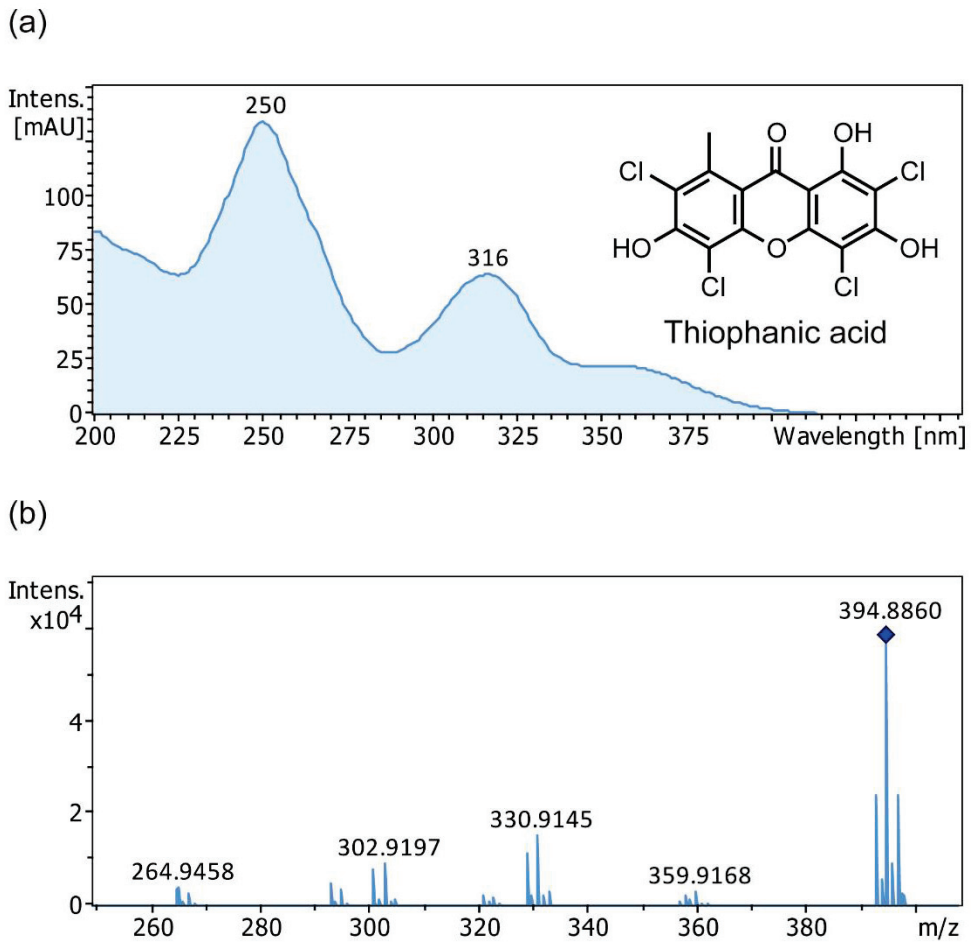

Figure 6. UV-visible spectrum (a) and MS/MS fragmentation spectrum (b) for thiophanic acid, **17**.

The other related components were also identified as trichlorinated xanthones, likely with similar functions, including three isomers of $C_{14}H_7Cl_3O_5$, (Figure 4a), and two isomers of $C_{15}H_9Cl_3O_5$ (Figure 4c).

Xanthones are a class of oxygenated heterotricycles present as secondary metabolites in plants, fungi, and lichens. Their pharmacological properties, including antimicrobial, anti-inflammatory, and antioxidant activity, have been studied in depth [42]. Although xanthones are not lichen-specific compounds, a rare biosynthetic pathway in lichen leads to substitution patterns not found in other species; the lichexanthone type pattern is a 1,3,6-trihydroxy-8-methylxanthone, whereas plants produce mostly 1,3,5- or 1,3,7-trihydroxyxanthones [43,44]. Furthermore, of the naturally occurring xanthones in nature, only a small percentage contain one or more chlorine atoms [45]. The majority of these chlorinated xanthones are synthesized exclusively by lichen [44,46].

