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Special Issue Reprint

Dyes in History and Archaeology 41

Edited by
Marei Hacke, Sara Norrehed, Joanne Dyer, Jo Kirby, Art Proaño Gaibor,
Ilaria Degano, Zvi Koren and Edith Sandström

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Preface

Dear Colleagues,

This Special Issue features contributions from the conference DHA41. Dyes in History and Archaeology (DHA) is an annual international conference that focuses on the academic discussion of dyes and organic pigments which have been used in the past. Every year since 1982, this meeting has drawn together conservators; curators; (technical) art historians; craftspeople; artists; independent scholars; and scientists and academics from museums, universities, research centers and other public or private institutions. Their common interest is to delve deeply into the history, production, application, and properties of organic colorants, as well as their analytical characterization and identification, often in textile objects, but also in other substrates as well as painted surfaces. In the autumn of 2022, the 41st DHA conference was hosted by the Swedish National Heritage Board in Visby. This was the first DHA conference held in Scandinavia, and it attracted over 50 in-person participants, 70% of whom travelled from other countries to attend this conference on the beautiful island of Gotland. During the morning sessions of the three-day conference, the attendants in Visby had the opportunity to participate in workshops, tours, and activities. The afternoons were reserved for the scientific conference sessions, with all lectures broadcasted live and over 650 online participants. The book of abstracts is published on the DiVA portal (Digitala Vetenskapliga Arkivet), and many of the presented posters are available for download from the conference program. We are very grateful to the authors of the following 16 articles in this Special Issue for submitting their manuscripts and allowing us to put together a publication that presents the fascinating breadth of research into Dyes in History and Archaeology.

For more information about the future meetings of the Dyes in History and Archaeology group, see https://www.dyesinhistoryandarchaeology.com.

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Editorial

Dyes in History and Archaeology 41: Reflections on the Conference and Its Assembly of Articles

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1. Introduction

In 1982, eight people—archaeologists, colour scientists and analysts—met in a room in King's Manor, York University, to discuss a subject of significance to them all: the analysis of dyes on archaeological and historical textiles. The meeting generated so much interest that another was held the following year, and the event has been repeated every year ever since (Figure 1). The name of the meetings, Dyes in History and Archaeology (DHA), represents the broad range of interests of the participants, as reflected in the sixteen articles in this Special Issue of *Heritage*.

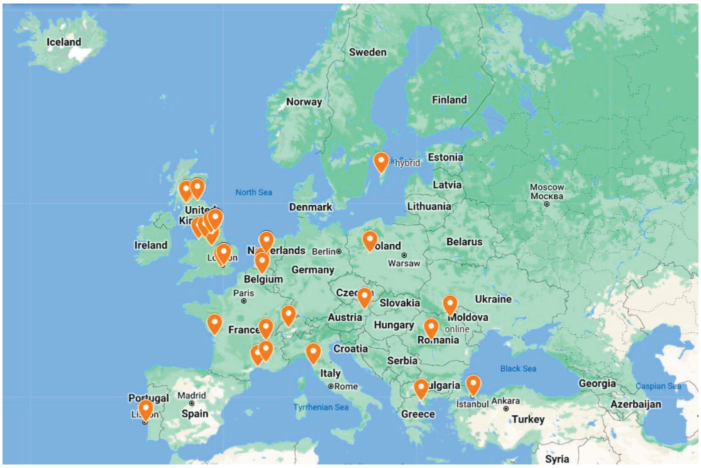

Figure 1. DHA conference locations 1982–2022. (Map assembled by Marei Hacke using Map data ©2023 Google, INEGI).

An important feature of DHA conferences is that they are interdisciplinary: those attending include historians, archaeologists, conservators, curators, scientists, independent scholars and craftspeople from museums, research centres, universities, archives and other institutions. Their central interest is dyes, both naturally occurring and synthetic, and their history. The analysis, characterisation and identification of dyes and the development of analytical methods may form a substantial part of the programme of events, but always within a historical context: the item being studied was created for a reason; it had a purpose and was made in a particular way under certain local circumstances or regulations and based on the availability of raw materials. Such a broad base of interests in the audience stimulates discussion, an important and desirable feature of any conference.

2. Reflections on the Conference in Visby

In the autumn of 2022, the 41st DHA conference was hosted in person and online by the Swedish National Heritage Board with financial support from the Marcus Wallenberg Foundation for International Scientific Collaboration. The 60 or so participants attending the conference in person in the medieval city of Visby on the island of Gotland, Sweden, could join in with practical workshops and guided tours as well as the scientific sessions that were also accessible to the online audience of over 650 registered participants (Figures 2 and 3). Prior to the conference, the book of abstracts was published https://urn.kb.se/resolve?urn=urn:nbn:se:raa:diva-6625 (accessed on 27 June 2023) and posters were made available for download (https://www.raa.se/in-english/events-seminars-and-cultural-experiences/dyes-in-history-and-archaeology/publication-dha41/ (accessed on 27 June 2023)). We are very grateful to the authors of the following 16 articles in this Special Issue of *Heritage* for submitting their manuscripts and allowing us to put together a publication that presents the fascinating breadth of research into dyes in history and archaeology.

Figure 2. Impressions of the practical workshops and tours held at the 41st DHA conference. (Photos: Sara Norrehed, Kathrin Hinrichs Degerblad and Elyse Canosa, CC BY).

The 41st DHA conference was the first to be held in Scandinavia, and several of the papers have a Scandinavian theme. Scandinavia has a long tradition in the arts and crafts, including the production and dyeing of textiles. Some dye sources could be found growing locally, but, like other regions of Europe, Scandinavia also relied on the trade of goods, exporting products in which the Scandinavian countries were rich and importing materials necessary for dyeing or painting for which there was no local equivalent. The island of

Gotland lies in the Baltic Sea, east of the Swedish mainland. In medieval times, Visby, with its natural harbour, dominated Baltic sea trade until the formation of the German Hanseatic merchant association in the mid-12th century, and still played a role thereafter. The history of the Hanseatic trading association can be found in many cities all around the Baltic coast, from Novgorod in the east, through the sound between Denmark and Sweden, or over land from Lübeck, west to the North Sea and on to cities in Norway and northwestern Europe. The goods traded undoubtedly included materials necessary for the textile and colour industries, and archival and other sources record the economic importance of the international trade in dyes and associated materials.

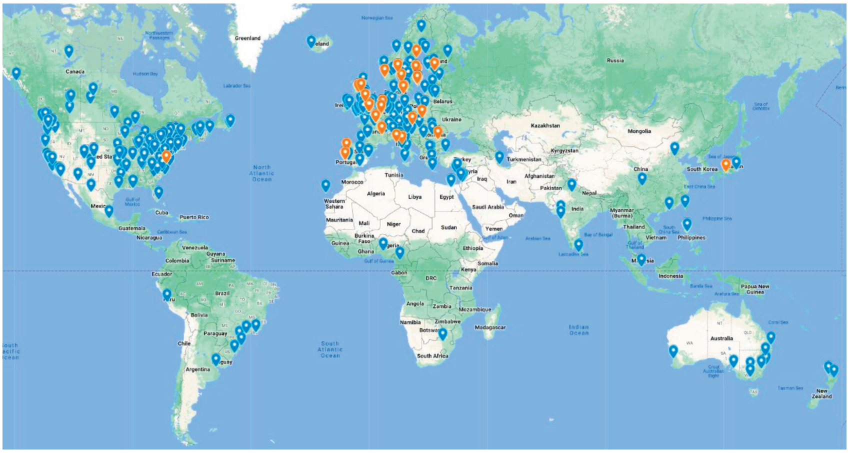

Figure 3. Places of registration for participants at the 41st DHA conference, in person (orange) and online (blue). (Map assembled by Marei Hacke using Map data ©2023 Google, INEGI).

3. Assembly of Articles in This Special Issue

To take an 18th-century example of the significance of trade, Margaret Knudtzon describes how the increased import of dyes and pigments into Norway during this period indicates a growing consumer society, a cycle probably driven by increased exports. The import of indigo from tropical regions increased during the 18th century. Imported cochineal, madder and brazilwood catered to different uses for dyeing red: from the luxury end of the market, represented by cochineal, to more everyday purposes, represented by the widely used brazilwood. Probate and other records also indicate a growing preference for more brightly coloured clothing as the 18th century progressed, a move away from the sombre colours of the previous century. The author demonstrates that, as both luxury and consumer goods, imported pigments and dyes had a range of values to society: material, economic, aesthetic and psychological [1].

The 18th century was also a time when intellectual and scientific curiosity was driving discovery and progress in many fields, not least the study of plants. In Sweden, Carl Linnaeus developed a system for the hierarchical classification of plants and animals, based on shared observable physical features. The consistent binomial naming of plants and animals he developed is still in use today. His studies included dye plants, but this study was greatly developed by one of his students, Engelbert Jörlin, whose dissertation was first published in 1759. Jörlin described both local Swedish plants and imported dyes, including the scale insect dyes and shellfish purple. Regina Hofmann-de Keijzer and Matthijs de Keijzer provide a detailed interpretation of Jörlin's work, arranged by colour and including the current taxonomic names of the dye sources: taxonomy has moved on since Linnaeus's day [2].

Eighteenth-century indigo-dyeing recipes, earlier archival sources and the traditional processing and couching of woad, the European source of the indigo dye, have been extensively studied by Dominique Cardon to obtain a quantitative estimate of the amount of woad actually grown and used and also the efficiency of the indigo vat process, assessing the contributions of both woad and imported indigo. Hisako Sumi compared the use of the couched woad in dyeing with *sukumo*, dyers' knotweed, used in Japan, which is processed in a rather similar way. The bacterial species responsible for the indigo reduction in the dye vats were also studied. Zvi Koren studied the development of indigotin, indirubin and isatin in fresh and couched woad and *sukumo* using high-performance liquid chromatography. All this has been put together to present a fascinating study on a dye of considerable importance [3].

By 1800, advances in the very new science of chemistry had led to the development of the earliest synthetic dyes and the discovery of new inorganic pigments. The huge growth in the use of synthetic dyes during the later 19th and 20th centuries was yet to come, however, and in practice, the transition between natural and synthetic dyes was quite gradual. This is demonstrated in two papers describing the continued use of naturally occurring dyes well into the 20th century in one case and the transition itself in the other. The preliminary study described by Athanasia Tsatsarou and co-authors drew on a large number of documentary sources and interviews carried out during fieldwork to record dyeing methods, traditions and the natural dyes used in the 19th and early 20th centuries to decorate clothing. Altogether, a great many plants were used across Greece, some well-known, and others quite unusual. Botanical dictionaries enabled the researchers to identify plants known under local names in different regions [4].

The work described by Irina Petroviciu and co-authors also has an anthropological significance in that the embroidered shirts examined have recently been accepted as part of the UNESCO National Inventory of Active Intangible Cultural Heritage Elements. The embroidered decorative bands over the shoulders of the shirts examined, all from the same region of Romania and dating from between the 1850s and the 1930s, are traditional in design, but analysis by liquid chromatography with diode array detection (HPLC–DAD) and, in some cases, coupled mass spectrometric examination revealed the change in the dyes used over time. In some examples from the late 19th century, a mixture of natural and synthetic dyes had been used, but soon synthetic dyes, with their popular bright colours, entirely replaced natural dyes [5].

It is important to remember, however, that while synthetic dyes were still in their infancy, fundamental research was also carried out on one of the most important natural dyes, that extracted from madder root. The most significant work took place in France and resulted in considerable improvements in both dyeing and pigment technology. However, research into madder dye for the production of pigments was also carried out in England from the beginning of the 19th century, exemplified by the work of the company founded by William Winsor and Henry Newton in 1832. Madder recipes are the subject of study in two funded projects, 'REDiscovering madder colours: Science & Art for the preservation and creation of cultural heritage' (2022.02909.PTDC) and 'Magic Lantern—Study, Safeguard, Uses and Reuses in 19th-Century Portugal' (PTDC/ARTPER/1702/2021), and the first experimental results are described by Tiago Veiga, Vanessa Otero and co-authors. They prepared rose-coloured madder pigments following three recipes, examining the results by spectrometric methods and high-performance liquid chromatography (HPLC). They were also able to compare their pigments with a 19th-century tube of Winsor & Newton Rose Madder oil paint by means of micro-Fourier transform infrared spectrometry (FTIR) and microspectrofluorimetry, and one gave a satisfyingly similar result [6].

By the end of the 19th century, a vast number and variety of synthetic dyes were being manufactured and their availability was spreading across the globe. This is demonstrated by Diego Tamburini and co-authors in an examination of the dyes used in the mounting textiles for three traditional Korean paintings—one, a rare example of portraiture, dating from the 18th century, the other two, a two-panel and a twelve-panel screen painting, from the late 19th century. As all were undergoing conservation treatment, it was possible to examine them via fibre optic reflectance spectroscopy (FORS), which indicated the areas from which it would be valuable to take a sample for analysis by means of high-performance liquid chromatography coupled with diode array and tandem mass spectrometry detection (HPLC–DAD–MS/MS). As expected, the earlier painting contained natural dyes, including indigo, sappanwood, amur cork tree and safflower. Sappanwood was also present in the later two-panel painting, along with indigo and a tannin in the twelve-panel screen, but Methyl Violet 3B, Methyl Blue, Fuchsin and Benzopurpurin 4B were also identified, an interesting result which helped to confirm the dating of the two later paintings [7].

The sheer number and variety of synthetic dyes appearing in the late 19th and early 20th centuries have presented challenges for analysts, not least because the methods of manufacture did not necessarily result in a pure product. This is particularly the case for analysts faced with a large collection of relatively early synthetic dyes, some of which are poorly labelled or unlabelled. Irene Bilbao Zubiri and Anne-Laure Carré were confronted with such a problem in a collection of synthetic dyes held at the Musée des Arts et Métiers, Paris, to be studied as part of the European Research Council (ERC) 'Project Chromotope, the 19th Century Chromatic Turn'. The dyes, which were probably used for educational purposes, are listed in a hand-written notebook, but as some of the dyes are unlabelled, their identity is unknown. The authors used electrospray ionisation mass spectrometry (ESI-MS) and Fourier transform infrared spectrometry (FTIR) to study a selection of labelled dyes, partly for later comparison with the unknown samples, and partly to assess their state of conservation. Some of the results indicated an impure product or a mixing of dyes, possibly before the dyes were marketed [8].

The use of liquid chromatography alone or coupled with a mass spectrometric method has been the principal analytical method for the examination of dyes for a number of years, backed up by spectrometric methods. However, mass spectrometric methods can be used without any previous chromatographic separation, as seen in the Chromotope Project analyses and in the two papers described below. Desorption electrospray ionisation mass spectrometry (DESI-MS), discussed by Edith Sandström and co-authors, is an ambient method whereby no preparation of the sample is necessary; electrically charged solvent droplets are directed onto the sample, in this case silk or wool dyed with a natural dye. Charged droplets containing dissolved and ionised dye are desorbed from the surface and transferred to the mass spectrometer inlet. The system was originally set up using a sample dyed with the synthetic dye Rhodamine B, and showed promising results with the direct dye turmeric, but it needs to be modified for mordant- or vat-dyed samples. However, the possibility that the method could be used in the examination of textiles printed with complex designs, non-invasively and with minimum damage to the fabric, is very attractive [9].

Direct analysis in real time mass spectrometry (DART-MS) is also carried out directly on the sample without previous treatment under normal pressure conditions, but in the case of very ancient, fragile archaeological samples, this is a challenging analysis to perform. Study of Tumulus MM, the tomb of the Phrygian King Midas or his father dating from the 8th century BCE, has been ongoing since its excavation in 1957. Initial results on the study of the textiles were reported in 2007 and 2010; intriguingly, the fragments of what appeared to be tabby cloth were actually skeletal lattices of goethite, α-FeO(OH) (yellow ochre). Using DART-MS, Mary Ballard and co-authors finally managed to identify madder and indigo on some of the textile fragments, revealing a sophisticated early dyeing technology [10].

Even with the aid of sophisticated analytical techniques and the wisdom contributed by archaeologists, historians and other colleagues, the results of scientific examination may still leave questions to be answered. This is demonstrated by three articles in this collection. Textile finds from the 13th century in south-west Finland are rare, and thus the examination of wool textile fragments from a 13th-century grave in Lieto Ristinpelto, discussed by Krista Wright and co-authors, was of particular interest. Indigo, probably from imported woad, was identified on several of the textiles, in many cases together with an unidentified orange dye. The orange dye, or others of very similar constitution, has been found on other Finnish textile finds from around this date, often in combination with indigo; clearly, the unidentified dye contributed towards a desirable colour combination. However, it is not known if this is an unknown local dye, or if the components seen are the consequence of deterioration caused by the burial conditions or were generated by sample extraction conditions used during HPLC analysis. Yellow dyes are rarely identified on textiles found in these burial circumstances, but unusually, a yellow flavonoid, luteolin, was detected on dark-red textile fragments. Here, too, the red colorant could not be identified. Much still remains to be explained about these intriguing results [11].

A different state of affairs is represented by the khipu cords examined by Lucrezia Milillo and co-authors. These bundles of knotted cords are described as a three-dimensional system of communication used by the Incas and earlier cultures as a means of encoding information. However, apart from the recognition of a decimal system, the means by which the position and spacing of the knots, the fibre types, the mixing of fibres and the wrapping of the cords, the colours and other features encoded and conveyed information is still unknown. This paper, in which two Wari khipus at the Museum of World Culture, Gothenburg, were studied using multiband imaging, X-ray fluorescence (XRF) and HPLC–MS, describes the first time the nature of the colours present has ever been examined scientifically. Some fibres were undyed; an iron mordant was used with some dyes, including a pink; the dyes used included cochineal, indigo and an unknown yellow; and the presence of the iron mordant on a particular thread within a strand of wrapped cord helped to indicate a more complicated pattern of coloration than the present condition of the cords might suggest. The results as a whole reveal a more complex picture than previously realised and a reassessment of earlier hypotheses proposed may be required [12].

The article by David Peggie and co-authors focussing on an unusual and unidentified pigment in a 13th-century panel painting from Arezzo, Italy, provides the third example. Recent conservation treatment on Margarito d'Arezzo's *The Virgin and Child Enthroned, with Scenes of the Nativity and the Lives of the Saints*, in the National Gallery, London, revealed yellow foliate decoration on the original red paint of the border below mid-19th-century repaint. Most of the scientific examination of the painting was carried out by means of fibre optic reflectance spectroscopy (FORS) and macro X-ray fluorescence scanning (MA-XRF); only very limited sampling was possible. A tiny sample of the original paint of the border could be examined via energy dispersive X-ray analysis in the scanning electron microscope (SEM–EDX) and other techniques. The decoration was painted using the golden-yellow arsenic sulfide pigment orpiment, over which was a yellow glaze containing a yellow lake pigment. Examination of documentary sources revealed that simple mixing of a plant dye with a white mineral was probably the principal way of making yellow lake pigments at this time; the unusual aspect was the presence of syngenite, a potassium calcium sulfate mineral, as the substrate. No firm conclusion could be reached as to whether syngenite had always been the substrate or was an alteration product formed during the pigment manufacture or at some other stage during the life of the painting [13].

Non-invasive methods of examination available today, such as X-ray fluorescence and hyperspectral imaging, particularly those that scan the object, are able to provide a wealth of information about the construction of the work, its condition and materials present. The examination of three 16th-century tapestries in the Royal Collection, Hampton Court Palace, UK, by means of hyperspectral imaging, described by Constantina Vlachou-Mogire and co-authors, is particularly interesting in this context, as the authors were able to use model samples prepared and dyed as part of the Monitoring of Damage to Historic Tapestries (MODHT) European research project between 2002 and 2005 as standards for comparison. Apart from the preliminary characterisation of the dyes used, the use of false colour images revealed some areas of restoration, while scanning using infrared radiation (VNIR and NIR) of certain areas that appeared to be a uniform colour revealed the use of different dyes [14].

The natural indigoid dyes, shellfish purple and indigo itself, provide particular fascination for both dyers and analysts. Two papers in this Special Issue of *Heritage* examine points of interest with the shellfish purple dye, 6,6′-dibromoindigo. Distinction between the three species of Mediterranean mollusc known to produce a purple dye and to have been used in Mediterranean regions in Antiquity, *Hexaplex trunculus*, *Bolinus brandaris* and *Stramonita haemastoma*, is based on the proportions of the isatinoid, indigoid and indirubinoid constituents and their brominated derivatives present. Zvi Koren describes a simple and useful formula to distinguish between dyes obtained from these three species, based on HPLC analysis of the dyes in archaeological samples, together with a ternary diagram, with axes indicating the colours of the dyes, in which the results of the analyses tabulated in the paper are plotted [15].

Keith Ramig and co-authors examine the strange fact that wool dyed with 6-bromoindigo (monobromoindigo), which is blue-violet in colour, turns blue when heated in water at 60 °C. Not only that, but further experiments also showed that wool dyed purple with dibromoindigo heated in water in the same way became redder in colour, and these changes appeared to be permanent. Chemical or physical changes in the molecules were ruled out as the cause; the possibility of aggregation of the molecules during dyeing remained, however. An elegant experiment showed that a change in the size of the aggregates upon heating in a polar solvent, water, is the cause of the colour change [16].

4. Conclusions

The variety of topics discussed in the papers included in this Special Issue of *Heritage* are typical of the range of subjects presented at Dyes in History and Archaeology conferences. The trade in dyes and their place in the economy of a society are rarely discussed, however; the paper on the trade in colorants in 18th-century Norway is therefore particularly welcome. The work of Engelbert Jörlin on dye sources available in Sweden, following on from Carl Linnaeus's work on the taxonomy and naming of plants and animals, is indicative of the intellectual climate in 18th-century Sweden. These papers are also examples of topics presented at the meeting that are relevant to the region, another feature of DHA conferences. The textile fragments in the 13th-century grave in Lieto Ristinpelto, Finland, provide a third example.

Many of the papers have several authors, a common feature in the scientific field. It is noticeable, however, that in these papers, the collaboration is often between authors from rather different disciplines: perhaps a combination of art or textile historians or archaeologists, conservators and scientists (Figure 4). As the subject of the discussion, the artefact, is often part of a museum collection or undergoing special conservation treatment, this is not surprising. The effect, however, is to provide a degree of breadth and insight to the discussion that is unique to such transdisciplinary studies and very apparent in several of the papers.

Until recently, non-invasive methods of examination have been more widely used on painted works than on dyed textiles, and the use of the scanning systems available is to some extent limited by the cost of the equipment. These are more likely to be found in museums, where there is a whole collection to be studied, and university research departments. Several papers in this collection demonstrate the value of examining an artefact using a non-invasive method before any samples are taken for more precise analysis, and it is certainly true that, depending on the method used, interesting and unexpected features of the artefact may be revealed: perhaps an early restoration or a change in the composition or materials used. Textiles are generally less complex in their three-dimensional structure than paintings, on the whole, but examination via a non-invasive method, scanning or not, may still reveal interesting features, including structural features, that are not obvious at first sight. The identification of organic colorants, in pigment form or as dyes, by non-invasive means can be challenging, however, more so than with inorganic pigments; this is particularly the case for yellow dyes.

The editors have found the wide-ranging topics in this group of articles, typical of DHA presentations, very interesting and enjoyable. We hope readers find something unexpected and thought-provoking in them as well. The enduring achievement of DHA meetings is that they act as a place to bring colleagues from many different disciplines together in a way that is at the same time intellectually stimulating, entertaining and friendly. We look forward to the continuing success of these meetings in their ability to unite subject areas in such a positive way.

Figure 4. Transdisciplinary authors and audience at the 41st DHA conference; a still from the film https://www.raa.se/2022/10/roster-fran-den-forsta-internationella-fargkonferensen-i-skandinavien/ (accessed on 27 June 2023. Film: Erik Larsson, CC BY).

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Increased Imports of Colorants and Constituent Components during the 18th Century Reflects the Start of the Consumer Society in Norway

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Abstract: The start of the consumer society in Norway is examined by studying the increased imports of colorants and their constituents during the 18th century. Based on historical customs records, 82 imported pigments and dyes, 27 binders and additives and nine mordants and auxiliaries are presented. Imports increased significantly in the middle and at end of the century, representing two chromatic "revolutions". This was especially evident for lead white and indigo; being the only particularly white and blue pigments used for painting and dyeing, respectively. Red dyes at different prices and properties (brazilwood, madder and cochineal) met the demands for red textile coloring in different social groups. The study presents a comprehensive overview of colorant imports and provides new insights in the development of consumption in Norway. Colorant imports were probably initiated by a supply-driven positive feed-back loop as a result of increased export trade. This was followed by a demand-driven loop, involving increased domestic trade, product preferences, "fashionability", consumer culture, economic conditions and enlightenment. A model is presented that can contribute to a further understanding of the start of the consumer society in the second half of the 18th century in Norway.

Keywords: 18th century; consumer goods; consumer society; colorant; dye; import; mordant; Norway; pigments; positive feedback loop

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1. Introduction

A consumer society is characterized by an increased use of new consumer goods. McKendrick, Brewer and Plumb showed in their 1982 book *The Birth of a Consumer Society* how the increased consumption of goods in England before the industrial revolution represented a consumer revolution [1]. Studies of probate records indicate that the increase in the number of clothing and household items in England started already in the 16th century and reached a peak around 1680–1720 [2]. Today, historians agree that a consumer society in Europe developed gradually over many years [3–5]. Some of the extensive historiography on the development of western consumer societies is summarized in Appendix A. In order to understand the development of the consumer society, emphasis has been placed on the importance of social and economic factors, and there has been a debate on the importance of supply and demand factors. As part of this debate, the present study has used colorant imports during the 18th century to analyze the development of the consumer society in Norway.

Colorants have been used as consumer and luxury goods for many centuries. Norwegian Vikings used an abundant amount of imported colorants both for decoration and dyeing [6,7]. Unn Plahter demonstrated the oldest known use of indigo in Norway on altar frontals from 1250–1350 [8]. Tropical indigo had already almost completely replaced the use of woad in Norway in the 17th century [9], which describes the close Norwegian trade relations with Europe. Norwegian export products such as timber, copper, klipfish and stockfish became important driving forces for European trade. The start of the Norwegian consumer society in the 18th century must be seen in the context of increased trade and the import of new consumer goods. During the 18th century, Norway experienced a color revolution when new imported colorants partly replaced the use of local produced pigments and dyes. Increased imports of colorants can therefore shed light on the start of the consumer society in the 18th century in Norway.

Based on digitized product lists from the Norwegian customs records, this survey provides an overview of color imports to Norway during the 18th century. This may be of interest within the disciplines of archaeology, building maintenance, conservation, ethnology and museology, as well as the disciplines of art, cultural, economics and textile history. Paint pigments and textile dyes have not previously been studied extensively with regard to the start of the consumer society. The present longitudinal study of imported colorants to Norway highlights that increased imports occurred in the middle of the 18th century, with a significant further increase in imports at the end of the century. Furthermore, factors and mechanisms are discussed which may partly clarify how a consumer society started in Norway in the 18th century [10].

2. Materials and Methods

The present study is based on imported goods declared at Norwegian customs offices and registered in customs records. Selected customs protocols have been transcribed from Gothic script and digitized as part of the project *Historical customs and ship call lists* [11]. The digitized product lists *alle varer* are available on the Internet, based on the protocols for 1685, 1686 and a selection of years during the 18th century, as well as digitized import data from trade statistics of 1835 [12]. Since only selected years have been digitized, the present study does not provide a complete evaluation of the annual imports throughout the 18th century. However, the results for a range of different colorants from these selected years provide a representative longitudinal picture of the flow of colorant items throughout the century.

From 1537 to 1814 Norway was part of the Kingdom Denmark-Norway. Goods registered in the customs records were mostly imported from European countries, and to a lesser extent from Denmark and other domestic customs ports. The colorants were imported to 25 different customs ports, mainly in Southern Norway. The largest custom ports of Bergen, Christiania (Oslo), Drammen and Trondheim contributed to most of the imported goods. Table 1 shows the years with the complete and "most" complete records for these ports (1686, 1731, 1733, 1754, 1756, 1786, 1788, 1790, 1792 and 1794) [12]. For five of these years data are missing or incomplete for Bergen, and for either Christiania, Drammen or Trondheim, data are missing for one of the years (Table 1). Additional information is available for Trondheim, where import data have been digitalized for several consecutive years. Dashed graph lines in the figures indicate a lack of data between the recorded years. When presenting the graphs, emphasis has been placed on the most complete registrations, but in cases where the imports for adjacent years show similar import quantities; these years have also been included. There are some sources of error with regard to the digitized product lists, including varying designations in units and under-reporting due to different names of the goods [13]. Smuggling, in particular, is a major under-reporting factor, which may have been as high as 20% [14]. However, the reported values are most likely comparable from year to year [15]. Colorant prices are stated in the customs records for only some years and goods. Most of the goods were weighed in pounds (Norwegian *pund*) of approximately 0.49 kg.

Some colorant items had multiple uses. Potash and sumac were imported in much larger quantities than other colorant items. Potash may have played a small role in dyeing to modify alkalinity, and sumac as a brown dye. However, they were probably mostly used in the glass industry and for tanning, respectively; in this study, they are therefore not included in calculations of colorant items. Other examples of agents with multiple uses were minium (red paint mostly used for ship-bottom paint), gallnuts (colorant, mordant but also used as ink), and saffron (the most expensive colorant at 8.6 daler/pound, probably almost exclusively used as a spice).

Table 1. The table gives an overview of the years with digitized product lists from the customs records for the largest custom ports Bergen, Christiania (Oslo), Drammen and Trondheim. The dark fields show customs records transcribed completely, the light fields show partially transcribed customs records and the white fields show customs lists that are missing.

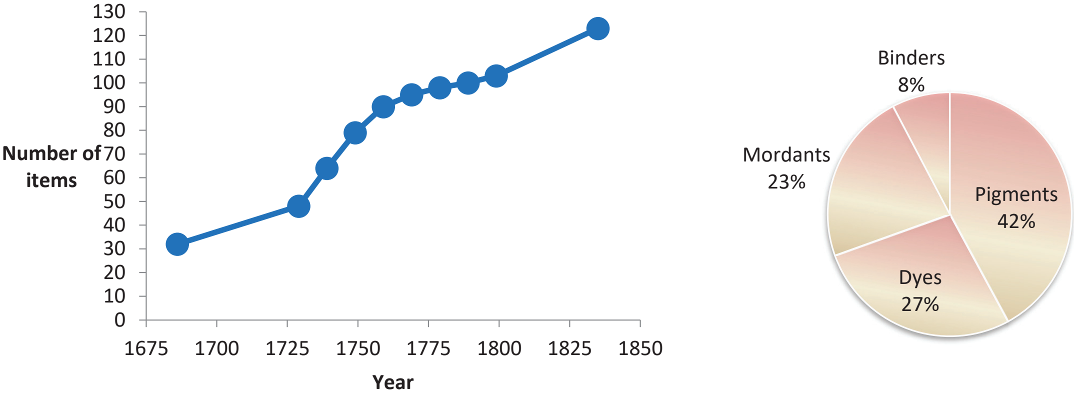
Town	**1686**	**1731**	**1733**	**1754**	**1756**	**1762**	**1774**	**1786**	**1788**	**1790**	**1792**	**1794**
Bergen	🟩				🟩		▨	🟩	🟩	🟩	🟩	🟩
Christiania	🟩	🟩	🟩	🟩	🟩	🟩	▨	🟩	🟩	🟩	🟩	🟩
Drammen	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	▨	🟩
Trondheim	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	▨

Historical descriptions have been studied with regard to the use of the colorants. During the first part of the 18th century, the best known Norwegian topographic descriptions in the broad sense are from 1743, based on responses to questions from the Danish Chancellery [16–20]. These descriptions provide a picture of Norwegian social conditions in the first part of the 18th century. In addition, local topographic descriptions, historical descriptions in travelogues and other historical literature throughout the century have been studied to provide information on the use of imported colorants. However, these descriptions are based on the reports of literate people and reflect mostly the view of civil servants.

3. Results

A total of 118 colorant items (Appendix B) were identified for paint and textile dyeing, of which 82 were pigments and dyes, 27 binders and additives (including constituents such as siccatives, diluents, resins and varnishes) and nine mordants and auxiliaries. As shown in the Appendix B, some products were used for several purposes. In all, 29 colorant items were imported in 1685/1686, a further 69 during the 18th century, and 20 more in 1835. A total of 65 colorant items with more than 10 registrations are used to calculate the quantity of imports in the 18th century. Data on price were also recorded for 61 of the examples. For some colorants, such as verdigris, dyer’s buckthorn and Prussian blue, the distinction between pigment and dyes can be arbitrary. Cobalt, lichen and tar are mentioned as export goods and Danish red, alum and lime as domestic goods (Section 3.5).

The number of imported colorants and constituents increased throughout the 18th century, with a large increase between 1730 and 1760 (Figure 1a). Figure 1b shows the distribution percentage of imported amounts of pigments, dyes, mordants and binders. Measured in weight, about 50% more paint pigments (622,576 pounds, one Norwegian *pund* approximately 0.49 kg) than textile dyes (405,749 pounds) were imported. The amount of pigments for house painting (brown red, caput mortuum, carbon black, Danish red, earth pigment, English earth, lead white, minium, yellow ochre) was approximately 20 times larger than the pigments used for decorative art. Linseed oil is not included among the binders, because it was imported in original volume units (converted to liters [21]. Linseed oil was mostly produced in Norway. This may explain why the imported binders (113,700 pounds), which generally make up the largest volume in paint, accounted for less than 20% of the imported colorant items. Moreover, paints based on auxiliary agents (“emulsion paints”) were often used, and basic components such as water, lime, flour and eggs have not been included. The amount of imported mordants (337,216 pounds) was similar to the amount of imported dyes, which is consistent with the use of equivalent amounts of dyes and mordants in textile dyeing recipes.



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

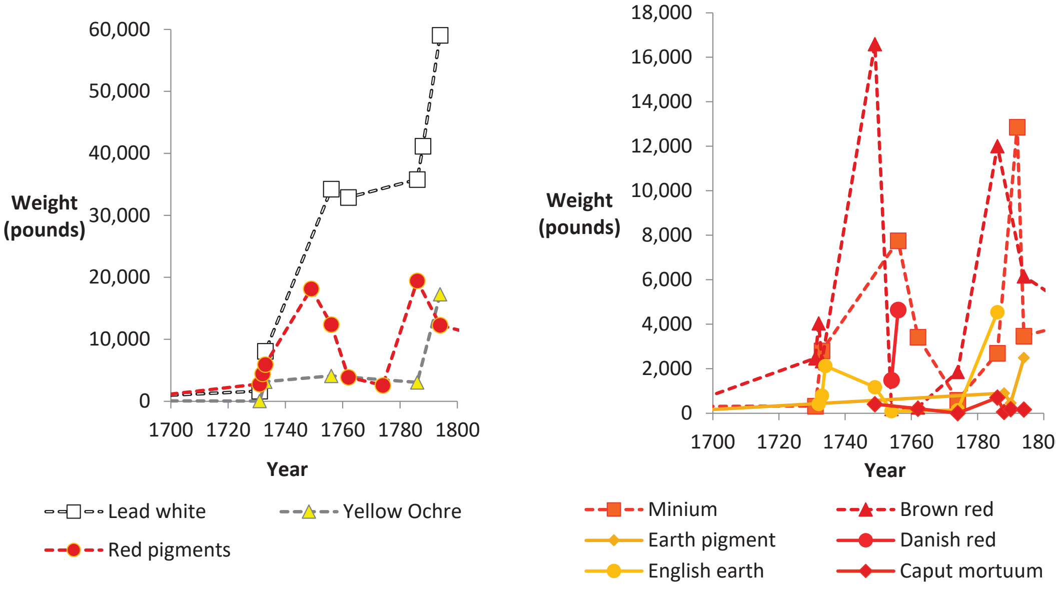
Figure 1. (**a**) The graph shows the cumulative number of colorant items imported from 1685/1686, in 10-year periods from 1720–1800, and in 1835; (**b**) percentage distribution of imported quantities of pigments, dyes, mordants (and auxiliaries) and binders (and additives) as they appear in the digitized customs records.

Bergen accounted for the largest import quantities relative to the population. There is limited information on the foreign trading partners, but when specified, most of the trade was with the Netherlands, followed by Altona–Hamburg and England–Scotland–Ireland. There were also local differences in the use of dyes. With regard to red dyes, Bergen imported mostly madder, Trondheim mostly redwood, while Christiania imported both cochineal and redwood. Saw-wort was used in Bergen while annatto, imported both as orleans and uldrian (the name is derived from the Danish pronunciation of orleans), was the preferred yellow dye in Christiania and Trondheim.

3.1. Pigments, Binders and Other Additives

Figure 2a shows import graphs for pigments for house painting. Lead white was imported in the largest quantities. Red pigments for house painting consisted of iron oxide pigments (brown red, earth pigment, Danish red, English earth and caput mortuum) and minium. Imports increased in the middle and end of the 18th century. The only blue color suitable for painting was Prussian blue (see bellow), imported from 1733. This pigment was expensive (1.51 Norwegian daler/pound), imported in small quantities (1,537 pounds) and probably mostly used as a decorative pigment color. Yellow ochre (0.05 daler/pound) was imported in larger quantities (48,543 pounds) at the end of the century (Figure 1a). Umber (0.13 daler/pound) was imported in small amounts (1,038 pounds) and probably mostly used for decoration.

Figure 3 shows imports of yellow and black pigments, mostly used for decoration. Imports of toxic orpiment (also imported as *rusgel*) more or less ceased in the second half of the 18th century. It was probably replaced by dyer's buckthorn lake pigment and an unspecified *kongegult* (transl. king's yellow and probably synthetic orpiment). Graphite and ink powder were used in the middle of the 18th century, while imports of carbon black increased significantly at the end of the century. Tar had been used for centuries, but its use was reduced due to being a fire hazard.



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

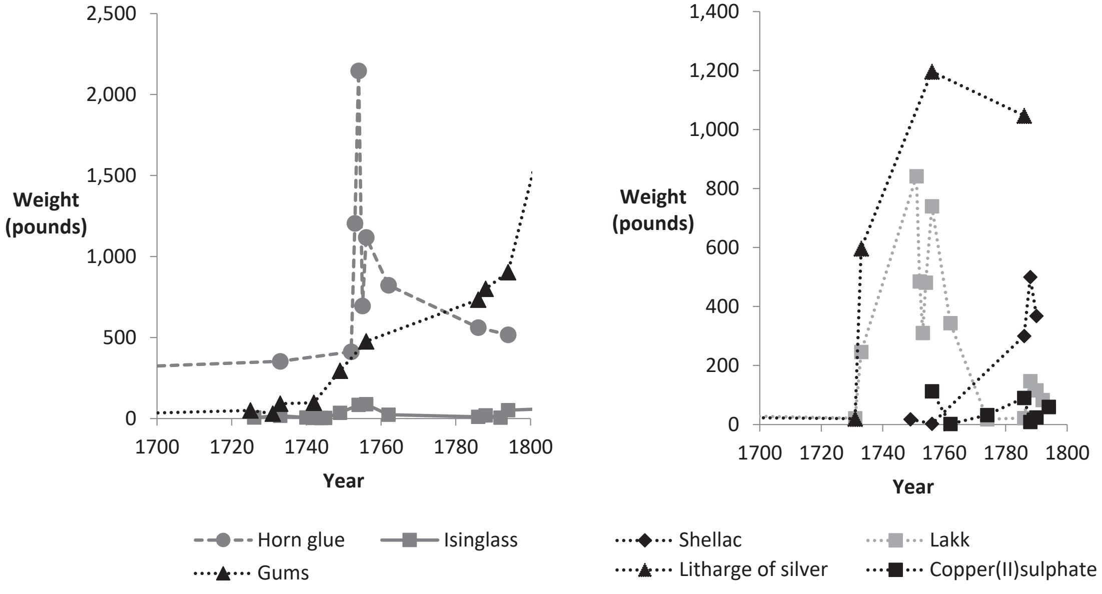
Figure 2. (**a**) Import graphs for white, red and yellow pigments for house painting; (**b**) import graphs for the individual red paint pigments consisting of iron oxide pigments (brown red, earth pigment, Danish red, English earth and caput mortuum) and minium. Markers refer to years 1731, 1732, 1733, 1749, 1754, 1756, 1762, 1774, 1786, 1788, and 1794. Dashed graph lines indicate a lack of data between the recorded years.

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

Figure 3. Import graphs for (**a**) yellow decorative pigments orpiment (including *rusgel*), *kongegult* and dyer's buckthorn; (**b**) and graphite, carbon black and ink powder. Markers refer to years 1724, 1725, 1731, 1733, 1740, 1742, 1749, 1751, 1752, 1753, 1754, 1756, 1762, 1786, 1788, 1792, and 1794. Dashed graph lines indicate a lack of data between the recorded years.

Red lake pigments made of cochineal, redwood and madder (Florentine lake, *kulelakk* and *kurlakk*) were also imported in small amounts. Blue cobalt color was imported as smalt, smalt *blausel* and smalt blue, while cobalt was an export product. Verdigris was used both as a paint pigment and a textile dye. Some imported dyes, such as indigo, litmus, turmeric and dyer's buckthorn, may also have been used for painting.

Figures 4 and 5 show the import of binders and other additives. Local produced paints were initially often made with cod liver oil [22]. Water-soluble binders were mainly used at the beginning of the 18th century, either as emulsion or glue paints. Emulsion paints contained mixtures of different auxiliary agents (such as wheat flour, wheat bran and rye flour) and solutions (like milk, beer and herring oil) [23]. Glue was boiled on site from calfskin. Horn glue and small amounts of isinglass were imported as water-soluble binders, with decreasing amounts in the second half of the century (Figure 4a). Gums were used in increasing amounts (Figure 4a). Their use as water-soluble constituents was most likely reduced, but gums were also used to thicken paints, as mordants, and to starch clothing.

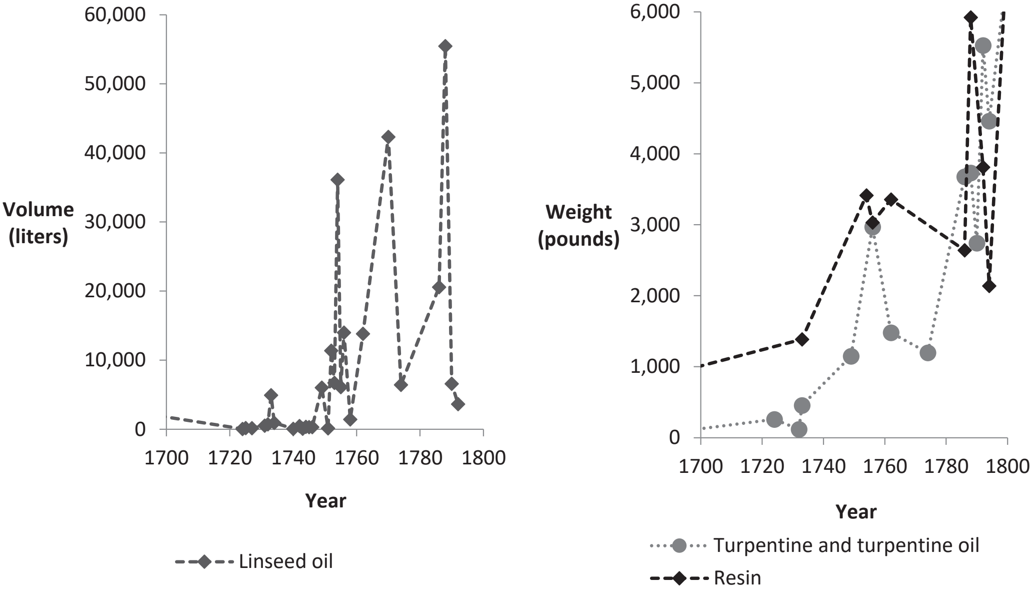


(**a**)

(**b**)

Figure 4. Import graphs for (**a**) the water soluble binders horn glue, isinglass and gums; (**b**) and non-water soluble shellac, lakk, litharge of silver and copper (II)sulphate. Markers refer to years 1725, 1726, 1731, 1733, 1740, 1742, 1744, 1745, 1749, 1751, 1752, 1753, 1754, 1755, 1756, 1762, 1774, 1786, 1788, 1792, and 1794. Dashed graph lines indicate a lack of data between the recorded years.

During the second half of the 18th century non-water soluble binders became more popular in use. Simplified, linseed oil (Figure 5a) became the typical binder for paint and turpentine oil (Figure 5b) the typical solvent. Siccatives (litharge of silver and copper(II)sulphate as *kobberrøg* and *blåstein* Figure 4b) functioned as drying agents. The varnishes increased the flexibility of the paint during application, were used as protective film and were also believed to harden the paint. The customs records include various varnishes, such as resin (*harpiks*, Figure 5b), shellac (Figure 4b, resin secreted by the Indian *Kerra Lacca*), *lakk* (Figure 4b, various forms of melted plant resins) and small amounts of unspecified *ferniss*. Based on Figure 4b, it seems as if shellac replaced the plant varnishes. Shellac was probably also used as a sealing wax and stamp varnish, as well as for polishing furniture. The quantities of imported turpentine and turpentine oil increased from the middle of the century (Figure 5b). Norway became largely self-sufficient with linseed oil, which explains the reduced import at the end of the century (Figure 5a) [24]. The price of linseed oil was as high as 0.16 daler/liter, and people continued to use cod liver or herring oil when painting houses.

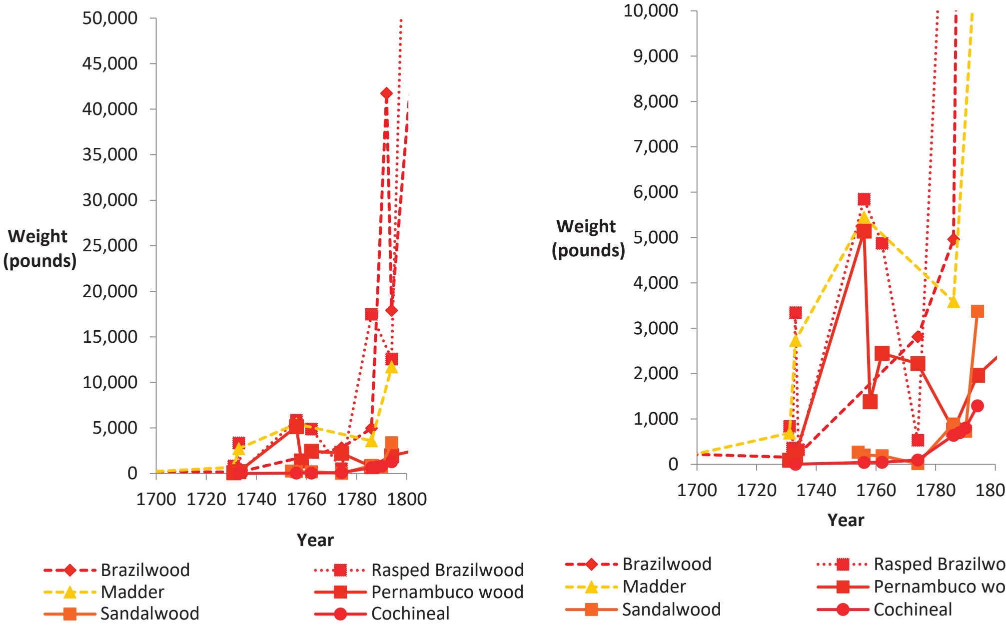


(a) (b)

Figure 5. Import graph for non-water soluble binders:(**a**) linseed oil (imported in volume units and converted to liters), Markers refer to all the years linseed oil has been registered in the digitized customs records; (**b**) and resin (*harpiks*), turpentine and turpentine oil. Markers refer to years 1724, 1732,1733, 1749, 1754, 1756, 1762, 1774, 1786, 1788, 1790, 1792, and 1794. Dashed graph lines indicate a lack of data between the recorded years.

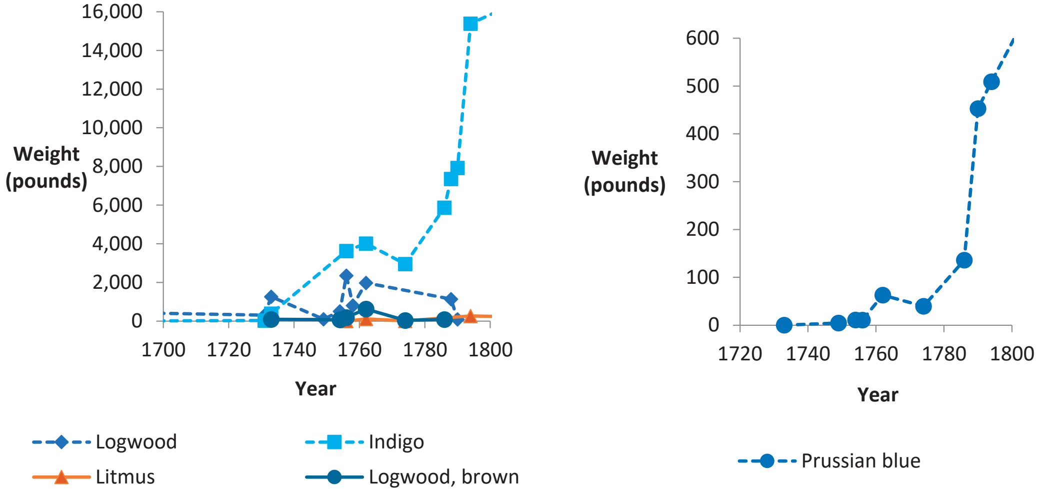
3.2. Dyes, Mordants and Auxilliaries

Brazilwood and rasped brazilwood were the red textile dyes that were imported in the largest quantities and especially at the end of the 18th century (Figure 6a). Madder was the second largest imported red dye. Other red dyewoods (sandalwood and the brazilwood pernambuco wood) and cochineal were imported in smaller quantities, and imports did not increase at the end of the 18th century (Figure 6b). Indigo was the blue dye imported in the largest quantities, with significantly increased imports at the end of the century (Figure 7a). Other imported blue dyes were logwood (called blauholt, campecheholt, and *brissel*). Together with litmus and brown logwood, they were imported in smaller quantities than indigo and without increased imports at the end of the century (Figure 7a). Logwood was used for coloring blues, mauves, grays and blacks, but according to the import data it was in limited use in Norway during the 18th century. Prussian blue (Figure 7b) was mostly used as a paint pigment, whereas its use as a dye became more popular in the 19th century. The increasing imports of yellow textile colors turmeric, annatto (orleans and uldrian) and saw-wort, are shown in Figure 8a. Turmeric was also used as a spice. Figure 8b shows import graphs for verdigris and gallnut. It can be noted that Figures 6–8 show increased imports of dyes in the middle and late 18th century.



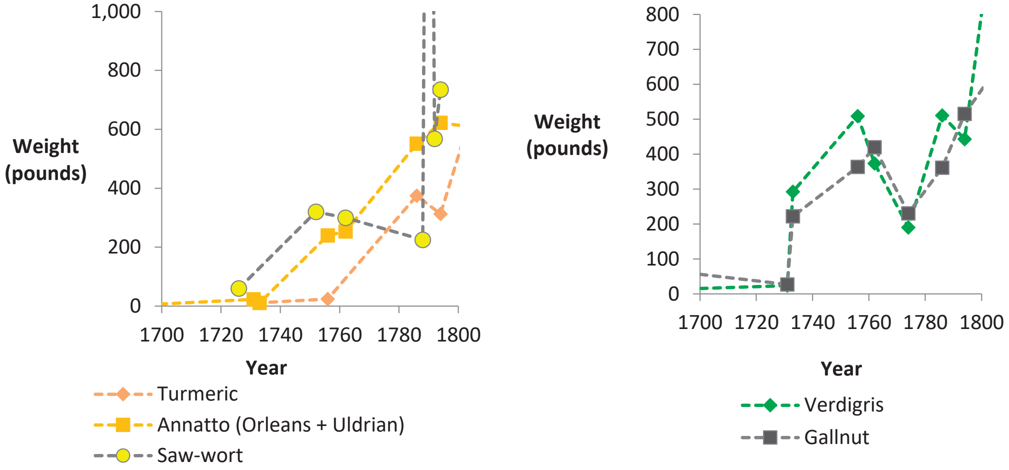
(**a**) (**b**)

Figure 6. Import graphs:(**a**) for red textile dyes brazilwood, rasped brazilwood, madder, cochineal sandalwood, and pernambuco wood for the entire century; (**b**) and same graph but with enlarged *y*-axis. Markers refer to years 1731, 1732, 1733, 1734, 1754, 1756, 1758, 1762, 1774, 1786, 1788, 1790, 1792, and 1794. Dashed graph lines indicate a lack of data between the recorded years. The graphs overlap each other but clearly show the increased imports in the middle and at the end of the 18th century.



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

Figure 7. Import graphs for:(**a**) logwood (*brissel*, campecheholt, and blauholt), indigo, litmus, and logwood, brown; and(**b**)Prussian blue. Markers refer to years 1731, 1733, 1749, 1754, 1756, 1758, 1762, 1774, 1786, 1788, 1790, and 1794. Dashed graph lines indicate a lack of data between the recorded years.