For lichenologists, the identification of secondary metabolites has long been critical to the taxonomic classification of lichen species, with species identifiable by a "chemosyndrome", or set of characteristic metabolites. A chemosyndrome often consists of a major metabolite and minor "satellite" compounds with similar biosynthetic origins [39,47]. Researchers use spot tests, chromatography, or even mass spectrometry to identify characteristic components, allowing morphologically similar species to be distinguished, which in some cases is necessary for species identification. There is, therefore, a record of chemical information for known lichen species, including those that have been documented as commonly used for dyeing, such as *Ochrolechia tartarea* ("cudbear"), *Parmelia saxatilis* ("light crottle" or "salted shield lichen"), and *Letharia vulpina* ("wolf moss") [1,8].

Lichens cannot be easily cultivated, and are, therefore, geographically constant, though their populations can be threatened by overharvesting and environmental changes. Furthermore, because secondary metabolites allow lichens to adapt to their environments, chemical composition is often closely related to geography [48,49].

Considering the specificity of lichen metabolites and the little information available about the *Caesar* tapestry, we hypothesized that the identification of the metabolites could offer a rare look into where or how the materials of the *Caesar* tapestry were sourced. However, despite an abundance of literature detailing lichen dye sources across the world, to the best of our knowledge, there are no accounts of TA-containing lichen species used for dyeing, either industrially or domestically [1,6–8,50,51]. This conclusion can be made after cross-referencing the available literature on lichen dye species with the extensive literature detailing the chemical composition of lichen species [13,14,39,40,44,52–54]. Apart from orchil lichens, most of the lichen species used for dyeing were employed in small, local industries, and the visual similarity of many lichens makes differentiation between species difficult in the absence of modern analytical techniques. A species of lichen could certainly have been used without knowing or recording its precise identity.

Within Europe, one of the only TA-containing species with common and large enough populations to be identified and collected for dyeing is *Lecanora sulphurata*, a species that is common in the Mediterranean area and does not occur in Central Europe [53,55]. Critically, chemotaxonomic reports have identified TA and several trichlorinated xanthones as major and minor components of this species.

To investigate the chemical composition of the specimen of *Lecanora sulphurata*, a small area was scraped off and extracted for an hour in acetone. LC-qToF-MS was used to identify the metabolites. The major components present in the reference sample were chlorinated xanthones and two depsides: atranorin **20** (a pale-yellow pigment), and chloroatranorin **21**.

Due to the condition and size of the samples, the concentration of the metabolites present in the tapestry was generally not high enough to be identified by their UV-visible spectra but could be validated by retention time and MS/MS fragmentation (Figures 5 and 6b).

TA was indeed a major component of the reference, allowing for the confirmation of its presence in the tapestry sample (Figures 7 and S1). Three of the trichlorinated xanthones from the tapestry were also present in the reference species, which were compared with reference material and identified as trichloronorlichexanthone isomers arthothelin **13**, asemone **14**, and isoarthothelin **15** [39,53]. In contrast with the available literature, the reference specimen also contains the fourth isomer of $C_{14}H_7Cl_3O_5$, **16**, but the chemical composition of this species has been reported to differ slightly between populations. The reference was not found to contain any isomers of the methylated xanthones ($C_{15}H_9Cl_3O_5$) that are present in the tapestry. We ruled out the possibility that methylation in the tapestry samples could have resulted from the extraction process by treating the lichen reference with the same mildly acidic extraction process used to extract the dye from the fibers (Figure S2). Oxalic acid extraction led to the appearance of peaks that may correspond to monoaromatic depside hydrolysis products [56]. However, no methylation was observed.