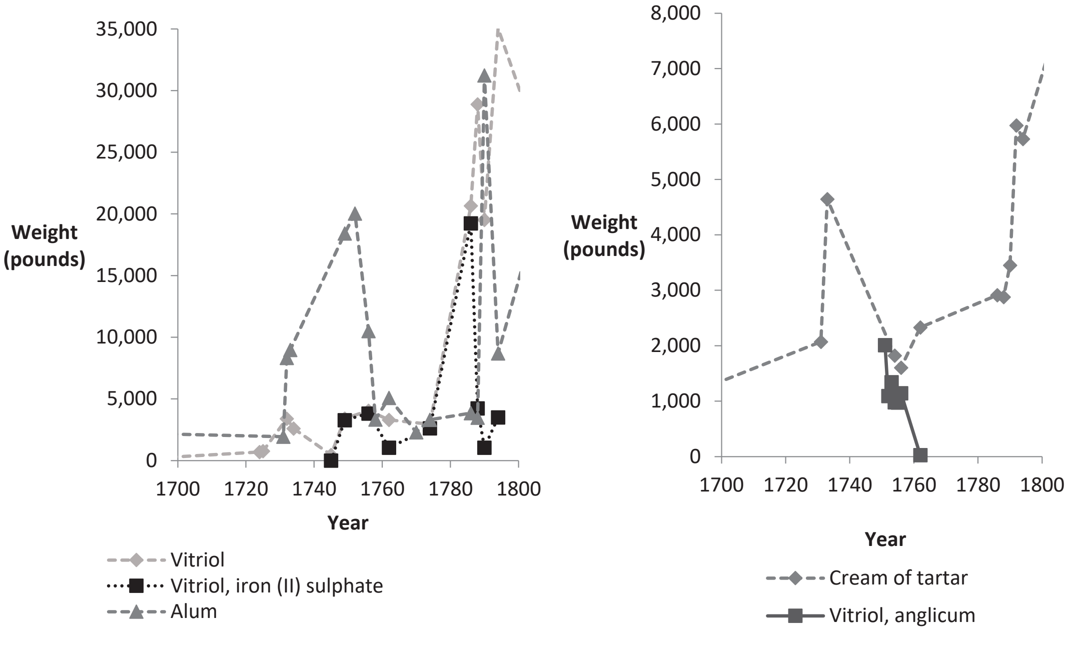
(**a**) (**b**)

Figure 8. Import graphs for:(**a**) yellow textile dyes turmeric, annatto (orleans and uldrian), and saw-wort; and (**b**) verdigris and gallnut. Markers refer to years 1726, 1731, 1732, 1733, 1752, 1756, 1762, 1774, 1786, 1788, 1790, 1792, and 1794. Dashed graph lines indicate a lack of data between the recorded years.

Dyes need mordants to bind to the textile fibers. Mordants are usually metal salts that form metal complexes with dyes. Textiles with cellulose fibers such as cotton, linen and hemp, also needed treatment with gallnuts or sumac in order for the mordants to adhere [25]. Among the highest amounts of imported mordants were alum, vitriol and the vitriol, *kobberrøg* (Figure 9a). The import of alum increased both in the middle and at the end of the 18th century at the same time as imports of dyes increased. The temporary decline in alum imports during the third quarter of the century was probably due to alum production in Christiania. Cream of tartar and vitriol anglicum were imported in smaller quantities (Figure 9b). Gums were used as auxiliary agents in the dyeing process. Lime played a minor role in vat dyeing with indigo to adjust alkalinity. The customs lists contain other goods which are added to the dyeing process, but which are not included in this study, like wheat bran, ash, urine, vinegar, chalk, nitric acid, ammonium chloride, bismuth, and lemon juice.

3.3. Prices

Figure 10 shows that there were no consistent changes in average prices of 31 colorants during the period 1774 to 1794, but with some variations at the end of the 18th century. The more expensive dyes were known as the greater dyes (*grands* or *bons teints* in French) since they gave more yield per unit and were more light-resistant. Imported red textile dyes had different prices. Cochineal (4.67 daler/pound) was the most expensive greater red dye followed by madder (0.16 daler/pound), while brazilwood (0.07 daler/pound) was called a lesser dye. Indigo (1.60 daler/pound), in spite of being an expensive greater dye, was the chosen imported blue dye in Norway during the 18th century. Logwood (0.06 daler/pound) was increasingly used only during the 19th century. Leadwhite as the only used white pigment (0.07 daler/pound) was somewhat more expensive than other imported pigments used for painting houses, such as yellow ochre (0.05 daler/pound) and brown red (0.02 daler/pound). Decorative pigments were more expensive such as vermilion (1.22 daler/pound), verdigris (0.60 daler/pound), orpiment (0.18 daler/pound) and umber (0.13 daler/pound). Other expensive pigments were Florentine lake (2.0 daler/pound) and Prussian blue (1.5 daler/pound). There is little information about the prices of local produced dyes and pigments, probably because these were to a lesser extent part of the colorant trade. According to a description from that time, a local dye was sold for 0.08 daler/pound, which is cheaper than most of the imported dyes [20]. Goods imported at the highest amounts during the 18th century were among the cheapest. Figure 11 shows that apart from indigo, all the colorants imported in greater quantities had prices below 0.2 daler/pound.



(**a**)

(**b**)

Figure 9. Import graphs for mordants: (**a**) alum, vitriol, and vitriol, *kobberrøg* (alum was measured both as pounds and barrels; barrels are converted to pounds based on the price of pounds and barrels.) Markers refer to all the years linseed oil has been registered in the digitized customs records; and (**b**) cream of tartar and vitriol, anglicum. Markers refer to years 1724, 1725, 1731, 1732, 1733, 1734, 1745, 1749, 1751, 1752, 1753, 1754, 1755, 1756, 1758, 1762, 1770, 1774, 1786, 1788, 1790, 1792, and 1794. Dashed graph lines indicate a lack of data between the recorded years.

Figure 12 shows 17 imported pigments and dyes sorted by total weight, with their corresponding total values (quantity multiplied by price), as they are registered in the digitized product lists. Lead white, brazilwood, indigo and madder were the most imported colorants by weight (Figure 11, markers). The three colorants with the largest costs during the 18th century were indigo (110,019 daler; high price 1.6 daler/pound and high quantity 68,762 pounds), lead white (23,636 daler; low price 0.07 daler/pound but high quantity 337,661 pounds), and cochineal (19,810 daler; high price 4.67 daler/pound but low quantity (4242, Figure 11, columns).

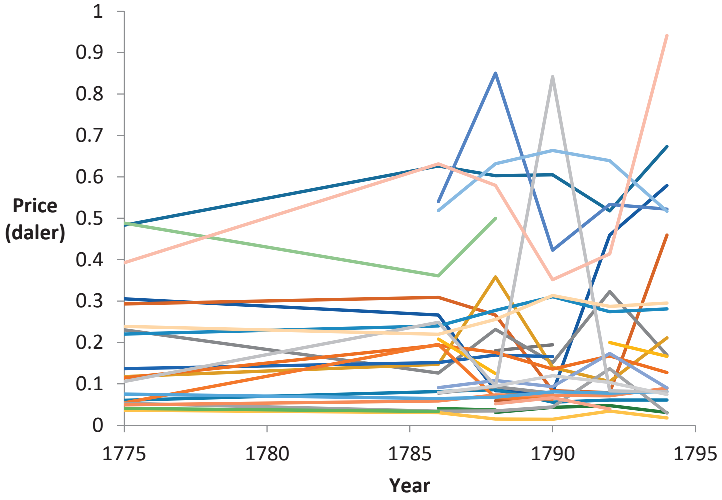


Figure 10. Average prices for the period 1774 to 1794 for 31 colorant items, with prices below 1 daler/pound (annatto (orleans and uldrian), brazilwood, brazilwood shavings, brown red, caput mortuum, carbon black, red chalk, dyer's buckthorn, earth pigment, English earth, gallnut, graphite, ink powder, king's yellow, lake pigments *kulelakk* and *kurlakk*, lead white and *skiferhvit*, litmus, logwood, logwood brown, madder, minium, pernambuco wood, sappanwood, saw-wort, smalt, turmeric, umber, verdigris, and yellow ochre). The colorants are not specified on the graphs, since the message is to show that the prices were mostly stable.

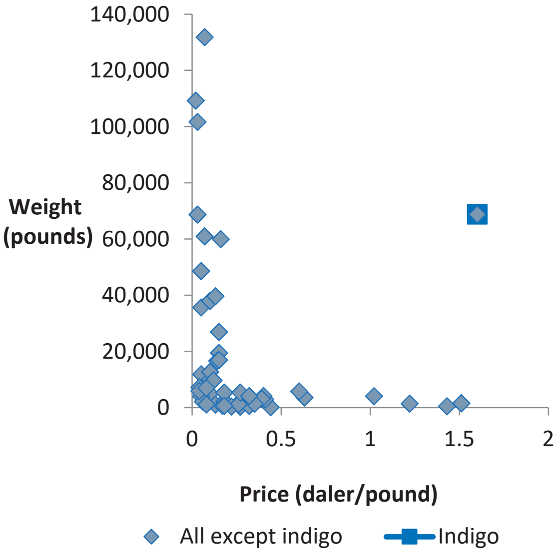


Figure 11. Prices versus import quantities. Values for two dyes with prices above 2 daler/pound are not included: saffron (8.6 daler/pound) and cochineal (4.67 daler/pound), both with low import quantities of 895 and 4, 242 pounds, respectively. Indigo (square marker) had a high price and high import quantity.

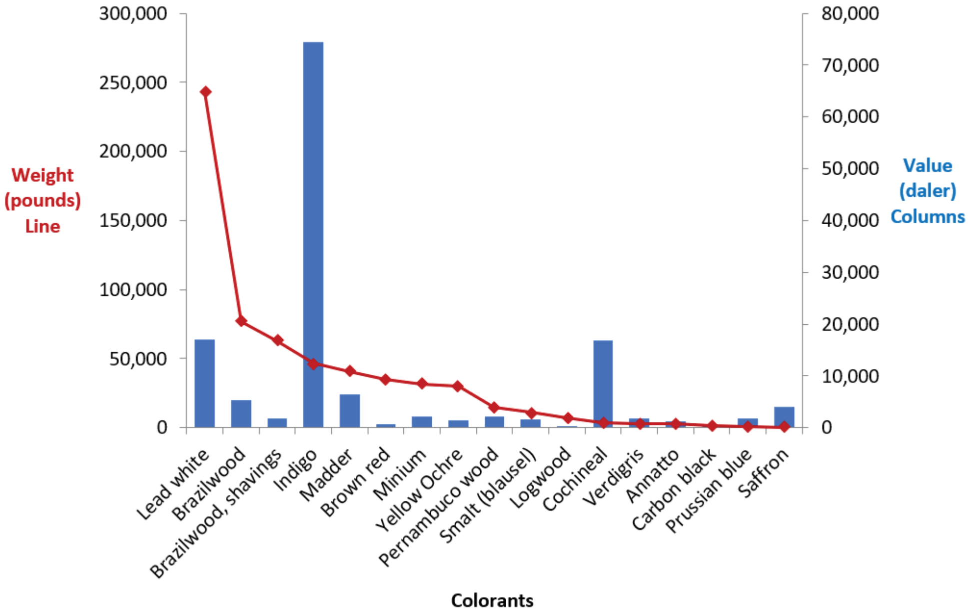


Figure 12. Total imported quantities (red, line) and the total values (quantity multiplied by price, blue columns) of imported pigments and dyes.

In terms of weight, the import of pigments was slightly higher than dyes (see below). In terms of values the imported pigments and dyes were similar in 1733 (1397 and 1530 daler, respectively). However, in 1790 the values of the imported textile dyes (21,541 daler) were five times higher than the values of the paint pigments (4343 daler). Consequently, more money was spent on dyeing clothes than painting houses, and the increased use of dyeing is even more evident since smaller amounts of dyes were used on textiles compared with pigments used on the larger areas of buildings.

3.4. Imports of other Consumer Goods

Textile fibers, including wool, were not produced in sufficient quantities in Norway. Figure 13a shows that a significant amount of hemp and flax were imported during the first part of the 18th century, and considerably less cotton and wool. In the middle of the century imports increased for all four fibers. Subsequently, imports of flax and hemp did not increase further, whereas cotton and wool imports increased considerably (Figure 13b). This clearly indicates a change in the use of raw material for clothing.

Figures 14 and 15 show imports of goods that traditionally have been considered as typical consumer goods. Like the rest of Europe, pepper was an important import product in the 17th century with significant quantities imported in 1686 (2186 pounds) and 1733 (2432 pounds). During the 18th century, increasing quantities of pepper were imported both from foreign places and from Denmark (Figure 14a). The increased imports of sugar exceeded the other products in weight, and also became part of Danish trade (Figure 14b). While tea and coffee imports into England increased steadily throughout the 18th century [26], tea and coffee imports into Norway only increased during the second half of the century, and again predominately from Denmark (Figure 15). These figures show that imports of traditional consumer goods also increased at the end of the 18th century in Norway.

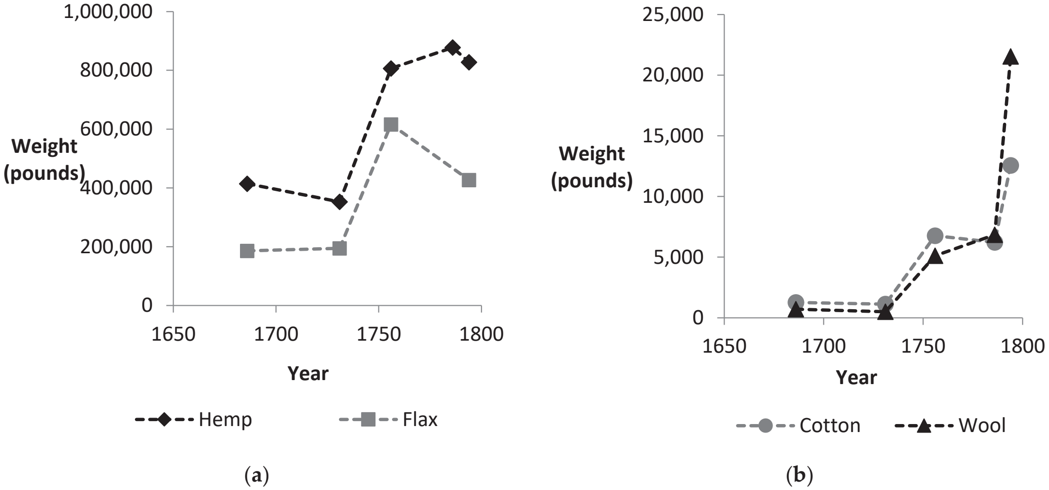


Figure 13. Import graphs for unprocessed:(**a**) hemp, flax; and (**b**) cotton and wool. Markers refer to years 1686, 1731, 1756, 1786, and 1794. Dashed graph lines indicate a lack of data between the recorded years.

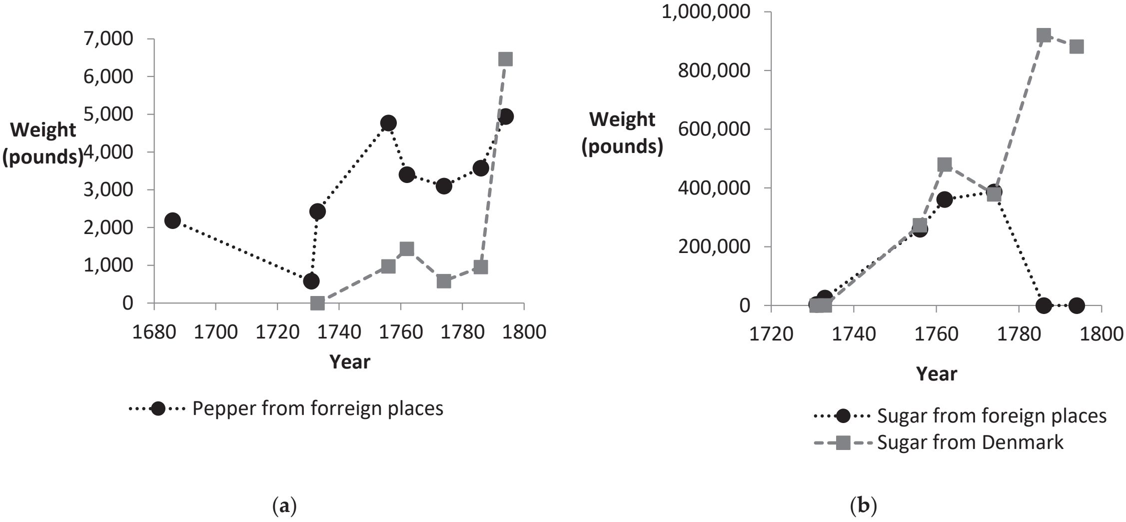
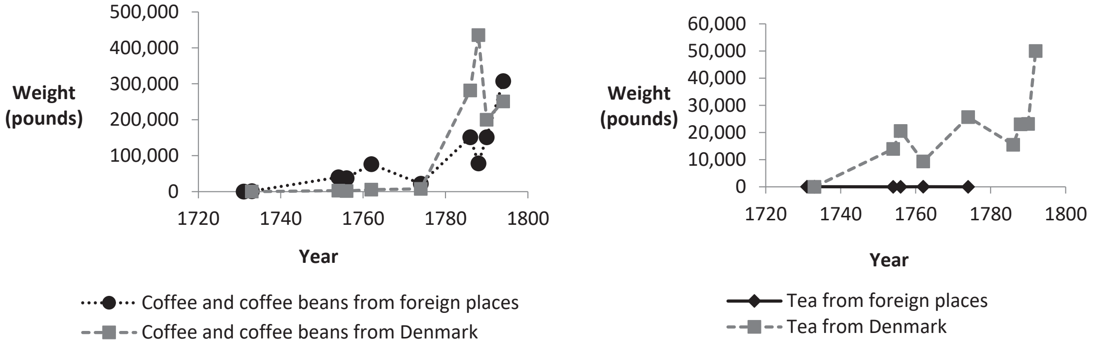


Figure 14. Import graphs for: (**a**) pepper; and (**b**) sugar. Markers refer to years 1686, 1731, 1733, 1756, 1762, 1774, 1786, 1788, 1790, and 1794. Dashed graph lines indicate a lack of data between the recorded years.

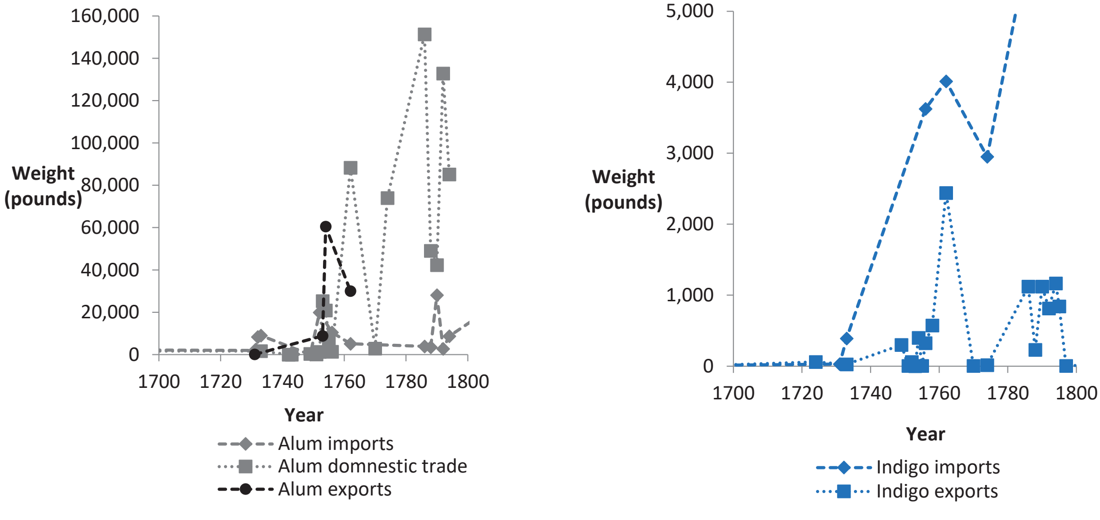


(**a**) (**b**)

Figure 15. Import graphs for: (**a**) coffee; and (**b**) tea. Markers refer to years 1731, 1733, 1754, 1756, 1762, 1774, 1786, 1788, 1790, 1792, and 1794. Dashed graph lines indicate a lack of data between the recorded years.

3.5. Export and Domestic Trade in the 18th Century and Imports in 1835

The quantities of tar exported exceeded the quantities of tar, which were imported or sold domestically. Exports of cobalt and lichen were also larger than imports. Tar, cobalt and lichen may therefore be classified as export products. Brown red was partly an imported and partly a domestic color from Denmark. Danish red, however, was a pure domestic color from Denmark, used for a short period during the 1750s. Alum and lime were produced in Norway. The domestic trade of alum was considerable, mostly shipped from Norway to Denmark (Figure 16a). Indigo was imported in large quantities during the 18th century (Figure 7a) and was also exported for a few years during the second half of the 18th century (Figure 16b).



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

Figure 16. Import, domestic and export graphs for:(**a**) alum; and (**b**) indigo. Markers refer to the years where data for the items have been registered in the digitized customs records. Dashed graph lines indicate a lack of data between the recorded years.

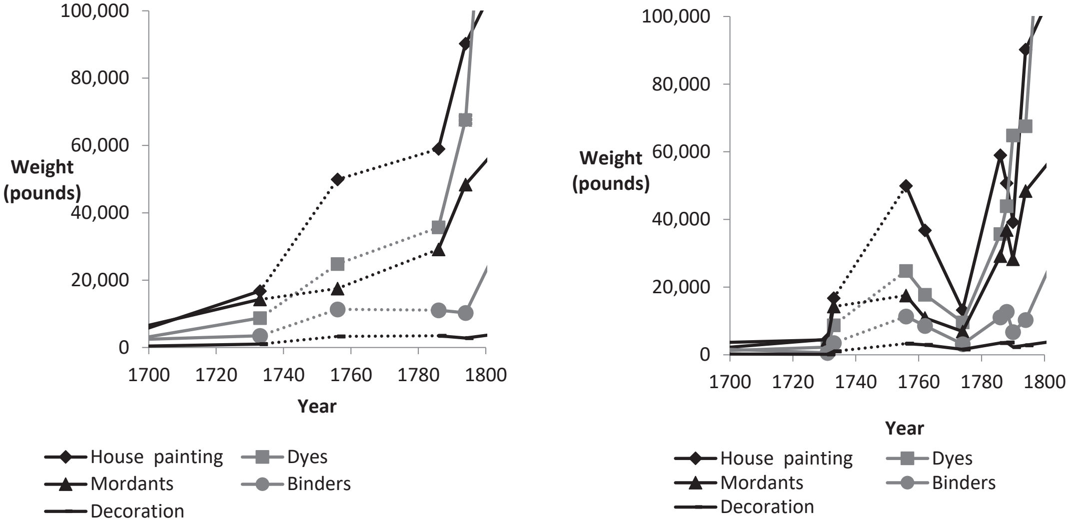
The most important Norwegian export products were timber, copper, klipfish and stockfish. Export graphs are difficult to present for timber and stockfish exports, since the digitized product lists from the Norwegian customs records do not contain sufficient data with uniform units. Export data for copper from Trondheim show an increase from 283, 434 and 618 ton for the periods 1721–1730, 1741–1765 and 1771–1790, respectively [27]. Similarly, Figure 17 shows that the amount of klipfish exported increased especially from the middle of the 18th century.

Figure 17. Export graph for klipfish during the 18th century. Markers refer to years 1731, 1732, 1733, 1746, 1749, 1756, 1762, 1774, 1786, and 1794. Dashed graph lines indicate a lack of data between the recorded years.

A total of 20 new colorants were registered in the trade statistics from 1835. Quercitron and sappanwood were examples of a new yellow and red dye for textile dyeing. Brunswick green and chrome yellow were new paint pigments, and ultramarine was imported as an expensive paint pigment known for centuries. The increased dyes from 1794 to 1835 (559,135 pounds) was significantly greater than the increase in paint pigments (88,238 pounds), indicating that textile dyeing constituted a considerable larger proportion of the colorant imports than those used for painting and decoration. Imports of toxic arsenic pigment (orpiment, *rusgel*) continued to decrease, but toxic lead-containing pigments (lead white, minium, chrome yellow and chrome red) were still imported in 1835. Similarly, toxic arsenic compounds were also used for make-up: lead to give a pale complexion and vermilion was used as rouge [28].

3.6. Two Periods of Increased Colorant Imports

Imported pigments have been divided into pigments used for painting houses (brown red, caput mortuum, carbon black, Danish red, earth pigment, English earth, lead white, minium, yellow ochre) and other pigments that were mainly used for decoration. Figure 18a shows import graphs for pigments for house painting, binders, dyes and mordants for the years 1733, 1756, 1786 and 1794with "most" complete records available. There was an increase in imports somewhere between 1733 and 1756, and a considerable further increase from 1786 to 1794. Figure 18b shows similar import graphs for the years 1731, 1733, 1756, 1762, 1774, 1786, 1788, 1790, and 1794 with "most" complete registrations. The figure shows a temporary decrease in imports in 1774, which will be discussed in Section 4.2. The increase in imported paint pigments and textile dyes in the 18th century was significant. The amount of imported dyestuffs increased from 1733 to 1756, 1786, and 1794 with factors of 4.5, 6.3, and 14.9, respectively, and the corresponding figures from 1731 were significantly higher 23.1, 32.4, and 76.6, respectively. Colorants with especially large increases in imports at the end of the century were brazilwood, indigo, cochineal, lead white, madder and sandalwood. As shown in Figure 1a, the number of new pigments and dyes also increased significantly. Figure 19 showing import graphs for selected dyes that were imported in larger quantities, further illustrates the increasing imports in the middle of the 18th century and significant additional increases at the end of the century.



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

Figure 18. Graphs for imported colorant items (pigments for house painting and decoration, binders, dyes and mordants) for: (**a**) 1733, 1756, 1786, and 1794; and (**b**) 1731, 1733, 1756, 1762, 1774, 1786, 1788, 1790, and 1794. In (**a**), the graphs are dashed between 1833 and 1786 because of the long time interval, while 1774 is included in (**b**). The graphs show increased imports in the middle and at the end of the 18th century, increases which the author has called the first and second Norwegian chromatic revolutions. According to the 1774 registrations imports were temporarily reduced before similar import levels as 1756 were reached in 1786, with further increases at the end of the century.

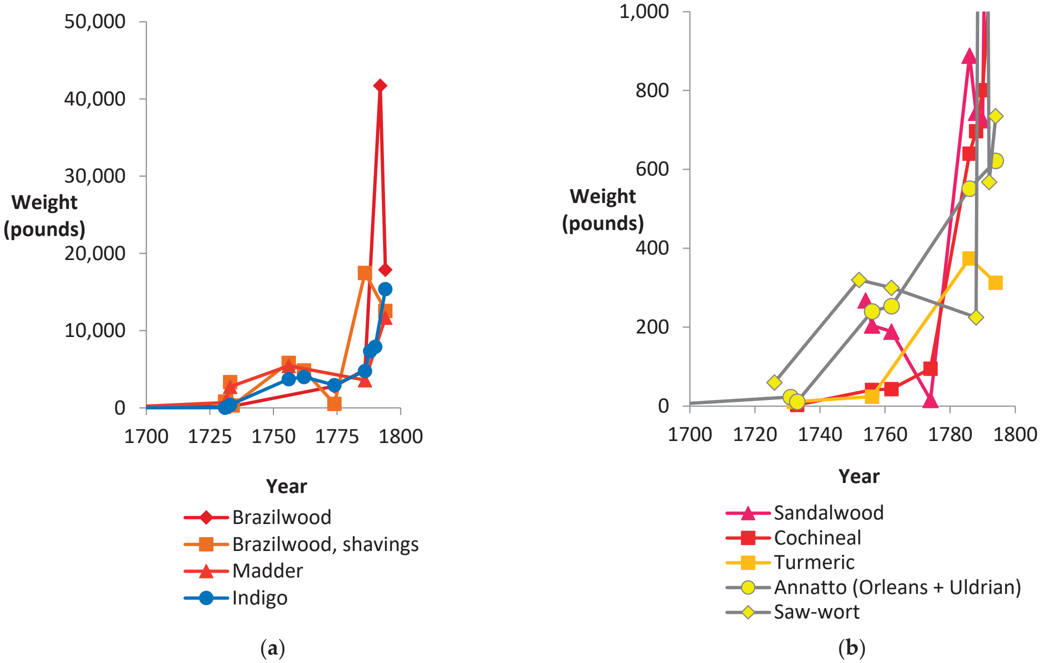


Figure 19. Import graphs for dyes imported in high quantities: (**a**) dyes imported in smaller quantities; and (**b**) show how imports of dyes increased in the middle and at end of the 18th century. Markers refer to years 1726, 1731, 1732, 1733, 1734, 1749, 1752, 1756, 1762, 1774, 1786, 1788, 1790, 1792, and 1794.

The digitized product lists from the Norwegian customs records include particularly frequent import registrations for the city of Trondheim in the mid-18th century. Figure 20 shows that imports of many dyes were low in the first part of the 18th century, and increased considerably during a short period 1745–1750. The increased dye import was maintained during the second part of the 18th century. A further increase of imports at the end of the century was most pronounced for lead white and indigo, as shown for the whole country in Figures 2a and 7a.

3.7. Imports by Color

Figure 21 shows the total import of pigments over the century, with lead white, red and yellow colors accounting for 96% of the weight of imported colors used. Figure 22 shows that red dyes made up the majority (approx. 3/4) of the imported dyes. The imported red dyes showed the greatest increase, as largely represented by brazilwood. Imports of indigo (20%) and yellow dyes (9%) also increased in the late 18th century. Blue and red became popular colors during the century, indigo due to its high color yield per unit was also used in large amounts, and yellow, green (2%) and black (1%) colors contributed to an increased color range.

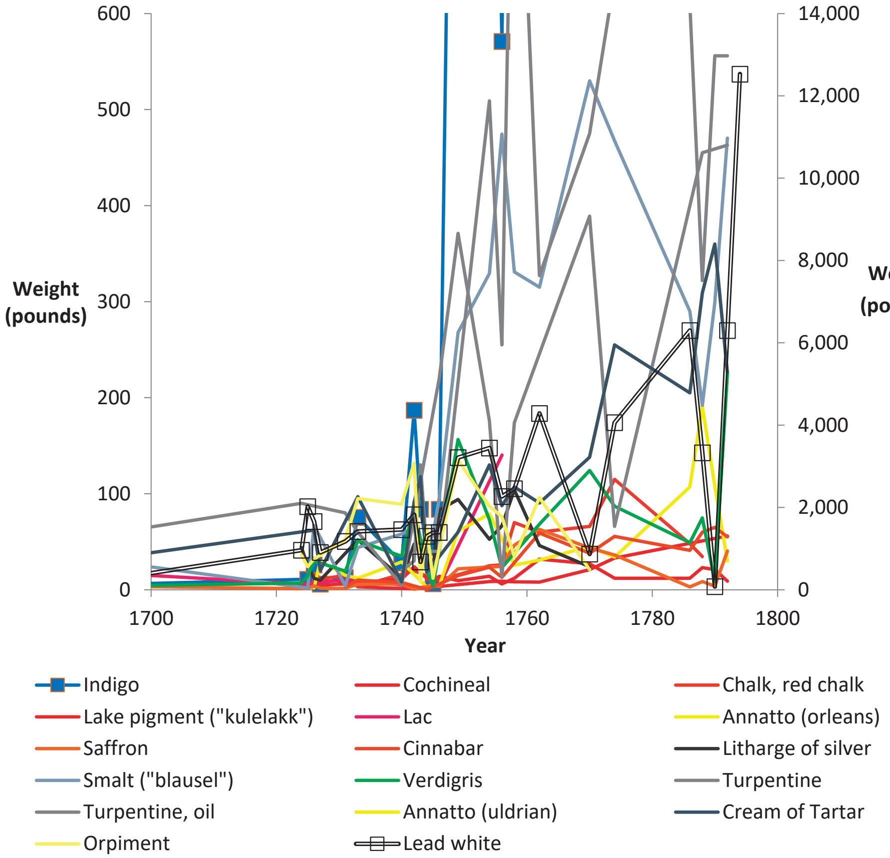


Figure 20. Imports of colorant items to Trondheim during the 18th century. The secondary right y-axis relates to indigo and lead white which were imported in considerable larger quantities. The graphs overlap each other but clearly show that import of many colorant items increased during the period 1745–1750. This increased colorant import was maintained during the second part of the 18th century.

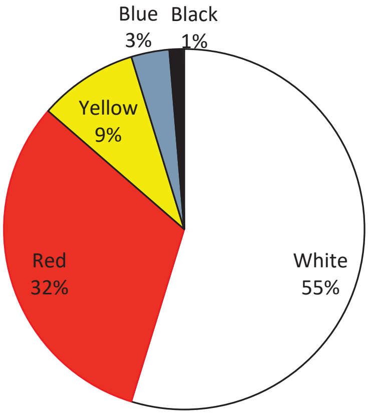


Figure 21. Percentage distribution of the colors of imported paint pigments as they appear in the digitized customs records.

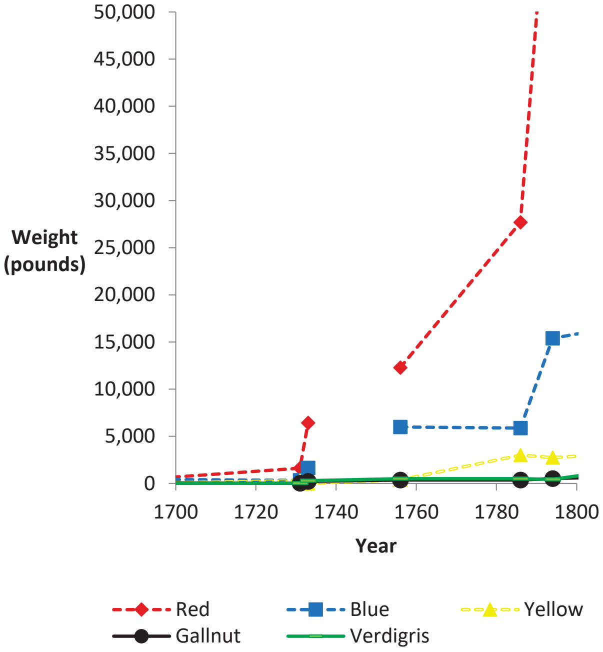


Figure 22. Import graphs for the textile dyes shown by color. Markers refer to years 1731, 1733, 1756, 1786, and 1794. Dashed graph lines indicate a lack of data between the recorded years, and missing graphs between 1733 and 1756 indicate a lack of these data concerning the start of the first chromatic revolution.

4. Discussion

In 18th century Britain, people spent more money on clothes and textiles than on any other consumer goods [26]. Dyes determined much of their attractiveness. Together with painted houses and objects, dyes represented an increased splendor of color as a visible part of the consumer society. In the previous Section, increased imports of colorants in Norway during the 18th century are presented, representing the increased supply of imported colorants especially during the second part of the century. This Section discusses how increased imports of colorants as consumer goods can shed light on the beginnings of the consumer society. Factors to be discussed include the increased imports reflecting two chromatic revolutions, how increased export trade may have stimulated increased colorant imports and domestic trade, and how different factors may have stimulated the use and demand for colors. All these elements may be compiled in a model to visualize processes, which may have contributed to the development of the early consumer society.

4.1. Colorants as Consumer Goods

Goods from the colonies accounted for 10% of the value of English imports in the mid-16th century and increased to 36% in 1770 [29]. From 1664–1679 to 1731–1740, the share of pepper among imported goods had fallen from 20% to 4.3%, with increasing amounts of other imported consumer goods such as tea, coffee, sugar, and tobacco [26,29]. Figures 14 and 15 show a similar increased import of these consumer goods to Norway. While the traditional luxury often was associated with high costs and a lack of moral scruples, increased trade in consumer goods gave rise to a new luxury that was more closely linked to utility, comfort and pleasure. It became more accepted as an expression of wealth, and changed people's living habits and consumption culture [30]. The rise of the consumer society in England has largely been studied through the import of the classical new products from the colonies, such as pepper, coffee, tea, sugar and tobacco [31]. Other new consumer products, such as porcelain and textiles, had high quality and aesthetic values. Traditionally, paint pigments and textile dyes have not been highlighted as typical luxury and consumer goods, but they have many similarities. The imported colorants competed with the domestically produced earth pigments and plant dyes, and formed a heterogeneous group in terms of both price and characteristics, used by a large part of the population. Like tobacco, coffee and sugar, they provided increased pleasure and well-being. They did not increase comfort or simplify daily life, but as semi-finished products the imported dyes were easier in use than local plant dyes. For all these reasons, colorant imports are particularly suitable for studying the start of the consumer society.

4.2. Two Chromatic Revolutions

The countries around the North Sea were the most important Norwegian trading partners, and only 17% of the colorants came as domestic trade from Denmark. The imported colorants were produced in Europe (such as lead white, madder and verdigris) or had been transported from the colonies. After the Great Nordic War (1709–1719), Denmark-Norway experienced a long period of peace. It started with economic depression, where also pietism prevailed. However, after a period with low climate temperatures from 1741 to 1743, prosperity increased. During The War of the Austrian Succession (1740–1748), Denmark-Norway increased its trading activity. There was a significant increase in European demand for the Norwegian export products during the 18th century, which is reflected by an increased export of timber, copper and fish to Europe. Increased exports of klipfish (Figure 17) may serve as an example of the increased Norwegian export trade from the middle of the 18th century, which opened the way for a new type of import trade with luxury and consumer goods, including new colorants.

Lead white and indigo imports are of particular interest, since these colorants were exclusively imported and were the only white pigment and blue dye in use. There is no evidence that colorants were stored in large quantities in Norway. Therefore, import graphs of lead white (Figure 2a) and indigo (Figure 7a) may be representative for the use of imported colorants during the 18th century, characterized by increased imports during the middle and at the end of the century. Import graphs for the different dyes (Figure 19) clearly show increased imports in the middle and at the end of the 18th century. Similar graphs for pigments as a group are not presented for several reasons. Firstly, the largest amounts of pigments were used for house paintings, which followed periods of different styles. Secondly, with the exception of lead white, the amounts of imported pigments do not reflect their total use, since there was an abundant local production as well [32,33]. Finally, pigments for decoration represented a heterogeneous group imported in smaller quantities. However, individual import graphs for pigments basically not related to style show the same tendency towards increased imports during the second part of the 18th century, such as lead white (Figure 2a), Prussian blue (Figure 7b), dyer's buckthorn (Figure 3a), carbon black (Figure 3b), verdigris (Figure 8b), gums (Figure 4a), turpentine and turpentine oil (Figure 5b).

Correspondingly, imports graphs showing the total amounts of pigments for house painting, dyes, mordants and binders (Figure 18), and colorant items to the city of Trondheim (Figure 20), show the same import patterns. Imports of pigments for decoration did not show significant increases at the end of the 18th century, presumably because there were more of them and each pigment was used to a lesser extent. The data for 1774 Figure 18b may be misleading due to incomplete data from Bergen and Christiania. Complete import data from Trondheim, however, do not show a similar significant decrease in colorant imports in 1774 (Figure 20). It is however noteworthy that the graphs indicate a transient stagnation in colorant imports from the middle of the 18th century. The slight increase in export trade of indigo in this period (Figure 16a) may indicate saturation of the domestic colorant market, possibly as part of mercantilist politics with customs and law restrictions. Moreover, the early 1770s were designated as crisis years due to unsuccessful grain crops and due to negative impacts of the Seven Years' War (1756–1763) when Denmark-Norway had to mobilize the navy to protect their neutral merchant ships. Limited transport, sales and production opportunities may also transiently have hampered a steady increase in the use of colorants during the 1770s. Import graphs for the textile dyes sorted by color show that the sum of the blue and red dyes also followed the two chromatic revolutions (Figure 22b). Similar increases are apparent for the yellow, green and black textile dyes, when the scale for the Y-axis is enlarged. The 18th century has been called the century of revolutions, and the author has designated the two periods of increased colorant import in the middle and late 18th century as the first and second Norwegian chromatic revolutions, respectively.

Colorants with particularly large increases in imports at the end of the century were brazilwood, indigo, cochineal, lead white, madder and sandalwood. However, although most colorant items followed similar import patterns corresponding to the two chromatic revolutions, each of the colorants also had individual factors influencing their import. Some colorants such as cochineal (Figure 6a) and Prussian blue (Figure 7b) were new and expensive and their import increased later in the century. Imports of orpiment (Figure 3a) declined due to toxicity, and pernambuco wood (Figure 6a) due to deforestation in America. Increased local production can explain periods of reduced imports of alum (Figure 9a), iron oxides (Figure 9b), yellow ochre (Figure 2a), earth pigments and linseed oil (Figure 5a). Increased imports of annatto, turmeric and saw-wort (Figure 8a) suggest that yellow dyes also became popular. The increased import of turpentine and resin (Figure 5b) follows the increased use of oil-based additives. The heterogeneous import graphs of the colorants reflect the differentiated use of the imported colorants, but there was an overall tendency towards increased imports following the two chromatic revolutions.

4.3. Domestic Market

Many of the imported dyes in the 18th century were previously known, and had also been registered in the customs records of 1685 and 1686. The imported colorants were part of increasing amounts of other consumer goods that were imported and distributed within the domestic market. The domestic market of colorants also consisted of a large amount of local produced pigments and dyes, which had been used for centuries. These included many different local lichen, plants, soil colors and iron oxides [32,34,35]. There was little textile industry, and imports of ready-dyed textiles were significant already in the 17th century. During the 18th century, increasing amounts of pre-dyed materials and cloths were also imported. This widespread production and use of the local colorants and imports of colored textiles is not part of the present study, but must be born in mind as part of the overall picture of the increased use of colorants in the 18th century.

Imported colorants ended up in final products, such as painted houses, decorated objects, paintings, colored textiles and clothing. At the start of the 18th century, imported colorants could mostly be purchased only in cities [19]. Like other European countries, they were initially sold in pharmacies, but for larger projects colorants were also imported by merchants or brought to the country by foreign craftsmen. Increased transport, distribution, the expansion of trade networks and increased sales of imported colorants throughout the country can serve as an example of the widespread changes that took place in Norwegian society during the 18th century [36]. As semi-finished products, the imported dyes were part of a commodity trade with supply chains that processed them into final products. These commodity chains included a network of specialized labor (sellers, transporters, marketplaces, grocers, painters, dyers, and some dye houses) and production processes (painting, spinning, weaving, and dyeing). The degree of specialization among sellers, painters, artists and dyers and the formation of guilds were, however, limited in Norway. The final products (painted houses, painted objects and dyed textiles) were used by consumers in all social levels. Social development also included increased enlightenment with information and advertising from newspapers and books, including recipe books. Thus, changes in the infrastructure in Norway during the 18th century gave an important premise to the development of the consumer society. Domestic trade, transport and sales increased following specialization, and development of a more efficient domestic transport and sales apparatus.

4.4. Increased Use

At the start of the 18th century, the value of the workers' wardrobe in Paris was 9% of the value of that of the nobility, while by 1789, the figure had dropped to 1.4% [37]. The final consumers of the more expensive imported colorants in Norway were probably also the wealthiest. However, descriptions from that time show that an increasing portion of the lower social groups also afforded ownership of more colored textiles and some decorated objects. The costs of the colorants may be compared with the cost of a cup of coffee. Assuming a price of 0.21 daler/pound for a cup of 12 g coffee [38,39], the total value of imported textile dyes in 1762, 1786 and 1794 represented not more than 4.4, 5.8 and 15.6 cups of coffee per inhabitant, respectively (all ages included). For comparison, based on coffee imports the consumption of cups of coffee annually in the population these years were on average 15.9, 125.2 and 112, respectively. The consumption of 125 coffee cups on average per year in 1786 corresponded to an expenditure of 62.5 shillings/years, while the value of the textile dyes constituted 2.9 shillings/year. Consequently, the costs of imported dyes were considerably lower than coffee, but still coffee became relatively more popular than imported textile dyes during the 18th century. The main consumers of both coffee and colorants were the wealthier part of the population. This part of the population increased proportionally during the century and led to increased social divergence [40].

4.4.1. Increased Use of Imported Pigments

Originally, houses were not painted. Churches were usually tarred with red iron oxides, but tar treatment of other buildings was limited due to the risk of fire. Houses were painted to a greater extent as they were paneled. During the 18th century, tar was replaced by paint, log houses became more frequently paneled, brick buildings appeared in the cities and linseed oil replaced earlier glues and composition paints. Pigments for house painting accounted for a large part of the consumption of paint pigments. The import graph for lead white (Figure 2a), which was the only white paint pigment in use, reflects the increasing amount of house painting during the 18th century. However, the colors of houses also followed the styles. The temporary increased import of iron oxides (Figure 2b) and yellow ochre (Figure 3a) in the middle and the end of the 18th century indicates that houses were painted red and yellow at the end of the Norwegian Baroque and Rococo periods [41,42]. However, these pigments were also largely produced locally. The increase in the import of lead white in the late 18th century may indicate the start of Classicism. Houses became more decorated using other colors as well. Lamp black was imported as black color. Verdigris (Figure 8b) dominated as an imported green color, both for painting and dyeing. Prussian blue was a new synthesized paint pigment, while indigo was used for both dyeing textiles and for painting. The use of house painting was still limited to the wealthiest. The façade of the house could be painted with lead white, while the walls facing the backyard were unpainted or painted in cheaper colors. Painted houses in the countryside were less common than in the cities, and still most houses in Norway during the 18th century remained unpainted.

As houses acquired windows, and wood burning stoves in the middle of the room were replaced with iron stoves, interior decoration became more common. The period of the first chromatic revolution marks the beginning of increased use of imported pigments for the decoration of objects. Traditional Norwegian decorative floral painting (*rosemaling*) increased from the middle of the 18th century, and easel painting became more common at the end of the century. An anonymous person published a painting book in 1794 with an overview of pigments used for easel painting and decoration in Denmark-Norway. Almost all the pigments mentioned can be found in the digitized product lists from the Norwegian customs records [43]. The imported pigments include red pigments (earth pigments and various types of iron oxide presumably of finer grades, bolus, vermilion, red chalk and red lake pigments), blue pigments (indigo, Prussian blue, litmus, mountain blue, smalt blue), yellow pigments (dyer's buckthorn, orpiment, turmeric, yellow ochre) and lead white, including the finer and more expensive form *skiferhvit*. In 1794, 59,059 pounds of lead white were imported, which was equivalent to 19,686 L of white paint (3 pounds of lead white per liter paint) and about 0.02 L of lead white paint per inhabitant. Compared to the figures of approximately 1 L white paint per inhabitant sold in Norway today, 50 times more white paint is sold in Norway today compared with 1794. In short, few houses were painted, and only by the wealthy.

4.4.2. Increased Use of Imported Dyes

The 17th century was somberly dominated by black, gray and brown clothing, and colored cloths were used mainly by the wealthy. The 18th century became increasingly colorful, with colored clothing used by all social levels. The new color fashion was evident with the increasing use of red and blue colors [44]. This reflects the increased imports of brazilwood, madder, cochineal, and indigo, following the two chromatic revolutions. The use of the textile dyes was largely determined by color choice (fashion), prices, the dye's properties and availability compared to locally produced plant dyes. Cochineal and madder were the more expensive and light-resistant (*grand teint*) red dyes. The cheaper brazilwood was imported in the largest quantities and used by a larger part of the population. The imported indigo, yellow, green, brown, and black dyes contributed to a varied color range. Increased wool and cotton imports (Figure 13b) harmonize with increased use of imported dyes.

Studies of epitaphs and probate records show that clothing became more colorful [45]. Before the 18th century, it is stated that around 60% of the garments were black, while the proportion had dropped to 40% in the 1720s [46]. From 1730, there was a tendency towards increased use of lighter colors as well as checks and stripes in clothing [47]. Brighter reds, blues, pastels and whites were popular [46,48]. From around 1760, probate surveys estimate that it was mostly elderly and poor women who wore black [47]. The use of the imported dyes is described in detail in two Danish dye books from 1768 and in a number of handwritten "black books" (magic books), which also dealt with recipes for dyeing [49–51]. These dye books show that local plant dyes were still in use. Compared to the topographical descriptions from 1743, where imported dyes are only barely mentioned, the two Danish-Norwegian dye books 25 years later show many recipes with imported dyes. The imported dyes largely reflect the use of the dyes abroad, but some foreign dyes were rare in Norway, such as kermes, Polish cochineal, logwood, woad, weld, yellow wood (old fustic) and turnsole. Other dyes were imported to a small extent, such as *Reseda luteola*, weld (1732) and safflower (1756).

Table 2 shows total values of imported indigo, cochineal, madder, brazilwood, indigo, logwood and annatto, based on the prices and quantities of imported dyes. When it comes to the costs of textile dyeing, however, one must also take into account what Engel has called the color yield per unit, which determines the material cost of a dye [52]. A calculation based on Engel's values for color yield per unit for six dyes, shows that indigo, brazilwood, madder, cochineal, logwood and annatto accounted for 67%, 17%, 8%, 3%, 3% and 2% of the colored textiles, respectively. There seems to be a difference between Norway, where indigo was almost exclusively used, and England, where logwood was used for a range of colors. In other words, indigo with a high color yield per unit was responsible for most of the textiles dyed with imported colorants. Moreover, despite lower import quantities of cochineal and madder, these dyes with high color yields per unit contributed significantly compared to larger quantities of imported brazilwood with lower color yield per unit. In Table 2 (column 9) the material costs in daler/pound are calculated converted to £/ton based on the assumption that 1£=4 dalers [53], and compared with corresponding material costs £/ton reported for England for the period 1760–1789 (Table 2, column 10) [52].

The material costs according to the Norwegian customs records were roughly the same as in England.

Table 2. Comparison of dye cost between Norway and England. The table shows amounts of imported dye (based on the digitized product lists from the Norwegian customs records), mutual weight in percentage (of the registered amounts), color yield per unit [52] of textile dyeing, coloring ability measured as weight multiplied with color yield per unit, mutual coloring ability in percent, price as stated in the customs records for the period 1774–1794, material cost and calculated material cost in Norway and England.

	Weight (pounds)	**Weight (%)**	**Color Yield per unit**	**Weight * Color Yield per unit (pounds)**	**Weight*Color Yield per unit (%)**	**Price (daler)**	**Dye Cost (daler/pound)**	**Dye Cost Norway (£/ton)**	**Dye Cost England [52] (£/ton)**
	A		B	A*B		C	D=C/B	D	
Indigo	68,762	27	17.8	1,223,964	67	1.60	0.09	44.9	40.3
Cochineal	4,242	2	14.5	61,509	3	4.67	0.32	161.0	115.3
Annatto	4,637	2	9.2	42,660	2	0.38	0.04	20.7	15.7
Logwood	13,294	5	3.9	51,847	3	0.04	0.01	5.1	1.9
Brazilwood	102,549	40	3.0	307,647	17	0.07	0.02	11.7	6.8
Madder	59,920	24	2.3	137,816	8	0.16	0.07	34.8	32.5

4.5. Increased Demand

The use of indigo and cochineal in Norway was less than 0.08% of total imports of these colors to Europe [54,55]. Therefore, changes in the European availability of colorants can hardly explain any changes of colorant imports into Norway. The first chromatic revolution was most likely the result of increased supply of imported colorants following increased Norwegian exports and trade with Europe. The merchant fleet returned with many different consumer goods. Pigments and dyes were particularly suitable as return goods, as they were valuable in relation to their weight and very popular in the population. The capacity to transport colorants was good. Assuming a cargo capacity of 80 tons per ship, an estimated total import of 6800 tons colorants during the 18th century would require no more than 85 ships. Colorants were initially available in the cities and custom ports, and could only be afforded by wealthy people. However, their use was noted by the rest of the population. With increased supply following increased imports, increased desire for the goods sparked increased demand.

4.5.1. Preferential Use

Local produced colorants from plants and soil were probably commercially available to a very limited extent. Moreover, imported colorants were ready to use and replaced the laborious and time-consuming preparation of local colorants. The imported colorants met a variety of tastes, preferences and expectations for the users. Depending on the price, they had better color properties and qualities with regard to color yield per unit, light stability, washing fastness and color intensity. Widespread use of indigo back to the 17th century and increasing imports of the more expensive colorants such as cochineal, indigo, Prussian blue and lead white during the 18th century, show that their color preferences were highly valued by those consumers who had the financial means to buy them. The imported colorants with different properties and qualities and with versatile uses represented a significant change in the material culture of colorants during the 18th century. As luxury and consumer goods, the imported pigments and dyes represented many forms of value. Their economic value represented a wide range of different prices. They had their material value in terms of their preferential use. They had aesthetic and psychological values in their ability to please, to decorate and to promote styles, trends and fashion [31,56]. The visual dependence of colors should not be underestimated. Although not as addictive as tobacco and coffee, colors contribute to beauty and well-being that can stimulate body endorphins. The cultural value of colorants varied in different social groups. Their use had political, economic and social implications that affected norms and values in society [2]. The colors, like many other consumer products, stimulated a heterogeneous society, and contributed to a mental shift towards a consumer society. The imported colorants also maintained and developed further socio-cultural class distinctions and traditions, which influenced their preferential use in different parts of society.

4.5.2. Fashionability and Consumer Culture

The start of the consumer society was characterized both by changes in individual desires, and consumer behavior determined by taste, fashion and style and changes in consumer culture. Consumption was not only driven by a desire to show off, but also represented an expression of identity and became part of the social codes. Inspired by Parthasarathi and Riello, I will use the broad term, fashionability, to describe the many factors that may have improved personal appearance, satisfaction, comfort and ownership through material goods in the 18th century [57]. Fashionability covered the characteristics of consumer products, consumers, consumption itself, and the society in which the products were used [57]. The concept of fashionability included many different terms and qualities, such as trends, aesthetics, beauty, performance, pleasure, inspiration, desire, preferences, expectations, education, excitement, purchase, novelty, ownership and use. Fashionability in the 18th century thus became a broad term that influenced social, economic and cultural standards and norms in society [58]. Colorants constitute a complex group of products, where fashionability not only included color and color combinations, but also the use of different colorants, textiles, patterns, cuts and styles. The preferences for imported colorants and their fashionability became a self-reinforcing part of positive feedback loops. The use of colorants increased fashionability and consumer culture, which in turn increased their consumption. The business elite were trendsetters in Norway. They introduced the population to the new European fashion and style, and conveyed new standards for fashionability. Various theories have been discussed to explain social influences, including emulation, imitation, conspicuous consumption, inconspicuous consumption and the trickledown theory (Appendix A). These factors may have been part of the concept of fashionability, and may also have played a role in Norway.