Finally, a molecule with the chemical formula of $C_{14}H_6Cl_4O_6$, **10**, possibly an oxidized form of TA based on MS/MS fragmentation, was found to match a compound present in trace amounts in the tapestry (Figure S3). This compound has not yet been reported as a lichen metabolite, and further experimentation will be necessary to identify it.

With the goal of identifying the two isomers of $C_{15}H_9Cl_3O_5$ present in the tapestry, two of the eight isomers (3-*O*-methyl-2,4,5-trichloronorlichexanthone and 3-*O*-methyl-2,5,7-trichloronorlichexanthone) were obtained in pure form as reference standards. References of *Lecanora alboflavida* and *Lecidella asema*, which contain 3-*O*-methyl-2,4,5-trichloronorlichexanthone (thuringione) and 3-*O*-methyl-2,5,7-trichloronorlichexanthone, respectively, were prepared as extracts in acetone and analyzed for comparison (Figure S4). The chemical composition of these references can be found in Table S1. Based on retention time, compound **19** at 27.5 min could be 3-*O*-methyl-2,5,7-trichloronorlichexanthone. Unfortunately, the isomers have nearly identical

MS/MS fragmentation, and without knowing if the remaining six isomers co-elute, we are currently unable to definitively identify these components in the tapestry.

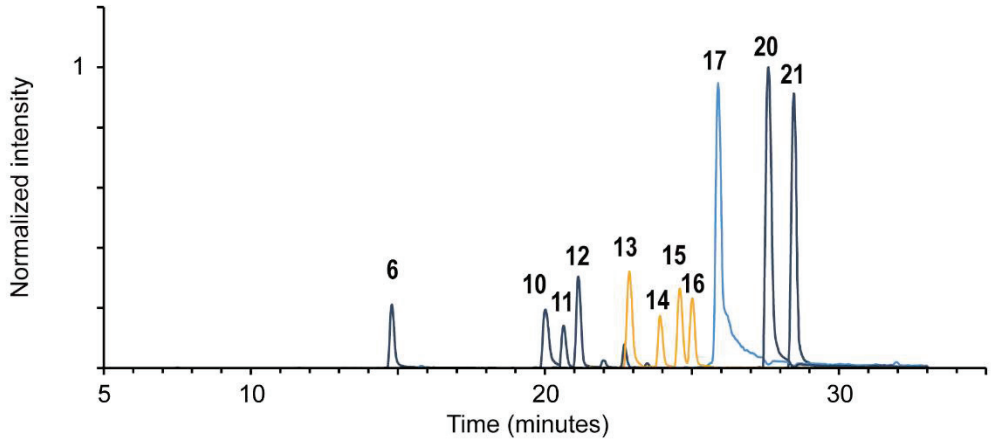

Figure 7. Extracted ion chromatogram (EIC) of acetone extract of *Lecanora sulphurata*.

Finally, since the process of dyeing can also lead to changes in composition, a small amount of lichen (*Lecanora sulphurata*) was heated with a sample of wool in Milli-Q water for several hours to observe the effects of the BWM process that may have been used. After boiling, the dye was then extracted from the fiber with a mildly acidic oxalic acid extraction and analyzed by LC-qToF-MS. The major component that was present in the wool sample was TA, with atranorin and chloroatranorin having almost completely degraded (Figure S5). This supports our hypothesis that the stability of chlorinated xanthones relative to lichen pigments may allow them to serve as markers for lichen dyes.

4. Discussion

Due to the age of the tapestry and the condition of the dyes, it may not be possible to definitively identify the lichen source (or sources) present in the dark brown dye. The reference specimen of *Lecanora sulphurata*, chosen as a candidate for its composition and population size, contained several of the chlorinated xanthones present in the tapestry, but not all. Most lichens containing these chlorinated xanthones are crustose lichens that grow on saxicolous or vegetal supports and would have to be scraped off the substrate to be used as a dye. Crustose lichens often form patches, and many species can have similar morphology. Therefore, more than one species could have been mixed, possibly along with parts of the support (see the composition of *Lecanora alboflavida* extract, Table S1).

Regardless of the species, the presence of distinct, lichen-specific xanthones raises the question of why a lichen source would be used to make the dark brown dye of the tapestry. No lichen dye source in the TA chemosyndrome has been documented, but it is possible that a lichen species could have been used as a dye without recording its identity. This is especially likely in the medieval era before the development of detailed taxonomy and chemical tests to distinguish between morphologically similar species of lichen.

Although chlorinated xanthones form yellow crystals, they have not been reported to function as dyes. However, the use of lichens that contain depside pigments, such as atranorin, is well-documented [6,8,57]. In fact, atranorin is one of the main colorants found in crottle, a famous Scottish lichen dye made from *Parmelia saxatilis* that can be used for dyeing golden or reddish brown on wool. Many lichen species contain atranorin, including those producing chlorinated xanthones. No such depsides were detected in the tapestry, but this could be due to the age and condition of the tapestry. Ester-linked (β)-orsellinic derivatives, such as atranorin, have been shown to be photolabile under high exposure to UVA and UVB [58]. It is, therefore, possible that the lichen species was selected as a dye for the presence of a pigment that has since faded.

Lichens are also "substantive" dyes, meaning they can be used on their own or combined with other dyes without the need for mordanting [8]. This quality may be

explained by their high iron content: lichens contain an average of 5.16 milligrams of iron per gram of dry material, in contrast with 0.30 milligrams for land plants [59]. Crustose lichens access iron from the substrate by disintegrating it through chemical and mechanical means [60,61]. Some lichen compounds possess chelating properties with regard to metals. The high iron content of the lichen may also explain the poor condition of the dark brown areas, some of which (in the case of the double-headed eagle on Caesar's shield) have almost completely disintegrated and could not be analyzed.

The dark brown color of the wool and the co-occurrence of hydrolyzable tannins in all three of the samples raise the additional possibility that the lichen was considered a quality of the tannin dye rather than its own organism. Tannin dyes such as oak bark yield lighter, more beige hues unless combined with an iron mordant, which is necessary to achieve darker browns, grays, and blacks [1]. If the lichen was growing on the bark of a tree used for dyeing, the lichen and the tannin source could be added simultaneously to the boiling dye bath as an ingenious way to avoid spending time and material on a separate mordanting step. Not only would the iron contained in the lichen modify the color and improve its longevity, but any pigments produced by the lichen (such as atranorin) may have provided additional nuance to its appearance. Professional dyers were—and still are—experts at using the materials provided by nature to achieve a complex range of hues. Even if they did not understand the precise chemical processes at play, they would have recognized this combination as a source of a fast, dark brown dye.

Whether sought out for its own dyeing capabilities or combined with its substrate, the lichen source in the tapestry appears to be the first example of a non-orchil lichen dye that has been identified in a historic object. Though the earliest literature evidence of BWM dyes is from the eighteenth century, some experts believe they have been in use for much longer [8]. One possible explanation for this gap in the literature could be that medieval dyers had a different understanding of their materials than modern researchers. They may have considered the lichen and its substrate not as separate organisms but as a beneficial union, much like the symbiotic relationship between mycobiont and photobiont that allows the lichen to survive. Although it is not possible to establish a dyer's intent through scientific means, these findings present the first indication that BWM lichen dyes could have been employed as early as the medieval period, centuries before the first literature evidence appears.

Though an initial goal of this study was to investigate the tapestry's origins, the novelty of evidence supporting the use of BWM lichen dyes during the medieval period makes interpreting these findings challenging. It is not currently possible to precisely identify the species from which the lichen metabolites were derived. However, we hope these findings will initiate further research leading to new discoveries and additional information. We are currently investigating brown dyes from other medieval tapestries in the Met's collection to understand the prevalence and use of lichen dyes.