4.5.3. Economy

There has been an extensive historical and economic debate to explain the economic ability of the population to acquire and use an increasing amount of consumer products. Adam Smith (1723–1790) considered luxury products an expression of personal vanity, but they contributed to providing work. Simplified, increased consumption requires increased financial means, which can be linked to a financial reserve, increased income and reprioritization, reduced expenses or increased debt. The present study cannot clarify how the population in Norway could afford to acquire increasing amounts of consumer goods, including the increased import of colorants. The population in Norway was generally not that poor during the 18th century, since natural resources provided export trade with increased income for those who participated in the production chains. The standard of living for the lower social groups was above the subsistence minimum [59]. Parts of the population had increased income potential through seasonal work from several sources (pluri-activity) [36]. The motivation for increased income may have had elements of investment and/or consumption. This may correspond to de Vries' theory of the industrious revolution, where the population of the Netherlands increased their purchasing power for consumer goods through increased paid work [60–62]. Increased income potential for farmers through pluri-activity covered necessary expenses, improved housing standards and ensured future investments. The surplus was also used to achieve increased purchasing power for a better way of life and to acquire luxury goods and status symbols [63]. The population's desire for consumer goods may have been a driving force for increased income.

4.5.4. Enlightenment

More than 90% of the population in Norway lived in the countryside, and shopping played only a minor part in the spread of fashion and knowledge compared to larger European countries. However, the population was exposed to the increased amounts of imported colorants through increased domestic trade, and the increased use of the preferred imported colorants had its own inherent effects on fashionability. In addition to the previously mentioned black books and dye books, newspapers became important sources for the dissemination of knowledge that had an impact on increased demand for pigments and dyes. The effect of enlightenment on increased use of colorants became an important part of the positive feedback loops, where increased demand stimulated increased trade.

4.6. Colorant Imports and the Start of the Consumer Society

During many decades of the18th century, colorant imports were subject to mercantilist restrictions and customs regulations. At the end of the 18th century, most of these restrictions, as well as sumptuary laws, were removed; society developed in a direction of a more liberal ideology with a greater degree of free trade. As shown in Figure 10, stable prices despite increased colorant imports indicate that prices were not driven by market economic principles through the laws of supply and demand. Instead, price-independent market principles, such as an increase in supply and/or demand, may have explained the increased colorant imports.

Jack Homer has looked at the industrial revolution from a feedback perspective in a system dynamic model [64]. Similar positive feedback causal loops may be postulated to explain the growing consumer society following increased imports of consumer goods. Increased exports stimulated increased imports and thereby an increased supply of colorants. When these consumer goods gradually became more available, there was an additionally stimulated increase in demand. These positive feedback loops form the basis of a model that may contribute to understanding the development of the consumer society, illustrated by the increase colorant imports (Figure 23). The population showed a linear doubling during the 18th century. Consequently, the multifold increase in colorant imports with the two chromatic revolutions cannot be explained by an increase in population, only. I will elaborate on some of the factors that may have contributed to increasing the demand for the imported colorants during the second part of the 18th century. The factors are summarized in Figure 23. This figure presents a proposed explanatory model to illustrated increased colorant imports to Norway during the 18th century, based on increased supply and demand for new colorants. Increased imports of colorants during the first and second chromatic revolutions led to an increased supply and use of imported colorants. As previously discussed, increased imports during the first chromatic revolution in the middle of the 18th century may have been the result of increased export trade. In periods of prosperity, this would induce a positive feedback supply loop, which also was stimulated by the changes in society towards liberalism. At the same time, as there was an increased supply of imported colorants, significant changes occurred in the domestic market with increased transportations and sales. In the previous Sections, factors have been discussed that could explain increased demand for imported colorants, which thereby initiated and stimulated positive feedback demand loops with further increased colorant imports. The increased production of consumer goods may also represent a positive feedback loop for increased demand. With respect to the increased use of colorants in Norway, this may be exemplified by increased production of alum, chalk, cobalt, lichen and tar. Based on colorant imports as a motif or exemplary model, Figure 23 may also be applicable as a more general model to summarize factors that facilitated the increased use of other consumer goods contributing to the development of the early consumer society. The color revolution, illustrated by the two chromatic revolutions, was part of the general consumer revolution, which in Norway started approximately in the middle of the 18th century.

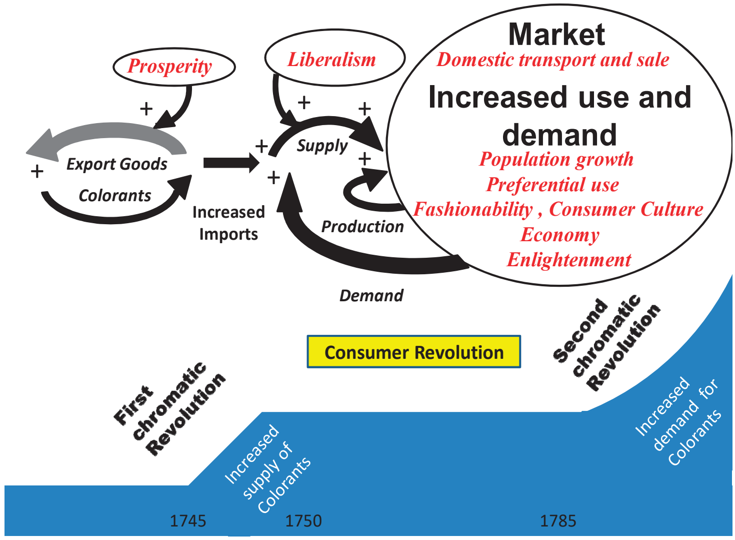


Figure 23. Model for the increased colorant imports into Norway. It also illustrates events that may have contributed to the development of the consumer society from the middle of the 18th century in Norway. This schematic representation includes to the left a positive feed-back supply loop, stimulated by prosperity with increased transnational export trade and import of colorants as return products. The first chromatic “evolution in the middle of the 18th century may represent a “supply (import)-driven increased consumption” for colorants. To the right a positive feed-back demand loop is driven by liberal politics, development of the internal market and factors that increase the demands for colorants, as well as production of consumer goods. This “demand-driven increased consumption” developed during the second part of the 18th century, which culminated in the second chromatic revolution at the end of the century.

Unaltered imports during the first half of the 18th century indicate that the supply of foreign consumer goods was largely adapted to the demand. From a traditional society stage 1, the first half of the 18th century may represent the end of Rostow’s stage 2 in the development of the modern consumer society [65]. Preconditions for economic growth were laid in this phase, prior to the take-off of stage 3 of increased colorant imports (the Norwegian chromatic revolutions) that started in the middle of the 18th century. In the mid-1700s, Norwegian society was “sensitized” to an increased amount of the consumer goods. A change in consumer culture and economic opportunities made it acceptable and possible for a consumer society to develop during the second half of the 18th century.

The start of the consumer society includes increased availability of new consumer goods. The colonial powers had a large intercontinental trade network that included their own colonies. Denmark-Norway had a few colonies (Danish West Indies and Tranquebar), from which the Danes imported colonial goods directly to Copenhagen. Norway had no significant part in this trade. Denmark also imported calico fabrics from India, and Denmark had its own production of colored and printed cotton textiles, which were re-exported. This separate textile “revolution” coincided in time with the Norwegian chromatic revolutions and contributed to the Danish consumer revolution [66]. Sweden had no colonies. The Swedes exported iron and timber, and used silver as a trade commodity to import Chinese silk and tea, which were also re-exported to Europe [29]. The Norwegian export products were the driving forces for the Norwegian trade within Europe. Norway had about half a million inhabitants, approximately the same number of inhabitants living in London. The rise of the consumer society in Norway, from the middle of the 18th century, can largely be attributed to a long period of peace. Prosperity developed to a certain extent, there was an increased domestic trade, which resulted in a flourishing use of consumer goods, including imported colorants. The start of a consumer society from the middle of the 18th century was not a smooth one-way process. It included a number of factors and mechanisms that contributed to a kind of exponential development driven by positive feedback loops.

Sara Pennell has advocated that the explanation for the development of a consumer society must be sought through interdisciplinary approaches, with emphasis on consumer mentality, motivation for increased consumption, qualitative features of possession, and the social and cultural capital that consumer goods can entail [67]. The present model for the development of the consumer society, in Figure 23, is highly simplified and by no means exhaustive, but it takes into account heterogeneous mechanisms and some of the qualitative factors that Pennell refers to.

5. Conclusions

In this study, the increased imports of a variety of colorants have been described, based on registrations from Norwegian customs records during the18th century. These pigments and dyes were used in increasing quantities throughout the country for house painting, decoration and textile dyeing. The imported lead white and tropical indigo comprised the main white and blue pigments used for painting and dyeing, respectively. Imports of red iron oxides and yellow earth pigments were supplements to the similar locally produced pigments. The imported colorants represented examples of both luxury and consumer goods, which together with increased imports and use of other consumer goods reflected a change in consumer culture. It marked the beginning of the consumer society in Norway from the middle of the 18th century. The increased imports were most probably a consequence of the increased Norwegian export trade. A significant further increase at the end of the 18th century seemingly expresses a substantial increased demand for consumer goods. A model for the development of the early start of the consumer society is presented, based on the increased imports of colorants, which takes into account many factors which may have contributed to the increased flow of consumer goods during the second part of the 18th century.

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Appendix A

Chronological overview of the histiography of the development of consumer society in Western countries.

Year	Author	Descriptions and Theories
1714	Bernard Mandeville [56]	Humans are self-absorbed, pleasure-seeking and vain, who sought luxury to fulfill these needs.
1776	Adam Smith [68]	Consumption was the sole purpose of all production.
1899	Thorstein Veblen [69]	Conspicuous consumption and pecuniary emulation.
1904	Georg Simmel [70]	Trickledown effect, mutual influence between social layers.
1932	ElizabethGilboy [71]	Supply and demand were equal driving forces.
1972	Franklin Mendels [72]	Proto-industrialization.
1977	Joel Mokyr [73]	Industrialization was mostly supply-driven. Increased demand requires increased income, falling prices or a change in preferences.
1982	Neil McKendrick [1]	Consumer revolution. Importance of emulation.
1988	Lorna Weatherill [5]	Consumption was promoted as part of a separate middle-class culture, semi-luxury goods.
1990	Carol Shammas [74]	Changes in households with increased demand.
1991	Maxine Berg [75]	Globalization and increased consumption of luxury products, cheaper products.
1991	Beverly Lemire [76]	Fashion was a driving force for the demand and distribution of cotton clothing, spread vertically and horizontally.
1993	Cissy Fairchilds [77]	Nation of shoppers, Dress fashion, populuxe goods.
1994	John Brewer [78]	The importance of demand and consumption.
1994	Jan de Vries [61]	Industrious revolution.
2006	Jonathan White [79]	Access to new goods in the 18th century led to increased consumption.
2009	Joel Mokyr [80]	Importance of enlightenment.
2011	Rene Girard [81]	Mimetic desire.
2016	Joel Mokyr [82]	Importance of consumer culture.

Appendix B

Summary of the colorant items, sorted by name, product type and color, first recorded import year, average price and import quantities.

Name	Product	First Import (year)	Price (daler/ pound)	Quantity Imported during the 18th Century (pound)	Quantity Imported 1685 and/or 1686 (pound)
Alum	Mordant for dyeing	1685	0.09	140,438	2,410
Amber	Additive (resin for painting)	1740			
Annatto (orleans and uldrian)	Yellow dye	1724	0.38	4,637	
Asphalt	Brown pigment	1756			
Berberis roots	Yellow dye	1835			
Bitgelrødt	Red pigment	1733			
Bole	Red pigment	1732			
Bone black	Black pigment	1835			
Bone brown	Brown pigment	1749			
Brazilwood	Red dye and pigment	1686	0.07	131,808	247
Brazilwood, rasped	Red dye and pigment	1724	0.03	68,664	
Brown red	Red pigment	1685	0.02	109,223	80
Brunswick green	Green pigment	1835			
Burnt Sienna	Brown pigment	1756			
Caput mortuum	Reddish purple pigment	1749	0.1	4,993	
Carbon black	Black pigment	1751	0.63	3,583	
Chalk, red chalk	Red pigment	1686	0.19	2,060	17
Chrome yellow	Yellow pigment	1835			
Ciginie red	Red pigment	1794			
Cochineal	Red dye and pigment	1724	4.67	4,242	
Cologne earth	Brown pigment	1756			
Colophony	Additive (varnish for painting)	1731			
Copper(II)sulphate (*blåstein*)	Additive (siccative for painting) and auxillary agent for dyeing	1762	0.18	609	
Copper(II)sulphate (*kobberrøg*)	Additive (siccative for painting) and auxillary agent for dyeing	1756	0.22	331	
Cream of Tartar	Auxiliary agent for dyeing	1685	0.1	37,952	1,063
Danish red	Red pigment	1754		Domestic	
Dyer's buckthorn	Yellow pigment and dye	1724	0.41	2,894	
Earth pigment	Red pigment	1730	0.05	3,904	
English earth	Red pigment	1732	0.05	11,813	
Florentine lake	Red pigment	1742	2	12	
Gallnut	Black dye and mordant	1686	0.27	5,322	69
Glue	Binder for painting	1686	0.07	11,906	736
Graphite	Black pigment	1725	0.1	2,198	
Gum	Additive (dyeing and painting)	1685	0.4	4,142	38
Gum arabic	Additive (dyeing and painting)	1770			
Gum copal	Additive (dyeing and painting)	1835			
Gum elemh	Additive (dyeing and painting)	1835			
Gum from *Burseraceae*	Additive (dyeing and painting)	1724			
Gum tragacanth	Additive (dyeing and painting)	1749			
Gum, ordinary	Additive (dyeing and painting)	1770	0.27	2,063	
Horn glue	Binder for painting	1685	0.1	10,815	490
Indigo	Blue dye and pigment	1686	1.6	68,762	12
Ink powder	Black pigment	1724	0.26	1,311	
Isinglass	Binder for painting	1726	1.43	432	
King's yellow (*kongegult*)	Yellow pigment	1752	0.56	292	
Lake pigment (*kulelakk*)	Red pigment	1725	0.59	645	
Lake pigment (*kurlakk*)	Red pigment	1724	0.44	115	
Lakk	Additive (varnish for painting)	1685	1.02	4,030	53
Lead white	White pigment	1685	0.07	337,661	80
Lead white (*skiferhvitt*)	White pigment	1733	0.19	77	
Lichen	Dye, different colors	1786			
Lichen, black	Dye, different colors	1835			
Lichen, color lichen	Dye, different colors	1835			
Lichen, Island lichen	Dye, different colors	1786			
Lichen, mountain lichen	Dye, different colors	1794			
Lichen, stone lichen	Dye, different colors	1835			
Lichen, white	Dye, different colors	1794			
Linseed oil	Binder for painting	1685	0.16	217,416	6,606
Litharge of silver	Additive (siccative for painting)	1686	0.12	9,645	24
Litmus	Blue dye and pigment	1749	0.17	585	
Logwood (*blauholt*)	Dye, different colors	1749	0.06	2,111	
Logwood (*brissel*)	Dye, different colors	1685	0.04	7,194	610
Logwood (*brown brissel*)	Dye, different colors	1733	0.08	1,105	
Logwood (*campecheholt*)	Dye, different colors	1732		3,989	
Logwood, red	Red dye and pigment	1733			
Madder	Red dye and pigment	1686	0.16	59,920	30
Mastic	Additive (varnish for painting)	1725		43	
Mineral blue	Blue pigment	1835			
Mineral green	Green pigment	1749			

Name	Product	First Import (year)	Price (daler/ pound)	Quantity Imported during the 18th Century (pound)	Quantity Imported 1685 and/or 1686 (pound)
Mineral yellow	Yellow pigment	1835			
Minium, red lead	Red pigment	1685	0.07	60,485	424
Montain blue	Blue pigment	1762			
Naples yellow	Yellow pigment	1749			
Ochre, brown	Brown pigment	1733			
Ochre, yellow	Yellow pigment	1685	0.05	48,543	170
Old fustic or dyer's mulberry	Yellow dye	1774			
Orpiment (orpiment and *rusgel*)	Yellow pigment	1686	0.18	2,197	51
Paris green	Green pigment	1835			
Parrot green	Green pigment	1835			
Peach-stone black	Black pigment	1835			
Pernambuco wood	Red dye, Brazilwood	1724	0.15	26,896	
Potash	Mordant for dyeing	1762	0.18	766,431	
Prussian blue	Blue pigment	1733	1.51	1,537	
Quercitron	Yellow dye	1835			
Reseda luteola, weld, (vav)	Yellow dye	1732			
Resin	Additive (resin for painting)	1686	0.05	35,602	852
Rye oil	Binder for painting	1754			
Safflower	Red/Yellow dye	1756			
Saffron	Yellow pigment	1685	8.61	895	12
Sandalwood	Red dye and pigment	1732	0.08	6,989	
Sandarac	Additive (dyeing and painting)	1742			
Sappanwood	Red dye	1835			
Saw-wort	Yellow dye	1726	0.04	5,894	
Shellac	Additive (varnish for painting, polishing agent)	1749	0.26	1,189	
Sky blue	Blue pigment	1685			
Smalt (*blausel*)	Blue pigment	1685	0.15	19,522	130
Smalt (*oljeblått*)	Blue pigment	1749			
Smalt blue	Blue pigment	1762			
Spike oil	Additive (diluent for painting)	1727			
Sumac	Brown dye	1731	0.1	378,379	
Tar	Black pigment	1685			
Turmeric	Yellow dye and pigment	1724	0.25	1,890	
Turpentine	Additive (diluent for painting)	1685	0.14	16,589	100
Turpentine, oil	Additive (diluent for painting)	1732	0.15	16,913	
Turpentine, venetian	Additive (resin for painting)	1762			
Ultramarine	Blue pigment	1835			
Umber	Brown pigment	1686	0.13	1,038	36
Varnish	Additive (varnish for painting)	1733			
Verdigris	Green dye and pigment	1686	0.6	5,741	12
Vermilion	Red pigment	1686	1.22	1,410	22
Vitriol	Auxiliary agent for dyeing	1685	0.03	101,615	170
Vitriol, anglicum	Auxiliary agent for dyeing	1751		7,571	
Vitriol, blue	Auxiliary agent for dyeing and additive (siccative for painting)	1835			
Vitriol, green	Auxiliary agent for dyeing	1835			
Vitriol, IronI(II)sulfate	Auxiliary agent for dyeing	1749	0.13	39,629	
Vitriol, white	Auxiliary agent for dyeing	1835			
Woad	Blue dye	1724			
Yellow pigment (*blekgult*)	Yellow pigment	1762			

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heritage

Article

Plantae tinctoriae: The 1759 Dissertation on Dye Plants by Engelbert Jörlin

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Abstract: In the late 1750s, the Swedish botanist Engelbert Jörlin (1733–1810), one of Carl Linnaeus' students wrote his dissertation *Plantae tinctoriae* on more than one hundred dye plants. The article presents a systematic study on these dyeing materials and reflects the knowledge in the mid-18th century. His dissertation focused on domestic plants that could be suitable instead of expensive imported trade goods and was published during the Age of Utility (1719–1771). The Latin text of Jörlin's dissertation was first converted into a digital version by the 'Noscemus General Model' from Transkribus and then translated into English. The current scientific names were obtained from various biological websites. The dyestuffs were assigned to four groups: native and applied in Sweden (A); imported trade products (B); native to Sweden with potential use for dyeing (C); non-native and used abroad (D). They were mainly applied for dyeing textiles, less frequently for pharmaceuticals, cosmetics (make-up), inks and artists' pigments. In his dissertation, Jörlin refers to scriptures from antiquity, Latin botanical literature from the 16th and 17th centuries but especially to the publications of Carl Linnaeus.

Keywords: Engelbert Jörlin; Swedish dye plants; traded dyeing materials; Carl Linnaeus; Age of Utility

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1. Introduction

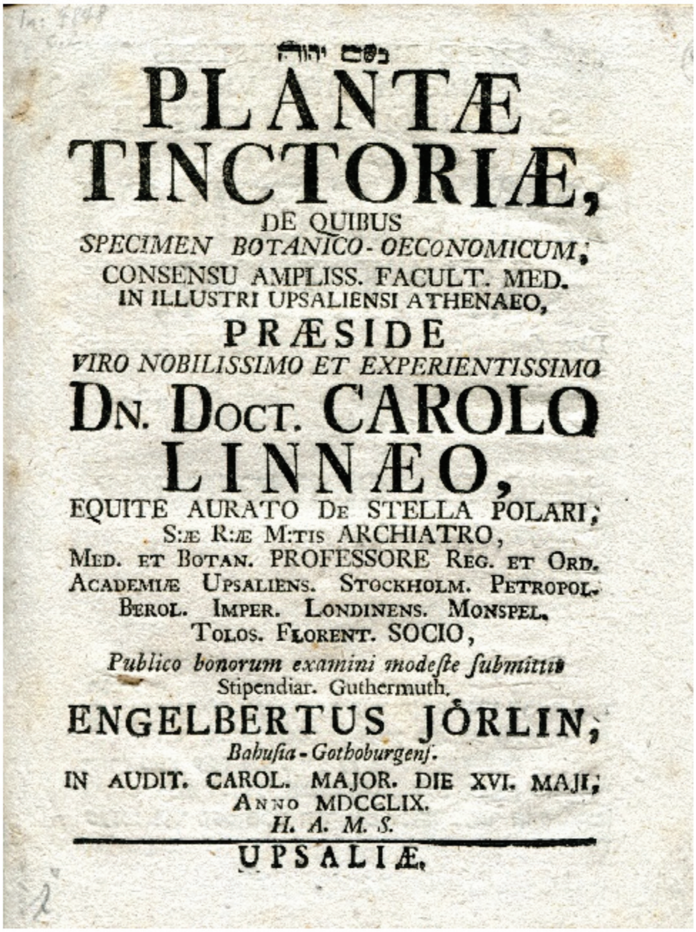
The famous Swedish botanist, zoologist and physician Carl Linnaeus (1707–1778) published 185 dissertations by his students in his 10-volume work of *Amoenitates Academicae* (1749–1790) [1,2], including Engelbert Jörlin's thesis in the fifth volume from 1760 [3]. At the beginning of the 19th century, in 1813, the Austrian naturalist Johann Georg Megerle von Mühlfeld (1780–1831) wrote his book on Austrian dye plants and cited Jörlin's dissertation as "*Linné Dissertatio de plantis tinctoriis in den Amoen. Academ. V. Theil. S. 314*" [4].

In 1759, Jörlin's thesis was published in Sweden during the Age of Utility (Age of Freedom, 1719–1771) [5]. At that time, domestic products were encouraged and sciences, which supported the Swedish economy received subsidies. The research focused on finding indigenous plants and animals that could be substitutes for expensive imported dyeing goods. Pioneers in the field of Swedish dye plants are the botanist Johan Linder (1676–1724) with his 1720 publication *Swenska Färge-Konst* (*Swedish Dye Craft*) and Linnaeus, who describes many dye plants in his scientific writings.

The article presents 130 materials from dye plants and dye insects, reflecting the state of knowledge about domestic and traded dyeing products in the mid-18th century. Furthermore, the publication gives an overview of Engelbert Jörlin's life, followed by a general description of his dissertation. The dyeing materials are discussed according to the colors given by Jörlin and the last chapter is dedicated to lichens, which were of particular interest during the Age of Utility in Sweden. To explain the dyeing properties, current scientific literature served to classify the dyeing materials into chemical dye classes such as flavonoids, anthraquinones, indigoids and tannins [6–8]. The information of Jörlin's dissertation is presented in the present tense without quoting Jörlin’s name each time, and the remaining information is written in the past tense. At the end of each chapter, a table provides information on the dyeing materials, the numbers used by Jörlin, the names by Jörlin and Linnaeus and their current scientific names.

2. Engelbert Jörlin’s Life

Engelbert Jörlin was born in Jörlanda, Västra Götaland County, Sweden on the 8th of June 1733 [9]. He was the second eldest of ten children of the farmer Sven Börjesson (1703–1757) and his wife Börta Engelbrektsdotter (1709–1797). During a parish visit, young Engelbert was noticed by Bishop Georg Wallin, who took him as his foster son and let him study. From the 20th of September 1757, he studied at the Uppsala University, where he became one of Linnaeus’ most talented students. In 1759, Jörlin defended his dissertation *Plantae tinctoriae* in front of his supervisor Linnaeus and became Magister of Philosophy in 1761 (Figure 1).

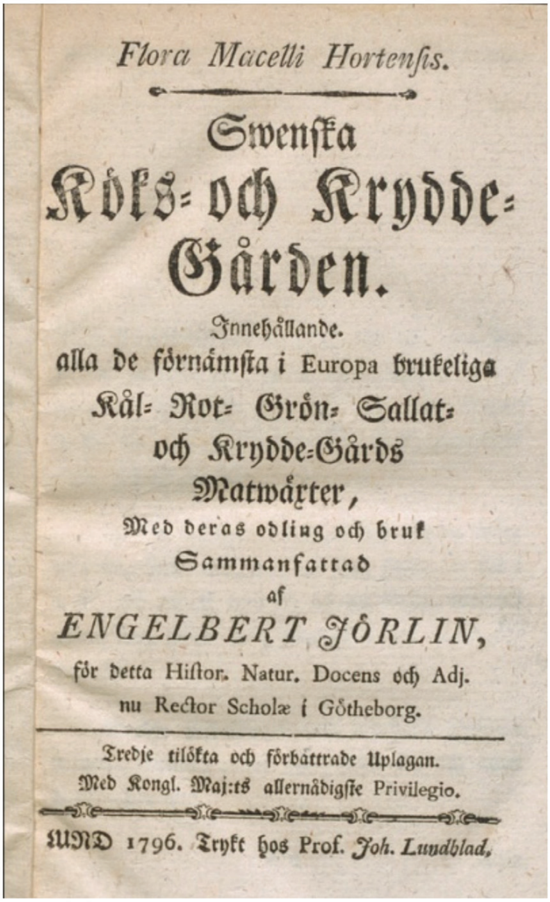


בשם יהוה
PLANTÆ
TINCTORIÆ,
DE QUIBUS
SPECIMEN BOTANICO-OECONOMICUM;
CONSENSU AMPLISS. FACULT. MED.
IN ILLUSTRI UPSALIENSI ATHENAEO,
PRÆSIDE
VIRO NOBILISSIMO ET EXPERIENTISSIMO
Dn. Doct. CAROLO
LINNÆO,
EQUITE AURATO De STELLA POLARI;
S:æ R:æ M:tis ARCHIATRO,
Med. et Botan. PROFESSORE Reg. et Ord.
Academiæ Upsaliens. Stockholm. Petropol.
Berol. Imper. Londinens. Monspel.
Tolos. Florent. SOCIO,
Publico bonorum examini modeſte ſubmittit
Stipendiar. Guthermuth.
ENGELBERTUS JÓRLIN,
Bahuſia-Gothoburgenſ.
IN AUDIT. CAROL. MAJOR. DIE XVI. MAJI;
Anno MDCCLIX.
H. A. M. S.
UPSALIÆ.