5. Conclusions

High-resolution LC-qToF-MS was performed on yarn samples from a rare fifteenth-century tapestry from The Cloisters collection at The Metropolitan Museum of Art, suggesting the presence of a lichen dye source. Comparison with reference material confirmed the identity of several lichen metabolites. Though we could not identify any known lichen pigments in the tapestry, chlorinated xanthones, such as thiophanic acid, may prove to be valuable markers for certain lichen dyes due to their high stability and the uniqueness of their isotopic patterning.

This study presents the first time that lichen xanthones, and possibly a BWM lichen dye, have been identified in a historic object. This is a significant finding that raises additional questions about the use of lichen and the production of artistic materials during the medieval period. This work would not be possible without high-resolution mass spectrometry (HRMS), which can be used to identify unknown colorants at low concentrations and enables molecular-level insights into the use of organic dyes and pigments in art objects.

The insights provided by HRMS highlight the strength of a micro-invasive approach which, while requiring sampling from a precious cultural object, can uncover chemical fingerprints, even at low concentrations, of a complex mixture of known and unknown dyes. These deep insights have profound implications for understanding how art objects were made centuries ago and are especially critical for objects with lost or non-existent records, such as *Caesar* and the remainder of the *Heroes* tapestries.

The question of which lichen species (or mixture of lichen species) could have ended up in a French or Southern Netherlandish tapestry presents a compelling mystery and the need for additional experimentation. LC-qToF analysis of tapestries from the South Netherlands or France, particularly those with well-documented provenance, may allow us to understand how common these dye sources were and if their use was geographically specific or widespread. Work is ongoing at the Met to analyze the brown dyes in medieval tapestries, including but not limited to the rest of the *Heroes* tapestries from the series. Trace amounts of arthothelin, a trichlorinated xanthone identified in *Caesar*, have already been detected in another tapestry from the Met's collection, this time from the sixteenth century (data not shown). The results of this research may provide connections between objects that were previously hidden and deepen our understanding of the ancient art of lichen dyeing.

Furthermore, though there has been extensive analysis of orchil/AFM dyes, BWM lichen dyes in general have received minimal attention. This is unfortunate, considering the local nature of BWM dyes and the chemical specificity of lichen species. A thorough investigation of these lichen species, using both non-invasive and micro-invasive techniques, may reveal markers for local lichen dyes, which can be useful in cases where an object's origins are uncertain. We hope that these findings will spark renewed interest in these fascinating colorants within the fields of conservation science and art history.

Finally, this work highlights the power of a collaborative approach to studying works of art. The detection of unusual molecules in a medieval tapestry led to the unexpected connection of researchers from across the globe with specializations in lichenology, natural product chemistry, conservation science, and art history. Like a tapestry born from individual warps and wefts, the breadth and depth of this collective expertise unites as we weave a new history of lichen dyes from a single serendipitous discovery.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/heritage7050112/s1, Figure S1: *Lecanora sulphurata* extracted with acetone; Figure S2: *Lecanora sulphurata* after extraction with 0.01 M oxalic acid (aqueous)/pyridine/methanol solution (3:3:4 v/v/v); Figure S3: UV-visible spectrum (a) and MS/MS fragmentation spectrum (b) for the unidentified compound **10** with chemical formula $C_{14}H_6Cl_4O_6$ at 20.2 min in both the tapestry, *Lecanora sulphurata,* and *Lecidella asema*; Figure S4: 350 nm UV chromatograms for *Lecanora sulphurata* (top), *Lecanora alboflavida* (middle), and *Lecidella asema* (bottom) extracted with acetone; Table S1: Chemical composition of three lichen references: *Lecanora sulphurata, Lecanora alboflavida,* and *Lecidella asema*; Figure S5: 350 nm UV chromatograph of *Lecanora sulphurata* after boiling with wool for 3 h followed by mild extraction with oxalic acid.

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Conflicts of Interest: The authors declare no conflicts of interest.

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