Figure 1. Engelbert Jörlin’s dissertation. Image: Courtesy of Hunt Institute for Botanical Documentation, Carnegie Mellon University, Pittsburgh, PA, USA.

A group of students, named the ‘Apostles’ of Linnaeus, undertook botanical and zoological expeditions to various parts of the world. Unfortunately, nearly half of them died during their journey [10]. After graduating, Jörlin also wanted to become an Apostle intending to study the flora and fauna of South Africa. However, the Dutch did not give him permission to travel to the Cape. He then wanted an employment at the Dutch East India Company, warmly recommended by Linnaeus. Again, he was unsuccessful because he did not have a full medical education. Despite all efforts, Jörlin did not become one of Linnaeus' Apostles. Both rejections may have had a positive influence on his lifespan.

After completing several scientific journeys through Sweden, Denmark and northern Germany, he became docent in natural history at the Lund University in 1769 and associate professor (Swedish: extra ordinarie adjunct) in 1781. He also lectured at the gymnasium in Gothenburg; in 1784, he was appointed rector of the Trivial School in Gothenburg, a post he held for several years. In addition to his teaching activities, Jörlin devoted himself to the cultivation of Swedish plants, which is reflected in his publications *Flora macelli hortensis—Svenska Koks-och Kryddgården* (Flora macelli hortensis—Swedish Kitchen and Herb Garden, 1784) and *Svenska vilda träds och buskars plantering* (Planting of Swedish Wild Trees and Shrubs, 1801) (Figure 2). The 2nd and 3rd volume of the *Flora macelli hortensis* were published in 1786 and 1794, and a joint edition was issued in 1796 [11] (p. 288). On the 27th of May 1787, he married the painter Christina Elisabeth Carowsky (1745–1797) and they had one daughter, Britta Maria Jörlin (1789–1848). Engelbert Jörlin passed away on the 20th of June 1810 in Gothenburg.


Flora Macelli Hortenſis.

Swenſka
Köks- och Krydde-
Gården.
Innehållande.
alla de förnämſta i Europa brukeliga
Kål- Rot- Grön- Sallat-
och Krydde-Gårds
Matwärter,
Med deras odling och bruk
Sammanfattad
af
ENGELBERT JÖRLIN,
för detta Hiſtor. Natur. Docens och Adj.
nu Rector Scholæ i Götheborg.

Tredje tilökta och förbättrade Uplagan.
Med Kongl. Maj:ts allernådigſte Privilegio.

LUND 1796. Trykt hos Prof. *Joh. Lundblad,*

Figure 2. *Flora macelli hortensis*—Swedish Kitchen and Herb Garden (1796) [12]. Swedish Literature Bank https://litteraturbanken.se/om/english.html (accessed on 23 November 2022).

3. Research Aim and Investigation Methods

The aim of the research was to study Jörlin's dissertation from various points of view and to make this historical document accessible to various disciplines, such as biology, art history, dye history and heritage science. The following investigation methods were performed: first, a digital version of the Latin text was obtained by the 'Noscemus General Model' from Transkribus [13]. The Latin text was then translated into English. The next step was to create a Microsoft Access database with fields for the plant names, Linnaeus' plant systematic and the distribution and application of the dyestuffs. Jörlin took over the scientific names and the classification of the plants from Linnaeus. Linnaeus' taxonomy and classification has evolved, leading to changes in scientific names of plants and animals and their categorisation into specific families. Several websites served to find out the current scientific names, family names and information about the species' distribution: the International Plant Name Index [14], the Plants of the World Online [15], the Linnaean Plant Name Typification Project [16] and the Global Biodiversity Information Facility websites [17]. Finally, queries were made concerning color and use. One topic of this study was the classification of the dyeing materials into groups according to their occurrence, trade and use (Figure 3).

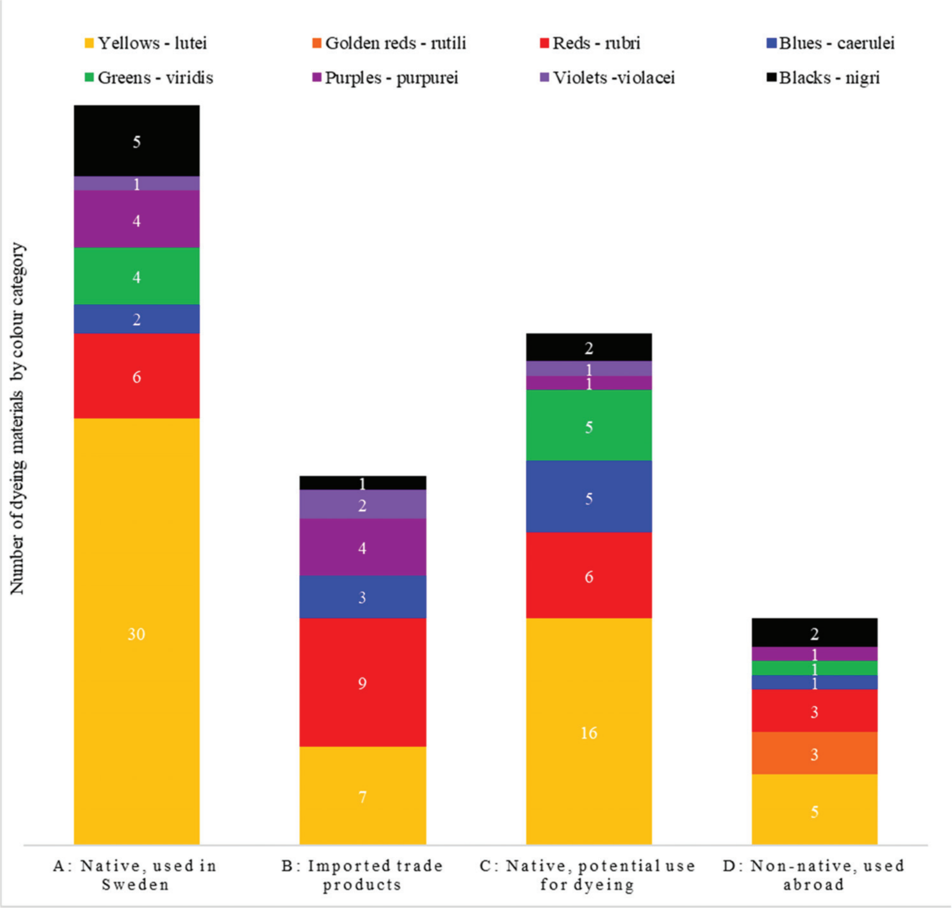
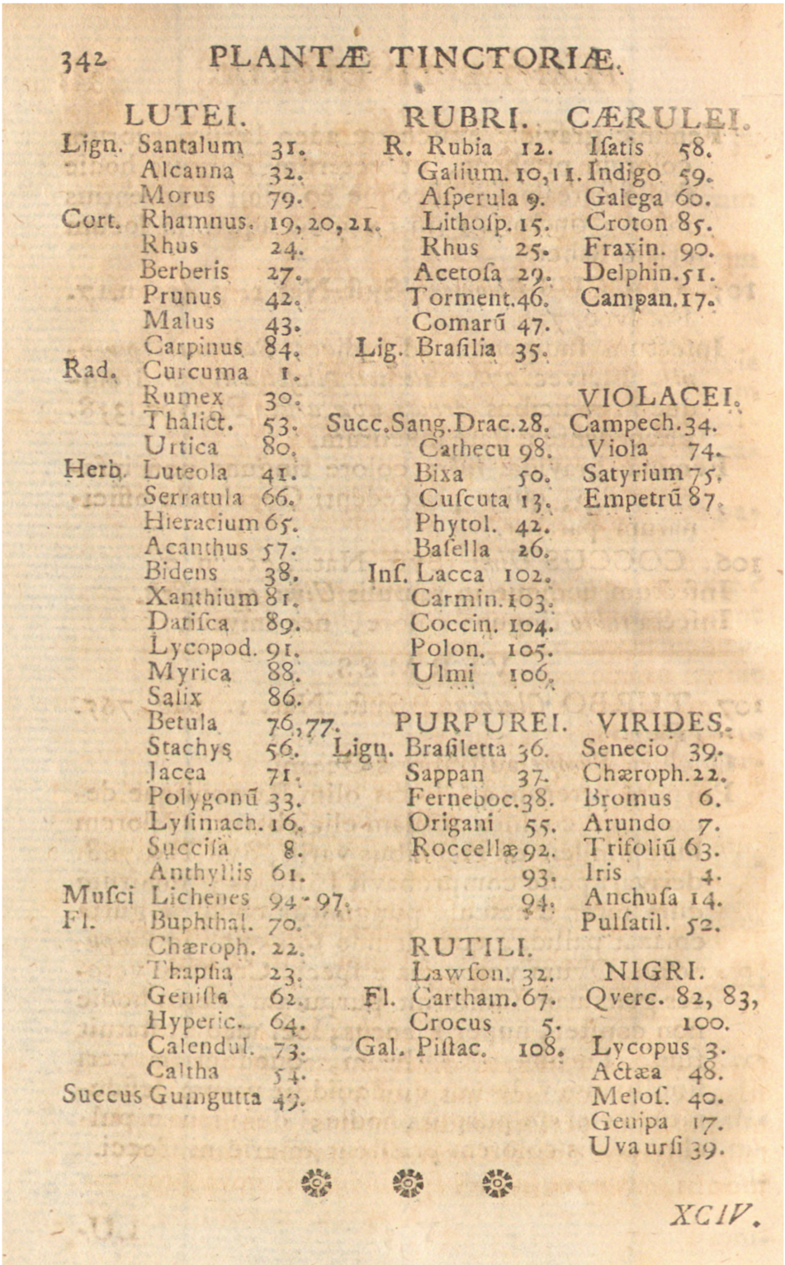


Figure 3. The 130 dyeing materials, sorted into four groups according to their occurrence, trade and use.

4. Jörlin's Dissertation

Jörlin's thesis gives information on 130 dyeing materials, originating from 117 different plant and animal species assigned to 107 numbers. In the 5th volume of Linnaeus' *Amoenitates Academicae,* the dissertation includes an index of only 102 dyeing materials (Figure 4). Some numbers differ, as can be seen from the asterisked numbers in the Tables 3–14.



342 PLANTÆ TINCTORIÆ.

LUTEI.
Lign. Santalum 31.
Alcanna 32.
Morus 79.
Cort. Rhamnus. 19, 20, 21.
Rhus 24.
Berberis 27.
Prunus 42.
Malus 43.
Carpinus 84.
Rad. Curcuma 1.
Rumex 30.
Thalict. 53.
Urtica 80.
Herb. Luteola 41.
Serratula 66.
Hieracium 65.
Acanthus 57.
Bidens 38.
Xanthium 81.
Datiſca 89.
Lycopod. 91.
Myrica 88.
Salix 86.
Betula 76, 77.
Stachys 56.
Jacea 71.
Polygonũ 33.
Lyſimach. 16.
Succiſa 8.
Anthyllis 61.
Muſci Lichenes 94-97.
Fl. Buphthal. 70.
Chæroph. 22.
Thapſia 23.
Geniſta 62.
Hyperic. 64.
Calendul. 73.
Caltha 54.
Succus Gumgutta 49.

RUBRI.
R. Rubia 12.
Galium. 10, 11.
Aſperula 9.
Lithoſp. 15.
Rhus 25.
Acetoſa 29.
Torment. 46.
Comarũ 47.
Lig. Braſilia 35.
Succ. Sang. Drac. 28.
Cathecu 98.
Bixa 50.
Cuſcuta 13.
Phytol. 42.
Baſella 26.
Inſ. Lacca 102.
Carmin. 103.
Coccin. 104.
Polon. 105.
Ulmi 106.

PURPUREI.
Lign. Braſiletta 36.
Sappan 37.
Ferneboc. 38.
Origani 55.
Roccellæ 92.
93.
94.

RUTILI.
Lawſon. 32.
Fl. Cartham. 67.
Crocus 5.
Gal. Piſtac. 108.

CÆRULEI.
Iſatis 58.
Indigo 59.
Galega 60.
Croton 85.
Fraxin. 90.
Delphin. 51.
Campan. 17.

VIOLACEI.
Campech. 34.
Viola 74.
Satyrium 75.
Empetrũ 87.

VIRIDES.
Senecio 39.
Chæroph. 22.
Bromus 6.
Arundo 7.
Trifoliũ 63.
Iris 4.
Anchuſa 14.
Pulſatil. 52.

NIGRI.
Querc. 82, 83, 100.
Lycopus 3.
Actæa 48.
Meloſ. 40.
Genipa 17.
Uva urſi 39.

XCIV.

Figure 4. Index of dyeing materials published in Linnaeus' *Amoenitates Academicae,* 1760 vol. 5, p. 342 [3]. Digitalisierungsplattform der Zentralbibliothek Zürich e-rara.ch.

The majority of the plant species belongs to seed plants (Spermatophyta). Further, Jörlin mentions one clubmoss, seven lichens, molluscan purple, six gall insects and five dye insects: kermes, Polish cochineal, American cochineal, Indian lac and an indigenous insect found on elm trees. Some species provide more than one dye source, so he lists a total of 130 different dyeing materials: 52 from native species used in Sweden, 26 imported products, 36 materials of native origin having the potential to be used in dyeing and 16 materials of non-native species applied abroad (Figure 3). The bar chart shows that the color yellow dominates among the Swedish dye sources, while the majority of traded products are for dyeing red and purple.

The thirty pages of his dissertation begin with religious words of gratitude in Hebrew, which is not found in the 1760 publication. It should be noted that Hebrew, Greek and Latin were taught in Swedish gymnasia. The Old Testament had to be read in Hebrew, the New Testament in Greek [18]. The following text is philosophical and addresses the wonders in nature we perceive with our sensory organs, like the tongue, nose, ears and eyes. The peacock (*Pavo cristatus* Linnaeus, 1758) and the amaryllis (*Amaryllis* L.) are his examples of color variation, and biblical quotations underline his treatise on the beauty and divinity of colors. The next pages are dealing with the aim of the thesis, explanations of terms, physics of colors, the creation of colors by mixing and a general part on the studied plants and animals. Jörlin obtained his information on dye plants from dyers, from his own experiments and from literature. He distinguishes between painting (*pictoriam*) and dyeing (*tinctoriam*). In painting, the pigments are applied on the surface and in dyeing, the dyes are soaked up by the fibres. The dyeing (*tingere*) of wool and silk is performed in the dye works (*infectorium*, *infectorii*).

He does not discuss the preparation of dyes, as there are already many library books published on this topic. He gives an overview of the common dye sources, most of them originate from the flora, some from the animal world but none from the kingdom of stones. He consulted dyers, lexica and many books of famous authors faced with countless names and general descriptions in many different languages. Jörlin obtained the information from ancient scriptures, Latin botanical literature from the 16th and 17th centuries but especially from Linnaeus' works in Swedish and Latin, including Linnaeus' 1758 publication on the journey to the Spanish countries in Europe and America by his Apostle Pehr Löfling between 1751 to 1756, who died in Venezuela. The literature is quoted in the form of abbreviations (Table 1).

Table 1. Literature cited by Engelbert Jörlin.

Author	Publication	Year	Language	Abbreviation
Publius Vergilius Maro (Virgil)	*Aeneid*	29–19 BCE	Latin	Virg.aen.
Pedanius Dioscorides	*De materia medica*	50–70	Greek	Dioscor.
Pliny the Elder	*Naturalis Historia*	77	Latin	Plin.
Johan Bauhin and Johann Heinrich Cherler	*Historia Plantarum Universalis*	1650–1651	Latin	Bauh. hist., Bauh. pin.
John Ray	*Historia Plantarum*	1686, 1688	Latin	(J.) Raj. hist.
Johan Linder (Lindestolpe)	*Swenska Färge-Konst*	1720	Swedish	Lind. tinct.
Georg Eberhard Rumpf (Rumphius)	*Herbarium amboinense*	1741–1750	Latin	Rumph. Amb.
Pehr Kalm	*Förtekning på någre Inhemska Färge-Grås*	1745	Swedish	Act. Stockh. 1745

Table 1. *Cont.*

Author	**Publication**	**Year**	**Language**	**Abbreviation**
Pehr Adrian Gadd	*Försök til en oeconomisk beskrifningöfwer satacunda häraders norra del*	1751	Swedish	Gadd. Satag.
Carl Linnaeus	*Förtekning, Af de Fargegras, som brukas påGotland ock Oeland*	1742	Swedish	Act. Stockh. 1742
Carl Linnaeus	*Systema Naturae*	1735	Latin	Syst. Nat.
Carl Linnaeus	*Flora Lapponica*	1737	Latin	Fl. Lapp.
Carl Linnaeus	*Öländska och Gothländska Resa*	1745	Swedish	It. Oel., It. Gothl.
Carl Linnaeus	*Flora Suecica*	1745	Latin	Fl. svec, Fl. sv.
Carl Linnaeus	*Fauna Suecica*	1746	Latin	Fn. svec.
Carl Linnaeus	*Wästgöta Resa*	1747	Swedish	It. W. goth., Itin. W. Gothico
Carl Linnaeus	*Flora Zeylanica sistens plantas indicas Zeylonae insulae, quae olim 1670–77 lectae fuere a Paulo Hermanno*	1747	Latin	Fl. Zeyl.
Carl Linnaeus	*Skånska Resa*	1751	Swedish	It. scan., Iter Scan.
Carl Linnaeus	*Species Plantarum*	1753	Latin	Sp. pl., Spec. Plant.
Carl Linnaeus	*Iter Hispanicum, eller resa til Spanska Länderna uti Europa och America 1751 til 1756*	1758	Swedish	Loefl. It.

A problem for Jörlin was to receive dyeing materials (*tinctoriae materiae*) from botanists, especially those from Asia and America (*Indiae alterutri*). Therefore, he searches in nature for local plants and collects all the parts that dyers need. Based on literature studies, he knows very well which dyestuffs were used in the other parts of the world.

The next topic is an introduction into the creation of colors. It is not Jörin's intention to explain the physics of color because the English physicist Isaac Newton (1642/43–1726/27) and others already did that. He mentions six primary colors (*colores primarios*): white (*album*), yellow (*luteum*), red (*rubrum*), blue (*caeruleum*), green (*viridem*) and black (*nigrum*). Color variations are obtained by mixing: grey (*cinereus*) from black and white; opal (*opalinus*) from white and blue; pink (*roseus*) from red and white; purple (*purpureus*) from blue and red; violet (*violaceus*) from blue and black; pale green (*pallide viridis*) from yellow and blue and dark green (*obscure viridis*) from blue and yellow.

He observed that some plants change color in the first stage of rotting, concluding that these plants could provide suitable dyes. The dried dog's mercury (*Mercurialis perennis* L.) and the yellow rattle (*Rhinanthus crista-galli* L., Rhinanthus minor L.) become grey and the flowers of *Lotus corniculatus* L. and *Anthyllis vulnerara* L. blue. Black discolorations are known from the black pea (*Orobus niger* L., current name: *Lathyrus niger* (L.) Bernh.), the gipsywort (*Lycopus europaeus* L.) and many roots of parasites, like *Hypocistis* (*Cytisus*), *Cynomorium*, *Monotropa* and *Lathraea* species.

In the case of gall and scale insects, Jörlin notes a close link between animals and plants. Galls are formed when insects lay their eggs in plants, like the *Quercus, Pistacia, Salix*, *Populus*, *Rosa*, *Glechoma*, *Hieracium* and *Statice* (*Limonium*) species. He names the host plants of the scale insects, like cacti (*Opuntia*) for American cochineal, oak (*Quercus*) for kermes, knawel (*Scleranthus perennis*) and bearberry (*Arctostaphylos uva-ursi*) for Polish cochineal.

White is created when naturally colored textile fibres of linen, wool and silk are properly rubbed and washed with soap. Although green is one of the most common colors in nature, it is rarely extracted from plants. According to Jörlin, a master dyer produces green colors by dyeing yellow and blue. Blue colors are hardly gained from indigenous plants. He states that the blue dyes occurring in the plant kingdom are wonderfully altered into a red color with acid and a green color with alkali (*colores caerulei, ab acido rubri, ab alcali virides evadunt*) with one exception, namely the stable indigo. The beautiful red color pleases the eyes with its brightness, but an even more intense color is created when acid is added. The dyers attribute the black color to the flora, which is not quite true because astringent (tannin-containing) plants need substances from the kingdom of stones, especially *martialia* (iron-containing agents). A strong and shiny blackness is achieved when the cloth is saturated with another color.

Linnaeus, the 'father of taxonomy' published his *Clavis Systematis Sexualis* in *Systema Naturae* in 1735 and the binomial nomenclature, the modern system for naming organisms, was for the first time applied in his *Species Plantarum* (1753). Jörlin names the plants and animals after this binomial nomenclature and classifies the dye plants according to the Linnaean system (Table 2). The plants are categorized on the basis of the numbers and characteristics of their male and female reproductive organs. The Rubiaceae have four male organs and are assigned to the *Tetrandria* (tetra = four, andr- = male). Weld (*Reseda luteola*) belongs to the *Dodecandria* (dodec- = twelve) and possesses twelve male organs. Woad (*Isatis tinctoria*) from the *Tetradynamia* (dynam- = power) has four long and two short male organs.

In addition to the dye plants, Jörlin also describes plants for washing textiles, namely *Struthium*, the common soapwort (*Saponaria officinals* L.) and two *Gypsophila* species of the family Caryophyllacae. He cites the Greek physician, pharmacologist and botanist Pedanius Dioscorides (ca. 40-ca. 90 CE) and the Roman politician and scholar Pliny the Elder (23/24-79 CE). Dioscorides says in *De materia medica* (50–70 CE) that fullers wash and clean cloths and wool with *Struthium* (*Saponaria officinals* L.) (Dsc. 2.163). Pliny the Elder in his *Naturalis Historia* (77 CE) notes that the plant rootlet (*radicula*), named *Struthion* by the Greek, provides a juice for washing and makes wool whiter and softer (NH 19.48). *Gypsophila struthium* L., native to Spain, is used by the Spaniards in the province of La Mancha to wash clothes and gives the same result as soap. Jörlin therefore recommends testing the washing properties of the native *Gypsophila fastigiata* L.

Table 2. Classification of the dyeing materials based on the Linnaean system.

Linnaean System	**Jörlin's Numbers**	**Linnaean System**	**Jörlin's Numbers**	**Linnaean System**	**Jörlin's Numbers**
Monandria	1	Dodecandria	43	Gynandria	75
Diandria	2–3	Icosandria	44–47	Monoecia	76–85
Triandria	4–7	Polyandria	48–54	Dioecia	86–89
Tetrandria	8–13	Didynamia	55–57	Polygamia	90
Pentandria	14–26	Tetradynamia	58	Musci (1)	91
Hexandria	27–30	Diadelphia	59–63	Algae (2)	92–97
Octandria	31–33	Polyadelphia	64	Palmae	98
Decandria	34–42	Syngenesia	65–75	Animalia	99–107

(1) In Jörlin's work, *Lycopodium complanatum* (Lycopodiaceae) is classified as a moss. (2) In Jörlin's work, lichens are classified as algae.

5. Yellows—*Lutei*

The majority of dyeing materials in Jörlin's dissertation concerns the yellows. 58 are listed and the most important fifteen species will be discussed first (Table 3). The herbs, leaves, flowers, fruits and old fustic possess flavonoid dyes, saffron contains the carotenoid dye crocetin, gamboge supplies xanthone dyes, barks provide mainly tannins and Indian sandalwood possesses unknown dyes. Seven of the 15 materials were imported: saffron, Avignon berries, tanner's sumach and dyer's sumach from southern Europe or Asia, Indian sandalwood and gamboge from Asia and old fustic from Central and South America.

Jörlin notes that weld (*Reseda luteola*), abundantly imported from abroad, gives a beautiful chamois color and is favored by dyers. In a cloth factory in Norrköping, a city in the province of Östergötland, Linnaeus was told that weld had to be imported although it grew 'like a weed' everywhere in Lund, where it should be cultivated [19] (p. 10), [20] (p. 28). In the past, Sawwort (*Serratula tinctoria*), which dyes like weld, had to be imported, but in the mid-18th century the plant was so common that it was exported. Jörlin refers to Linnaeus, who wrote that double-dyeing for green with sawwort and indigo was practiced in the parish of Gothum on Gotland [19] (p. 224), [20] (p. 139). The plant grew wild around Uppsala, Stockholm, in Östergötland, Öland and Scania [19] (p. 10), [20] (p. 28). In the southern part of Sweden, the herb was gathered by poor people, mainly peasant women, sold to traders and exported to Copenhagen [21] (p. 156).

The bark of the alder buckthorn (*Frangula alnus*) as well as the bark of the common buckthorn (*Rhamnus cathartica*) provide beautiful yellow colors. Jörlin cites Linnaeus, who states, that the inhabitants of Isgärde on Öland dye with the bark of the common buckthorn. In Martebo on Gotland, both barks are used and on Fårö, an island north of Gotland, these barks served to dye cloths [19] (pp. 58, 175, 209), [20] (pp. 53, 115, 132). Persian berries belong to the Swedish imported goods, provide an excellent yellow, are highly esteemed and sold throughout Europe under the name of *grain d'Avignon*. Jörlin writes that these berries originate from the buckthorn species *Rhamnus minor* growing in southern Europe, especially in Spain and in the French commune Narbonne. The Linnaean Plant Name Typification Project website states that the precise synonymy of this name is uncertain and so the current name is *Rhamnus* sp.

The flowers of the dyer's broom (*Genista tinctoria*) are considered excellent for dyeing. The leaves of the moor birch (*Betula pubescens*), producing a faint yellow color, are used from time to time by farmers. Jörlin refers to the Finnish naturalist and chemist Pehr Adrian Gadd (1727–1797) who said that the leaves of the dwarf birch (*Betula nana*) provide a more excellent yellow dye than the moor birch [22] (p. 57). According to Linder, painters used the flowers of the dyer's broom to prepare the pigment *Schutgelb*, while the pigment *Sutgrön* was made from the leaves of the moor birch [23] (pp. 81–82). Dyer's broom, birch leaves, buckthorn berries and other flavonoid providing plants were suitable for the preparation of these pigments. Buckthorn berries were traded in Europe under the name Avignon berries (graines d'Avignon, French berries) and Persian berries (Aleppo berries, Smyrna berries) imported from the Levant. Depending on the ripeness of these berries, yellow and green pigments were prepared. Unripe berries were soaked in a lye (potash) and then precipitated with alum to create the transparent pretty yellow pigment *Schutgelb* (nowadays Stil de grain jaune, formerly pink or pinke). Stil de grain jaune was applied in medieval illuminated manuscripts, in 18th-century French and English paintings, in wallpapers and colored paper. *Sutgrön* (Stil de grain vert) was mostly made from ripe buckthorn berries precipitated with alum. The pigment was rarely used in painting. Both pigments have a poor lightfastness and fade rapidly [24].

The flowers of the dyer's chamomile (*Cota tinctoria*) give a bright yellow color and are highly valued among the native dyeing plants. Jörlin cites Linnaeus, who noted that in Gothum on Gotland the yarns are pre-mordanted with alum in a copper vessel and then boiled in a dye bath prepared with the dried flowers of dyer's chamomile, named *Johannis Blommor* (*Johannis Blomstor*) and *Flores Buphthalmi* [19] (pp. 223–224), [20] (p. 139). According to Linnaeus, *Chrysanthemum* flowers, similar to dyer's chamomile at first glance, were common in the southern Swedish provinces Scania and Halland. However, experiments showed that the *Chrysanthemum* flowers are not a proper substitute for dyer's chamomile.

Saffron, cultivated in southern Europe and Asia, consists of the stigmas of *Crocus sativus* and gives a very beautiful color, so it is widely known, not only for dyeing but also to color pharmaceuticals. The barks of the tanner's sumach (*Rhus coriaria*) and the dyer's sumach (*Cotinus coggygria*), both native to southern Europe and Asia, dye cloths. Jörlin claims that the *lignum medullaris* of Indian sandalwood (*Santalum album* L., Santalaceae) dyes yellow, while the exterior wood rarely occurs in the art of dyeing. The heartwood (*lignum medullaris*) has a darker yellow-to-brown color, while the outer sapwood is pale yellow-to-white [25] (p. 227, Figure 1). Gamboge, the thick yellow latex from *Garcinia hanburyi*, native to Indo-China, is more often used in painting than in dyeing. Old fustic, the wood of the dyer's mulberry (*Maclura tinctoria*) is an essential import commodity. The wood originates from a South American tree (*arbor Americae meridionalis*) and produces the most excellent color for dyeing yellow.

Table 3. Important native plants and trade products for yellow.

Group	**Jörlin-No.**	**Name in Jörlin** ***Linnaean Name***	**Material**	**English Name** ***Swedish Name***	***Current Scientific Name*** **Family**
A	19 19 *	RHAMNUS frangula *Rhamnus frangula* Linnaeus	Bark	Alder buckthorn *Tröske* (*brakved*)	*Frangula alnus* Mill. Rhamnaceae
A	20 20 *	RHAMNUS catharticus *Rhamnus cathartica* Linnaeus	Bark	Common buckthorn *Getapel*	*Rhamnus cathartica* L. Rhamnaceae
A	43 41 *	RESEDA Luteola *Reseda luteola* Linnaeus	Herb	Weld *Wau*	*Reseda luteola* L. Resedaceae
A	62 62 *	GENISTA tinctoria *Genista tinctoria* Linnaeus	Flowers	Dyer's broom *Ginst*, (*färgginst*)	*Genista tinctoria* L. Fabaceae
A	66 66 *	SERRATULA tinctoria *Serratula tinctoria* Linnaeus	Herb	Sawwort *Ängskara*	*Serratula tinctoria* L. Asteraceae
A	70 70 *	ANTHEMIS tinctoria *Anthemis tinctoria* Linnaeus var. tinctoria	Flowers (1)	Dyer's chamomile *Lettblomster*, (*färgkulla, Johannis Blomster*)	*Cota tinctoria* (L.) J.Gay Asteraceae
A	76 76 *	BETULA alba *Betula alba* Linnaeus	Leaves	Moor birch *Biork, björk*	*Betula pubescens* Ehrh. Betulaceae
A	77 77 *	BETULA nana *Betula nana* Linnaeus	Leaves	Dwarf birch *Skarre*, (*dvärgbjörk*)	*Betula nana* L. Betulaceae
B	5 -	CROCUS sativus (2) *Crocus sativus* Linnaeus	Stigmas	Saffron *Safran*	*Crocus sativus* L. Iridaceae
B	21 21 *	RHAMNUS minor *Rhamnus minor* Linnaeus	Fruits	Avignon berry *Grain d'Avignon*	*Rhamnus* sp. Rhamnaceae
B	24 24 *	RHUS coriaria *Rhus coriaria* Linnaeus	Bark	Tanner's sumach *Sumach*, (*bärsumak*)	*Rhus coriaria* L. Anacardiaceae
B	25 -	RHUS Cotinus *Rhus cotinus* Linnaeus	Bark	Smoke tree, dyer's sumach (*Perukbuske*)	*Cotinus coggygria* Scop. Anacardiaceae
B	31 31 *	SANTALUM album *Santalum album* Linnaeus	Wood	Indian sandalwood *Sandel*	*Santalum album* L. Santalaceae
B	49 49 *	CAMBOGIA Gutta -	Latex	Gamboge *Gummi-gutta*	*Garcinia hanburyi* Hook.f. and other *Garcinia* species Clusiaceae
B	79 79 *	MORUS tinctoria *Morus tinctoria* Linnaeus	Wood	Old fustic, dyer's mulberry (*Fustikträdet*)	*Maclura tinctoria* (L.) D.Don ex Steud. Moraceae

Swedish names between brackets are from other sources than Jörlin; * Number occurring in the index sorted by color in Jörlin [3] (p. 342); (1) *Flores Buphthalmi*; (2) Jörlin places saffron in the category of reds (*rutili*); A = native plant, used in Sweden; B = imported trade product.

Eighteen materials are of less importance for dyeing yellow in Sweden (Table 4). The herbs, leaves and flowers provide flavonoid dyes, bark and roots of the common barberry yield the alkaloid dye berberine, and other barks contain mainly tannins.

The herb of the three-lobe beggartick (*Bidens tripartita*) provides a yellow dye. It was known in Scania for yellow and brown, while yellow and orange colors were produced near Isgärde, Hulterstad and Sandby on Öland [19] (pp. 58, 98, 101), [20] (pp. 53, 73, 75), [26] (pp. 240, 277). Rather seldom peasants take the herb of the woundwort (*Anthyllis vulneraria*) to dye their clothes. In Scania, five plants are rarely used by farmers: the dried leaves of devil's bit (*Succisa pratensis*), the herb of Kalm's hawkweed (*Hieracium umbellatum*), the herb of bog-myrtle (*Myrica gale*), the dried leaves of the bay willow (*Salix pentandra*) and the dried leaves of the purple willow (*Salix purpurea*) [26] (pp. 277, 293, 342). The ground-cedar (*Lycopodium complanatum*) dyes a very beautiful yellow and is often applied in rural areas. It should be noted that this dye plant accumulates the element aluminum in the cell sap and can serve as a mordant. In the dye works of Växjö in Småland, the brown knapweed (*Centaurea jacea*) is used instead of sawwort (*Serratula tinctoria*), but experiments show that the brown knapweed dyes less perfectly than sawwort [19] (p. 307), [20] (p. 183).

The corollas of the common marigold (*Calendula officinalis*) yield a yellow dye after squeezing and boiling with alum, and sometimes farmers take the dried corollas instead of saffron. According to the Finnish botanist and naturalist Pehr Kalm (1716–1779), the inflorescences of lady's bedstraw (*Galium verum*), boiled with alum, dye woolen clothes yellow [27] (pp. 251–252), but the roots on the other hand dye red (chapter Reds—rutili). The flowers of St John's wort (*Hypericum perforatum*) taken by rural people are of lesser value. The yellow bark of the apple tree (*Malus* sp.) is used by dyers, the bark of the plum tree (*Prunus domestica*) by country dwellers and the yellow bark of the common hornbeam (*Carpinus betulus*) mainly by Scanians. In Poland, a very pale saffian color is obtained on leather with the yellow bark of the common barberry (*Berberis vulgaris*), and in Sweden its roots are soaked in lye to dye wool. By boiling eggs with the yellow roots of the common nettle (*Urtica dioica*), peasants color the eggshells, especially at Easter.

Table 4. Less important native plants used for yellow.

Group	**Jörlin-No.**	**Name in Jörlin** ***Linnaean Name***	**Material**	**English Name** ***Swedish Name***	***Current Scientific Name*** **Family**
A	8 8 *	SCABIOSA Succisa *Scabiosa succisa* Linnaeus	Leaves	Devil's-bit *Angwadd*	*Succisa pratensis* Moench Dipsacaceae
A	11 -	GALIUM verum *Galium verum* Linnaeus	Flowers	Lady's bedstraw *Mariae Sanghalm*	*Galium verum* L. Rubiaceae
A	27 27 *	BERBERIS vulgaris *Berberis vulgaris* Linnaeus	Bark	Common barberry *Berberis*	*Berberis vulgaris* L. Berberidaceae
A	27 27 *	BERBERIS vulgaris *Berberis vulgaris* Linnaeus	Roots	Common barberry *Berberis*	Berberis vulgaris L. Berberidaceae
A	44 42 *	PRUNUS domestica *Prunus domestica* Linnaeus	Bark	European plum *Plommonträd*	*Prunus domestica* L. Rosaceae
A	45 43 *	PYRUS Malus *Pyrus malus* Linnaeus	Bark	Apple tree *Appel*	*Malus* sp. Rosaceae
A	61 61 *	ANTHYLLIS Vulneraria *Anthyllis vulneraria* Linnaeus	Herb	Kidneyvetch, woundwort *Rafklor (getväppling)*	*Anthyllis vulneraria* L. Fabaceae

Table 4. *Cont.*

Group	**Jörlin-No.**	**Name in Jörlin** ***Linnaean Name***	**Material**	**English Name** ***Swedish Name***	***Current Scientific Name*** **Family**
A	64 64 *	HYPERICUM perforatum *Hypericum perforatum* Linnaeus	Flowers	St. John's wort *Johannisort*	*Hypericum perforatum* L. Hypericaceae
A	65 65 *	HIERACIUM umbellatum Hieracium umbellatum Linnaeus	Herb	Kalm's hawkweed *(Flockfibbla)*	*Hieracium umbellatum* L. Asteraceae
A	68 38 *	BIDENS tripartite *Bidens tripartita* Linnaeus	Herb	Three-lobe beggartick *Brunskär, (brunskära)*	*Bidens tripartita* L. Asteraceae
A	71 71 *	CENTAUREA Jacea *Centaurea jacea* Linnaeus	Herb	Brown knapweed *Knappar, (rödklint)*	*Centaurea jacea* L. Asteraceae
A	73 73 *	CALENDULA officinalis *Calendula officinalis* Linnaeus	Flowers	Common marigold *Ringblomma*	*Calendula officinalis* L. Asteraceae
A	80 80 *	URTICA dioica *Urtica dioica* Linnaeus	Roots	Common nettle *Näßla, (brännässla)*	*Urtica dioica* L. Urticaceae
A	84 84 *	CARPINUS Betulus *Carpinus betulus* Linnaeus	Bark	Common hornbeam *Afwenbok, (avenbok)*	*Carpinus betulus* L. Fagaceae
A	86 86 *	SALIX pentandra *Salix pentandra* Linnaeus	Leaves	Bay willow *Jolster*	*Salix pentandra* L. Salicaceae
A	86 86 *	SALIX purpurea *Salix purpurea* Linnaeus	Leave	Purple willow (*Rödvide*)	*Salix purpurea* L. Salicaceae
A	88 88 *	MYRICA gale *Myrica gale* Linnaeus	Herb	Bog-myrtle *Pors*	*Myrica gale* L. Myricaceae
A	91 91 *	LYCOPODIUM complanatum *Lycopodium complanatum* Linnaeus	Herb	Ground-cedar *Jemna*	*Lycopodiumcomplanatum* L. Lycopodiacae

Swedish names between brackets are from other sources than Jörlin; * Number occurring in the index sorted by color in Jörlin [3] (p. 342); A = native plant, used in Sweden.

Jörlin lists sixteen materials from native plants with the potential for dyeing yellow and five well-known dyestuffs used abroad (Table 5). Nearly all contain flavonoid dyes, turmeric the yellow dye curcumin and galls mainly tannins.

Persicaria maculosa and *Persicaria hydropiper* dye woolen cloths, mordanted with alum, the herb of yellow loosestrife (*Lysimachia vulgaris*) as well as the roots and leaves of the common meadow-rue (*Thalictrum flavum*) dye wool, and an ink can be prepared from the flowers of marsh-marigold (*Caltha palustris*). Furthermore, yellows are created with the herb of yellow loosestrife (*Lysimachia vulgaris*), the herb of hedge woundwort (*Stachys sylvatica*), herb and fruits of the rough cocklebur (*Xanthium strumarium*), the flower heads (umbels) of cow parsley (*Anthriscus sylvestris*) and galls occurring on willows (*Salix* sp.).

Jörlin observes that the green parts of the seashore dock (*Rumex maritimus*), the false hemp (*Datisca cannabina*) and the staghorn sumac (*Rhus typhina*) turn yellow during ripening in the summer. He concludes that they provide yellow dyes and suggests experiments with these plants.

Jörlin describes various plants from abroad. The roots (actually rhizomes) of two plants, namely turmeric (*Curcuma longa*) and the Chinese keys (*Boesenbergia rotunda*), both native to India, dye a rich but fugitive color. The Spaniards dye yellow with the flower heads (umbels) of the villous deadly carrot (*Thapsia villosa*). The English vernacular name points to the poison of the roots, which was applied by fishermen in Catalonia as ichthyotoxin to stun fish to make them easier to catch [28]. Referring to the French traveller and naturalist Pierre Belon (Petrus Bellonius, 1517–1564), Jörlin writes that the pistachio galls serve for the preparation of yellows in the Orient. Jörlin mentions that the herb of bear's breeches

(*Acanthus mollis*) has been known since ancient times, citing the epic Aeneid (1:653) of the Roman poet Publius Vergilius Maro, named Virgil (70–19 BCE): “And the veil woven around (with a border) with saffron-yellow acanthus” (*Et circumtextum croceo velamen Acantho*). Another explanation is that the border of the veil possessed a pattern of acanthus leaves as it occurs in Late Antique textiles.

Table 5. Native plants with potential use for yellow and non-native plants used abroad.

Group	**Jörlin-No.**	**Name in Jörlin** ***Linnaean Name***	**Material**	**English Name** ***Swedish Name***	***Current Scientific Name*** **Family**
C	16 16 *	LYSIMACHIA vulgaris *Lysimachia vulgaris* Linnaeus	Herb	Yellow loosestrife (*Strandlysing*)	*Lysimachia vulgaris* L. Primulaceae
C	22 22 *	CHAEROPHYLLUM Sylvestre *Chaerophyllum sylvestre* Linnaeus	Flowers	Cow parsley *Hundkaxa*	*Anthriscus sylvestris* (L.) Hoffm. Apiaceae
C	30 30 *	RUMEX maritimus (1) *Rumex maritimus* Linnaeus	Herb	Seashore dock *Hafssyra*	*Rumex maritimus* L. Polygonaceae
C	33 33 *	POLYGONUM persicaria *Polygonum persicaria* Linnaeus	Herb	*Jungfru-twäl*	*Persicaria maculosa* Gray Polygonaceae
C	33 33 *	POLYGONUM hydropiper *Polygonum hydropiper* Linnaeus	Herb	*Jungfru-twäl*	*Persicaria hydropiper* (L.) Delarbre Polygonaceae
C	53 53 *	THALICTRUM flavum *Thalictrum flavum* Linnaeus	Roots	Common meadow-rue; (*Ängsruta*)	*Thalictrum flavum* L. Ranunculaceae
C	53 53 *	THALICTRUM flavum *Thalictrum flavum* Linnaeus	Leaves	Common meadow-rue; (*Ängsruta*)	*Thalictrum flavum* L. Ranunculaceae
C	54 54 *	CALTHA palustris *Caltha palustris* Linnaeus	Flowers	Marsh-marigold *Kabbelek*	*Caltha palustris* L. Ranunculaceae
C	56 56 *	STACHYS sylvatica *Stachys sylvatica* Linnaeus	Herb	Hedge woundwort (*Stinksyska*)	*Stachys sylvatica* L. Lamiaceae
C	81 81 *	XANTHIUM strumarium *Xanthium strumarium* Linnaeus	Herb	Rough cocklebur, clotbur (*Gullfrö, ljust gullfrö*)	*Xanthium strumarium* L. Asteraceae
C	81 81 *	XANTHIUM strumarium *Xanthium strumarium* Linnaeus	Fruits	Rough cocklebur, clotbur (*Gullfrö, ljust gullfrö*)	*Xanthium strumarium* L. Asteraceae
C	89 89 *	DATISCA cannabina *Datisca cannabina* Linnaeus	Herb	False hemp, acalbir -	*Datisca cannabina* L. Datiscaceae
C	89 89 *	DATISCA hirta *Datisca hirta* Linnaeus	Herb	Staghorn sumac (*Rönnsumak*)	*Rhus typhina* L. Anacardiaceae
C	99 -	CYNIPS Salicis viminalis -	Galls	Galls -	*Euura viminalis* Kopelke, 2001; *Cynips salicis* subsp. viminalis Christ, 1791 Tenthredinidae

Table 5. *Cont.*

Group	**Jörlin-No.**	**Name in Jörlin** ***Linnaean Name***	**Material**	**English Name** ***Swedish Name***	***Current Scientific Name*** **Family**
C	99 -	CYNIPS Salicis amerinae *Cynips amerinae* Linnaeus, 1758	Galls	Galls on bay willow (*Salix pentandra* L.)	*Euura amerinae* (Linnaeus, 1758) Tenthredinida
C	99 -	CYNIPS Salicis strobili *Cynips salicisstrobili* Linnaeus, 1758	Galls	Galls -	*Pseudencyrtus salicisstrobili* (Linnaeus, 1758) Encyrtidae
D	1 1 *	CURCUMA longa *Curcuma longa* Linnaeus	Roots (2)	Turmeric *Garkmäja*	*Curcuma longa* L. Zingiberaceae
D	1 1 *	CURCUMA rotunda *Curcuma rotunda* Linnaeus	Roots (2)	Chinese keys *Garkmäja*	*Boesenbergia rotunda* (L.) Mansf. Zingiberaceae
D	23 -	THAPSIA villosa *Thapsia villosa* Linnaeus	Flowers	Villous deadly carrot -	*Thapsia villosa* L. Apiaceae
D	57 57 *	ACANTHUS mollis *Acanthus mollis* Linnaeus	Herb	Bear's breeches (*Mjukakantus)*	*Acanthus mollis* L. Acanthaceae
D	101 108 *	APHIDES Pistaciae (3) *Aphis pistaciae* Linnaeus 1767	Galls	Pistachio galls -	*Baizongia pistaciae* (Linnaeus, 1767) on Pistacia terebinthus L.; *Aploneura lentisci* (Passerini 1856) on *Pistacia lentiscus* L. Aphididae

Swedish names between brackets are from other sources than Jörlin; * Number occurring in the index sorted by color in Jörlin [3] (p. 342); (1) In the index, Jörlin lists the roots and not the herb; (2) actually rhizomes; (3) Jörin mentions these galls for dyeing yellow and red, but in the index, it is only placed for dyeing red (*rutili*); C = native plant with potential use for dyeing; D = non-native plant, used abroad.

6. Golden Reds—*Rutili*

For dyeing golden red, three materials are listed (Table 6). *Alkanna* (henna) contains the naphthquinone Lawson, safflower the red dye carthamin and pistachio galls mainly tannins.

Jörlin mentions *Lawsonia inermis* as *Alkanna*, a plant native to Asia and Africa, mainly cultivated in Egypt. It should be noted that the name *Alkanna* dates back to the Arabic term *al-ḥinnā*, meaning henna. Today, *Alkanna* is the genus name for alkanet, which Jörlin names *Pseudo Alcanna* (Table 8). He thinks that the dried herb of *Lawsonia inermis* applied by the Orientals yields an excellent yellow to dye parts of their bodies and further he believes that the roots treated with quicklime (*calx viva*, calcium oxide) yield a red dye to color teeth, nails, faces, manes of horses, hides, wood, waxes, ointments, decoctions and cloths. Today, it is known that the dye originates from the leaves, but not from the herb and roots. According to Jörlin, the corolla of safflower (*Carthamus tinctorius*) treated with acid provides a very bright pink color, which is especially charming on silk (*Corollae Roseum colorem acido praeparatae praebent nitidissimum, serica inprimis venuste colorantem*). For this reason, he proposes the cultivation of safflower, as Linnaeus recommended for southern Sweden twenty years earlier [19] (p. 34), [20] (p. 40). Jörlin quotes Belon, who wrote that the Orientals took pistachio galls to prepare red colors using acid.

Table 6. Non-native plants for golden reds.

Group	**Jörlin-No.**	**Name in Jörlin** ***Linnaean Name***	**Material**	**English Name** ***Swedish Name***	***Current Scientific Name*** **Family**
D	32 32 *	LAWSONIA inermis *Lawsonia inermis* Linnaeus	Leaves	Henna tree, henna *Alkanna*	*Lawsonia inermis* L. Lythraceae
D	67 -	CARTHAMUS tinctorius *Carthamus tinctorius* Linnaeus	Flowers	Safflower *Safflor*	*Carthamus tinctorius* L. Asteraceae
D	101 108 *	APHIDES Pistaciae *Aphis pistaciae* Linnaeus 1767	Galls	Pistachio galls -	*Baizongia pistaciae* (Linnaeus, 1767) on *Pistacia terebinthus* L.; *Aploneura lentisci* (Passerini 1856) on *Pistacia lentiscus* L. Aphididae

* Number occurring in the index sorted by color in Jörlin [3] (p. 342); D = non-native plant, used abroad.

7. Reds—*Rubri*

For dyeing red, 24 materials are listed, which are divided in two groups (Tables 7 and 8). The first group includes the roots (actually rhizomes) of four Rubiaceae species and five scale insects, which all provide anthraquinone dyes (Table 7). The following four materials were imported: dyer's madder and kermes from the Mediterranean region, lac dye from Asia and American cochineal from Central and South America.

Jörlin reports that the imported dyer's madder (*Rubia tinctorum*) as well as indigenous Rubiaceae species are commonly used by the dyers. On the Baltic islands, the roots of dyer's woodruff (*Asperula tinctoria*) are collected before the stems sprout. It is proved by dyers' experiments that these roots provide an excellent substitute for dyer's madder. He refers to Linnaeus: "It is essential that the roots be collected before the cuckoo starts calling, that is before the roots put up stems; since the roots are looser then and yield more color... One cooks them with the sourest beer, especially the kind of *Standebilla*, for the sourer the beer is the more intense the color becomes ... After boiling the roots, the yarns or stockings are put into the decoction, while it is still warm, then they are rinsed quickly in a weak lye" [19] (pp. 238–239), [20] (p. 147). The malt left over after the beer production was treated again with water to produce a very sour malt brew, which the Gotlanders gave in their dye baths because only limewater occurs on Gotland [29] (pp. 20–21). *Asperula tinctoria* was found near Päsnäs on Öland, on Stora Karlsö, an island off the west coast of Gotland and in the vicinities of Visby, Martebo, Rute, När and Alskog on Gotland, where it grew in such quantities that it could be collected for dye works [19] (pp. 115–116, 168, 187, 195, 238–239, 283), [20] (pp. 84, 111, 120, 125, 147, 171). Jörlin reports that the farmers in Finland take the roots of the northern bedstraw (*Galium boreale*) for dyeing wool. He cites Kalm who stated that the roots of lady's bedstraw (*Galium verum*) also give a red color [27] (p. 244).

Other anthraquinone sources are the female scale insects of American cochineal (*Dactylopius coccus*), kermes (*Kermes ilicis*), Polish cochineal (*Porphyrophora polonica*) and lac dye (*Kerria lacca*). In the tropical greenhouse (*Caldarium*) of the Botanical (Linnaean) Garden in Uppsala, Jörlin saw cochineal insects (*Dactylopius coccus*) vividly some years ago and writes enthusiastically about this dye: "Dried pregnant females give such a nice red color, that today we can easily live without the purple of our ancestors, and there is nothing more frequent in the art of dyeing".

He states that dyers and pharmacists use the insects of *Kermes ilicis*. It can be assumed that Jörlin means kermes (*Kermes vermilio* Planchon, 1864) because *Kermes ilicis* provides only "slightly pinkish beige-browns" [8] (p. 609). Jörlin considers *Kermes ilicis,* American cochineal (*Dactylopius coccus*) and redwood (*Caesalpinia*) as organic coloring matters precipitated on alum for a Florentine Lake. Jörlin claims that Polish cochineal (*Porphyrophora polonica*) is native to Sweden where he discovered the species in the summer of 1858. This dye insect is found on the roots of three plants, the perennial knawel (*Scleranthus perennis* L.), the mouse-ear hawkweed (*Hieracium pilosella* L.) and the bearberry (*Arctostaphylos uva-ursi* (L.) Spreng.). In his view, the color of Polish cochineal is not inferior to American cochineal. Regarding the oystershell scale (*Lepidosaphes ulmi*), he only says that it is a native insect that provides red. Jörlin describes lac insects (*Insecta laccifera*), referring to the German physician and botanist Paul Hermann (Hermannus, 1646–1695) who was a medical officer to the Dutch East India Company in Ceylon between 1670 and 1677, where he collected many plants, particularly in the area around Colombo. Hermannus stated that these insects, native to *Indiae orientalis*, provide a resinous secretion on *Croton aromaticus* L. (*Croton laccifer* L.), sold as lacca. According to Jörlin, lacca is often used for dyeing pharmaceuticals and clothlets (*bezetta*).

Clothlets were prepared according to a historic method by soaking small pieces of tissue in a juice or liquid mainly derived from plants, which were then dried in order to store a water-soluble coloring matter until needed. They were made from the finest crepon, cotton and Dutch linen especially in red hues but also in other colors, like pale or dark yellow, green, blue, brown and violet. The most expensive colors were rose and carmoisin. Dyes for red and violet clothlets were obtained from American cochineal (*Dactylopius coccus*) and dyer's croton (tournesol, *Chrozophora tinctoria*), but Jörlin knows that lac dye (*Kerria lacca*), dyer's alkanet (*Alkanna matthioli*) and inkberries (*Phytolacca americana*) served for red *bezetta* and Malabar spinach (*Basella alba*) for violet *bezetta*. When artists needed them as coloring agents, these tissues were moistened in a small container with a little water. This technique has been known since the Middle Ages, mainly in manuscript illumination and later in watercolor. The technique of making pezzette was already described by the Italian painter Cennino Cennini (c. 1360-before 1427) in his 1390 *Il libro dell'arte*. Clothlets also served in cosmetics for make-up and to color wax, liqueurs, confectionary, baked goods, confitures, jellies and creams [30].

The second group of reds contains eight materials with different red dyes and seven tannin-rich plants (Table 8). The roots of two Boraginaceae species contain the naphthoquinone dye alkannin, the ripe buckthorn berries and the European dodder anthocyanins, the red dye nordin occurs in dragon's blood, the homoisoflavonoid dye brazilein in brazilwood, the carotinoid bixin in annatto and the betacyanin dye phytolaccanin in inkberries. Tormentil roots, the root bark of tanner's sumach, the root bark of dyer's sumach, alder bark, common sorrel, native sorrel and catechu mainly provide tannins. The following five materials were imported: dyer's alkanet from the Mediterranean region, dragon's blood from India, the fruits the Areca palm from Asia, brazilwood and annatto from Central and South America.

Jörlin mentions that the roots of imported dyer's alkanet (*Alkanna matthioli*) give a color, which is not lightfast and is hardly applicable for dyeing pharmaceuticals except for *bezetta*. He explains that the roots of the common bugloss (*Anchusa officinalis*) can replace the roots of dyer's alkanet. Linnaeus reported that another Boraginaceae species served as a kind of make-up, particularly in Hälsingland, a province in central Sweden belonging to Norrland [31] (p. 46). Young women took the fresh roots of the field gromwell (*Buglossoides arvensis* (L.) I.M.Johnst., *Lithospermum arvense* L.), washed them slightly and colored their faces with them. It gave them a pleasant red color on their cheeks that was attractive to suitors [21] (pp. 158–159).

Table 7. Rubiaceae species and scale insects for red.

Group	**Jörlin-No.**	**Name in Jörlin** ***Linnaean Name***	**Material**	**English Name** ***Swedish Name***	***Current Scientific Name*** **Family**
A	9 9 *	ASPERULA tinctoria *Asperula tinctoria* Linnaeus	Roots (1)	Dyer's woodruff *Madra*	*Asperula tinctoria* L. Rubiaceae
A	10 10 *	GALIUM boreale *Galium boreale* Linnaeus	Roots (1)	Northern bedstraw *Mära*	*Galium boreale* L. Rubiaceae
A	11 11 *	GALIUM verum *Galium verum* Linnaeus	Roots (1)	Lady's bedstraw *Mariae Sanghalm*	*Galium verum* L. Rubiaceae
B	12 12 *	RUBIA tinctorum *Rubia tinctorum* Linnaeus	Roots (1)	Dyer's madder *Krapp*	*Rubia tinctorum* L. Rubiaceae
B	102 102 *	INSECTA laccifera -	Insects	Lac dye *Lacca*	*Kerria lacca* (Kerr, 1782) Kerriidae
B	103 103 *	COCCUS ilicis *Coccus ilicis* Linnaeus, 1758	Insects	- -	*Kermes ilicis* (Linnaeus, 1758) (2) Kermesidae
B	104 104 *	COCCUS cacti Coccus cacti Linnaeus, 1758	Insects	American cochineal *Coccionell*	*Dactylopius coccus* Costa, 1829 Dactylopiidae
C	105 105 *	COCCUS Polonicus *Coccus polonicus* Linnaeus, 1758	Insects	Polish cochineal -	*Porphyrophora polonica* (Linnaeus, 1758) Margarodidae
C	106 106 *	COCCUS Ulmi *Coccus ulmi* Linnaeus, 1758	Insects	Oystershell scale -	*Lepidosaphes ulmi* (Linnaeus, 1758) Diaspididae

* Number occurring in the index sorted by color in Jörlin [3] (p. 342); (1) actually rhizomes; (2) Meant is kermes, *Kermes vermilio* Planchon, 1864; A = native plant, used in Sweden; B = imported trade product; C = native animal with potential use for dyeing.

The herb of the European dodder (*Cuscuta europaea*) yields a pale reddish shade, and the ripe buckthorn berries (*Rhamnus cathartica*) provide a pink juice when picked in the late fall. The German naturalist, physician and explorer Engelbert Kaempfer (Kaempferus, 1651–1716) reported that the fruits of *Calamus rotang*, native to India, are a source of dragon's blood, but Jörlin assumes that also other genera provide this resinous substance. He further notes its application by doctors to color pharmaceuticals. Regarding imported brazilwood (*Caesalpinia brasiliensis*), he only says that it is very common in dyeing. Annatto from the American pokeweed (*Bixa orellana*) is used by dyers and the American Indians paint their naked bodies with these seeds. The juice of the inkberries (*Phytolacca americana*) gives a fugitive pink dye for tinctures and *bezetta*.

The tormentil roots (*Potentilla erecta*) provide a red color and Linnaeus reported that chewed roots were smeared on leather in Lapland [31] (p. 171, No. 213). The alder bark (*Alnus* sp.), the roots of the purple marshlocks (*Potentilla palustris*), the root barks of the tanner's sumach (*Rhus coriaria*) and the root barks of the dyer's sumach (*Cotinus coggygria*) are well suited for dyeing red. The dried roots of the native sorrel (*Rumex acetosa*) are distilled for pharmaceuticals but not for dyeing textiles. The unripe fruits of the betel palm (*Areca catechu*), growing in tropical Asia, are boiled in water with quicklime (*calx viva*, calcium oxide) to produce the 'catechu of pharmacists' that serves more for coloring medicine than for dyeing.

Table 8. Other dyeing materials for red.

Group	**Jörlin-No.**	**Name in Jörlin** ***Linnaean Name***	**Material**	**English Name** ***Swedish Name***	***Current Scientific Name*** **Family**
A	29 29 *	RUMEX Acetosa *Rumex acetosa* Linnaeus	Roots	Common sorrel *Syra,* (*ängssyra*)	*Rumex acetosa* L. Polygonaceae
A	46 46 *	TORMENTILLA erecta *Tormentilla erecta* Linnaeus	Roots	Tormentil *Blodrot*	*Potentilla erecta* (L.) Raeusch. Rosaceae
A	78 -	BETULA Alnus *Betula alnus* Linnaeus	Bark	Black alder and grey alder *Al*	*Alnus glutinosa* (L.) Gaertn. and *Alnus incana* (L.) Moench; Betulaceae
B	15 15 *	LITHOSPERMUM tinctorium *Lithospermum tinctorium* Linnaeus	Roots	Dyer’s alkanet *Pseudo Alcanna*	*Alkanna matthioli* Tausch, syn. *Alkanna tinctoria* Tausch subsp. *tinctoria* Boraginaceae
B	28 28 *	CALAMUS Rotang *Calamus rotang* Linnaeus	Resin	Dragon’s blood *Sangvis draconis*	*Calamus rotang* L. Arecaceae
B	35 35 *	CAESALPINIA brasiliensis *Caesalpinia brasiliensis* Linnaeus	Wood	Brazilwood *Brasilja*	*Caesalpinia brasiliensis* L. Fabaceae, subfamily Caesalpinioideae
B	50 50 *	BIXA Orellana *Bixa orellana* Linnaeus	Seeds	Annatto *Orlean*	*Bixa orellana* L. Bixaceae
B	98 98 *	ARECA Cathecu *Areca catechu* Linnaeus	Fruits	Areca palm *Terra Cathecu*	*Areca catechu* L. Arecaceae
C	13 13 *	CUSCUTA europaea *Cuscuta europaea* Linnaeus	Herb	European dodder *Snar-refwa*	*Cuscuta europaea* L. Convolvulaceae
C	14,15 -	ANCHUSA officinalis *Anchusa officinalis* Linnaeus	Roots	Common bugloss *Oxtunga*	*Anchusa officinalis* L. Boraginaceae
C	20 -	RHAMNUS catharticus *Rhamnus cathartica* Linnaeus	Berries	Common buckthorn *Getapel*	*Rhamnus cathartica* L. Rhamnaceae
C	47 47 *	COMARUM palustre *Comarum palustre* Linnaeus	Roots	Purple marshlocks *Krakfotter,* (*kråkklöver*)	*Potentilla palustris* (L.) Scop. Rosaceae
D	24 -	RHUS coriaria *Rhus coriaria* Linnaeus	Roots	Tanner’s sumach *Sumach,* (*bärsumak*)	*Rhus coriaria* L. Anacardiaceae
D	25 25 *	RHUS Cotinus *Rhus cotinus* Linnaeus	Roots	Smoke tree, dyer’s sumach (*Perukbuske*)	*Cotinus coggygria* Scop. Anacardiaceae
D	42 42 *	PHYTOLACCA americana *Phytolacca americana* Linnaeus	Berries	American pokeweed, inkberry (*Amerikanskt kermesbär*)	*Phytolacca americana* L. Phytolaccaceae

Swedish names between brackets are from other sources than Jörlin; * Number occurring in the index sorted by color in Jörlin [3] (p. 342); A = native plant, used in Sweden; B = imported trade product; C = native plant with potential use for dyeing; D = non-native plant used abroad.

8. Blues—*Caerulei*

For dyeing blue, ten materials are listed (Table 9). Four indigo plants provide the blue pigment indigotin, blue flowers of three species contain anthocyanins, yellow flowers of two species seem to provide unknown blue dyes, tournesol yields chrozophoridin and the ash bark an unknown blue dye. The following three materials were imported: woad from the neighboring countries, indigo from India and dyer’s croton from the Mediterranean region or Asia.

Jörlin writes on woad (*Isatis tinctoria*) that it is planted in Sweden, although more than a fair amount is imported from neighboring countries. Further, he points to a woad mill at Alingsås in Västergötaland as indicated by Linnaeus (Figure 5) [32] (pp. 127–128). For the processing of woad, Jörlin quotes the *Historia Plantarum* by the British botanist John Ray (1627–1705) [33] (p. 842). Woad was mixed with indigo in a *blåkyppen* (blue vat). Linnaeus observed that woad grows wild near Torp in the north of the island Öland and recommended its cultivation on Lillholmen, a small island near Stockholm, and on the island of Klasen north of Gotland, where he found the plant on the coast [19] (pp. 111–112, 144, 216), [20] (pp. 82, 98, 135).

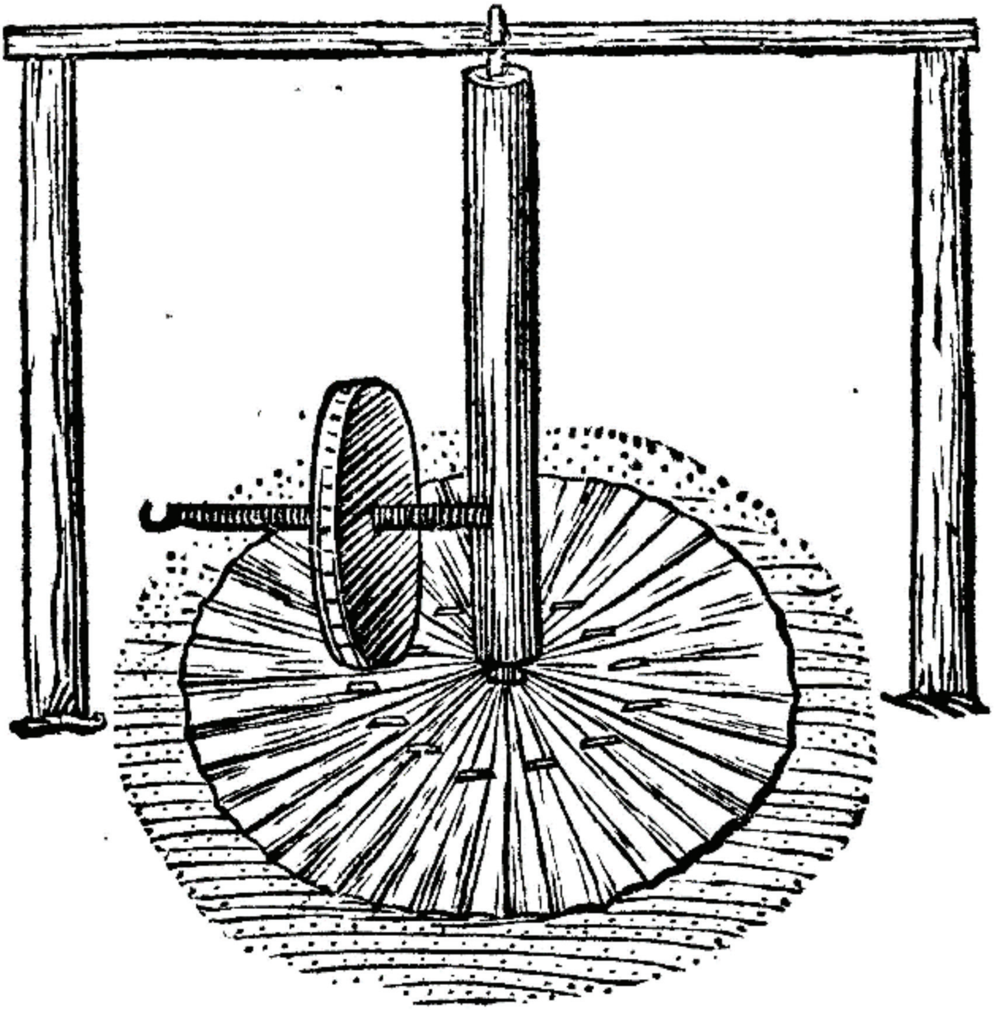


Figure 5. Woad mill in Alingsås in Västergotaland [32] (p. 128). Image: Niedersächsische Staats- und Universitätsbibliothek Göttingen, Germany, Signatur 8 H NAT III, 1380.

Indigo gained from *Indigofera tinctoria*, native to India and Indo-China, is the most excellent among all known dyestuffs and is therefore very popular. It has to be imported at a high price from foreigners, so efforts are still made to find a European plant as a substitute. Jörlin cites Ray's *Historia Plantarum*, which described the production of indigo as observed by the Spanish naturalist and court physician Francisco Hernández de Toledo (1514–1587) [33] (p. 927). Accompanied by his son, Hernández researched the plants of Mexico for their medicinal properties. It can therefore be assumed that he observed the indigo production process during this expedition (1570–1577). However, neither Jörlin (1759) nor Ray (1686) provide information on the country where the indigo production took place. The production is described as follows: The leaves are cut and put into a pot of boiling water, and after some time, the pot is taken off the fire to cool. To bring oxygen into the solution, shovels are moved vigorously. Then the solution is transferred into a vessel with holes higher up. After the sediment has sunk, the water leaves the vessel through the holes. The indigo is dried in the sun and small indigo balls are formed. Jörlin cites Hermann who reported that a blue dye, superior to indigo, is made from *Tephrosia tinctoria* by the Sinhalese but hitherto unknown to the Europeans [34] (p. 302).

Tournesol or lacmus originating from the dyer's croton (*Chrozophora tinctoria*), native to the Mediterranean region, Central Asia and Northwest India, provides a blue color for dyeing paper and pharmaceuticals [35]. As the color is easily changed by alkali and acid, it is also applied to test the water quality. Linnaeus used the dyer's croton when he tested the quality of a well at Roma Monastery on Gotland in 1741 [19] (p. 293), [20] (p. 175).

The juice of the flowers of the field larkspur (*Delphinium consolida*), boiled with alum, gives a blue color for scribes; the corollas of the harebell (*Campanula rotundifolia*) and the cornflower (*Centaurea cyanus*) are other sources for writing. The bark of the common ash (*Fraxinus excelsior*) turning blue in water is specified in a recipe by Linder: A cloth is pre-treated with the ground cedar (*Lycopodium complanatum*) and then dyed blue with the inner bark of the common ash (*Fraxinus excelsior*) [23] (p. 63). Interestingly, American settlers took the inner bark of the blue ash (*Fraxinus quadrangulate* Michx.) to dye yarns blue [36]. The yellow flowers of the woundwort (*Anthyllis vulneraria*) and the bird's foot clover (*Lotus corniculatus*) become blue after drying. From these color observations, Jörlin concludes that these flowers are suitable for dyeing blue.

Table 9. Dyeing materials for blue.

Group	**Jörlin-No.**	**Name in Jörlin** ***Linnaean Name***	**Material**	**English Name** ***Swedish Name***	***Current Scientific Name*** **Family**
A	51 51 *	DELPHINIUM Consolida *Delphinium consolida* Linnaeus	Flowers	Field larkspur *Riddar-sporre*	*Delphinium consolida* L. Ranunculaceae
A B	58 58 *	ISATIS tinctoria *Isatis tinctoria* Linnaeus	Herb	Woad *Weide, (vejde)*	*Isatis tinctoria* L. Brassicaceae
B	59 59 *	INDIGOFERA tinctoria *Indigofera tinctoria* Linnaeus	Leaves	Indigo *Indigo*	*Indigofera tinctoria* L. Fabaceae
B	85 85 *	CROTON tinctorium *Croton tinctorius* Linnaeus	Fruits	Dyer's croton, folium *Lacmus, tournesol*	*Chrozophora tinctoria* (L.) A.Juss. Euphorbiaceae
C	18 17 *	CAMPANULA rotundifolia *Campanula rotundifolia* Linnaeus	Flowers	Harebell, Scottish bluebell *Kläcka, (liten blåklocka)*	*Campanula rotundifolia* L. Campanulaceae
C	59,61 -	ANTHYLLIS Vulneraria *Anthyllis vulneraria* Linnaeus	Flowers	Woundwort, Kidneyvetch *Rafklor, (getväppling)*	*Anthyllis vulneraria* L. Fabaceae

Table 9. *Cont.*

Group	Jörlin-No.	Name in Jörlin *Linnaean Name*	Material	English Name *Swedish Name*	*Current Scientific Name* Family
C	59 -	Lotus corniculate *Lotus corniculatus* Linnaeus	Flowers	Bird's-foot trefoil (*Käringtand*)	*Lotus corniculatus* L. Fabaceae
C	72 -	CENTAUREA Cyanus *Centaurea cyanus* Linnaeus	Flowers	Cornflower *Blåklint*	*Centaurea cyanus* L. Asteraceae
C	90 90 *	FRAXINUS excelsior *Fraxinus excelsior* Linnaeus	Bark	Common ash *Ask*	*Fraxinus excelsior* L. Oleaceae
D	60 60 *	GALEGA tinctoria *Galega tinctoria* (Linnaeus) Linnaeus	Leaves	Orange Tephrosia -	*Tephrosia tinctoria* (L.) Pers. Fabaceae

Swedish names between brackets are from other sources than Jörlin; * Number occurring in the index sorted by color in Jörlin [3] (p. 342); A = native plant, used in Sweden; B = imported trade product; C = native plant with potential use for dyeing; D = non-native plant, used abroad.

9. Greens—*Viridis*

For dyeing green, ten materials are listed (Table 10). The herb of two plants, the panicles of two grasses, flowers of five species contain anthocyanins and the unripe alder buckthorn fruits provide flavonoid dyes.

In the general part of the dissertation, Jörlin mentions that green is created by dyeing yellow and blue, but nevertheless ten species are given. The unripe fruits of the alder buckthorn (*Frangula alnus*) dye wool in a green color. Swedish countrymen apply the panicles of the common reed (*Phragmites australis*). In Linnaeus' opinion, two plant species were known for dyeing green in Scania, the panicles of the rye brome (*Bromus secalinus*) by the farmers near the city of Ystad, and the flower heads of the red clover (*Trifolium pratense*) for woolen garments [26] (p. 277).

The flowers of the German bearded iris (*Iris germanica*), boiled with alum, and the juice of squeezed flowers of the pasqueflower (*Anemone pulsatilla*) yield green tinctures for writing. Woolen clothes can be dyed a saturated green with the roots, stems and leaves of the ragwort (*Jacobaea vulgaris*). They are picked before flowering, not dried and boiled with the textiles. However, the color is weakened by the solar rays ("*color autem, a radiis solaribus debilitatur*"). Pure and beautiful greens are obtained with the herb of the cow parsley (*Anthriscus sylvestris*), the freshly squeezed flowers of the common bugloss (*Anchusa officinalis*) and the flowers of the harebell (*Campanula rotundifolia*), the last two are boiled with alum.

Table 10. Dyeing materials for green.

Group	Jörlin-No.	Name in Jörlin *Linnaean Name*	Material	English Name *Swedish Name*	*Current Scientific Name* Family
A	6 6 *	BROMUS secalinus *Bromus secalinus* Linnaeus	Panicles	Rye brome *Losta, Swingel*	*Bromus secalinus* L. Poaceae
A	7 7 *	ARUNDO phragmites *Arundo phragmites* Linnaeus	Panicles	Common reed *Was, (bladvass, rörvass)*	*Phragmites australis* (Cav.) Trin. ex Steud. Poaceae
A	19 -	RHAMNUS frangula *Rhamnus frangula* Linnaeus	Berries	Alder buckthorn *Tröske, (brakved)*	*Frangula alnus* Mill. Rhamnaceae

Table 10. *Cont.*

Group	Jörlin-No.	Name in Jörlin *Linnaean Name*	Material	English Name *Swedish Name*	*Current Scientific Name* Family
A	63 63 *	TRIFOLIUM pratense *Trifolium pratense* Linnaeus	Flowers	Red clover *Rodwapling, (rödklöver)*	*Trifolium pratense* L. Fabaceae
C	14 14 *	ANCHUSA officinalis *Anchusa officinalis* Linnaeus	Flowers	Common bugloss *Oxtunga*	*Anchusa officinalis* L. Boraginaceae
C	18 -	CAMPANULA rotundifolia *Campanula rotundifolia* Linnaeus	Flowers	Harebell *Kläcka, (liten blåklocka)*	*Campanula rotundifolia* L. Campanulaceae
C	22 22 *	CHAEROPHYLLUM sylvestre *Chaerophyllum sylvestre* Linnaeus	Herb	Cow parsley *Hundkaxa*	*Anthriscus sylvestris* (L.) Hoffm. Apiaceae
C	52 52 *	ANEMONE Pulsatilla *Anemone pulsatilla* Linnaeus	Flowers	Pasqueflower *Backsippa*	*Anemone pulsatilla* L. Ranunculaceae
C	69 39 *	SENESIO Jacobaea *Senecio jacobaea* Linnaeus	Herb with roots	Ragwort *Stånds*	*Jacobaea vulgaris* Gaertn. Asteraceae
D	4 4 *	IRIS germanica *Iris germanica* Linnaeus	Flowers	German bearded iris *Swerdslilja*	*Iris germanica* L. Iridaceae

Swedish names between brackets are from other sources than Jörlin; * Number occurring in the index sorted by color in Jörlin [3] (p. 342); A = native plant, used in Sweden; C = native plant with potential use for dyeing; D = non-native plant, used abroad.

10. Purples—*Purpurei*

For dyeing purple, ten materials are listed (Table 11). Molluscan purple provides 6,6′-dibromoindigotin and other indigoid dyes, three species of soluble redwoods yield the homoisoflavonoid dye brazilein, berries of two species and flowers of one species contain anthocyanins. The following three sorts of soluble redwoods were imported: sappanwood from Asia, brasilletto from Central America and pernambuco wood from Brazil.

Jörlin writes that the purple of antiquity, once sung by the Greeks and Romans, was produced from a certain snail species. He mistakenly thinks that the snail gives off a liquid when pierced between its tentacles but knows very well that the pale liquid of the snail turns purple when exposed to the sun. He mentions *Turbo clathrus* as a possible species but is not sure that it is the right source. Whatever its origins, Jörlin states that molluscan purple is little missed because American cochineal (*Dactylopius coccus*) provides a beautiful color. Nowadays, it is known that real purple does not originate from this marine snail species but from the banded dye-murex the banded dye-murex, *Hexaplex trunculus* (Linnaeus, 1758), the spiny dye-murex, *Bolinus brandaris* Linnaeus, 1758, and the red-mouthed rockshell, *Stramonita haemastoma* (Linnaeus, 1767).

Three imported species of soluble redwoods are given: pernambuco wood (*Paubrasilia echinata*), sappanwood (*Biancaea sappan*) and brasiletto (*Caesalpinia vesicaria*). They give beautiful reds and purples, mainly for dyeing cloths. For pernambuco he points to Ray's *Historia Plantarum* [33] (p. 1737) and to the *Historia Plantarum Universalis* written by the Swiss botanists and physicians Johan Bauhin (1541–1613) and Johann Heinrich Cherler (1569–1609/10) [37] (p. 494).

The privet berries (*Ligustrum vulgare*) provide a purple dye and in his *Historia Plantarum*, Ray notes that these berries serve to illuminate playing cards and other pictures ("*qui chartulas lusorias aliasve picturas variis coloribus illuminant*") [33] (p. 1603). Black crowberries (*Empetrum nigrum*), boiled with alum, dye clothes a dark purple hue. Referring to Linnaeus, Jörlin states that farmers in the province Scania and on the island Öland gain purple colors from the flowering branches of the oregano (*Origanum vulgare*) [19] (pp. 58, 97, 101), [26] (p. 277). During the Öland journey, he observed that oregano created reds near Isgärde, brown colors in the neighborhood of Hulterstad and brownish reds in the area of Sandby [20] (pp. 53, 73, 76).

Table 11. Dyeing materials for purple.

Group	**Jörlin-No.**	**Name in Jörlin** ***Linnaean Name***	**Material**	**English Name** ***Swedish Name***	***Current Scientific Name*** **Family**
A	2 -	LIGUSTRUM vulgare *Ligustrum vulgare* Linnaeus	Berries	Wild privet *Liguster*	*Ligustrum vulgare* L. Oleaceae
A	55 55 *	Origanum vulgare *Origanum vulgare* Linnaeus	Flowers	Oregano *Dosta, (Kungsmynta)*	*Origanum vulgare* L. Lamiaceae
B	36 36 *	CAESALPINIA vesicaria *Caesalpinia vesicaria* Linnaeus	Wood	Brasilletto *Brasilletta*	*Tara vesicaria* (L.) Molinari, Sánchez Och. & Mayta; *Caesalpinia vesicaria* L. Fabaceae, subfamily Caesalpinioideae
B	37 37 *	CAESALPINIA Sappan *Caesalpinia sappan* Linnaeus	Wood	Sappanwood *Sappan*	*Biancaea sappan* (L.) Tod., syn. *Caesalpinia sappan* L. Fabaceae, subfamily Caesalpinioideae
B	38 38 *	LIGNUM rubrum -	Wood	Pernambuco wood, brazilwood *Fernbock*	*Paubrasilia echinata* (Lam.) Gagnon, H.C.Lima & G.P.Lewis, *Caesalpinia echinata* Lam. Fabaceae, subfamily Caesalpinioideae
C	87 87 *	EMPETRUM nigrum (1) *Empetrum nigrum* Linnaeus	Berries	Black crowberry *Kraklinge,* *(Kråkbär, kråkris)*	*Empetrum nigrum* L. Empetraceae
D	107 -	TURBO Clathrus *Turbo clathrus* Linnaeus, 1758	Snails	- *Purpur*	*Epitonium clathrus* (Linnaeus, 1758) Epitoniidae

Swedish names between brackets are from other sources than Jörlin; * Number occurring in the index sorted by color in Jörlin [3] (p. 342); (1) Jörlin mentions that the berries provide a dark purple color, but in the index, it is only placed for dyeing violet (*violacei*); A = native plant, used in Sweden; B = imported trade product; C = native plant with potential use for dyeing; D = non-native animal with historical use abroad.

11. Violets—*Violacei*

For dyeing violet, four materials are listed (Table 12). The flowers of two species and berries of one species contain anthocyanins and logwood the homoisoflavonoid dye haematein. The following two materials were imported: the Malabar spinach from tropical Asia and logwood from Central America.

Jörlin reports that the juice from the petals of the common violet (*Viola odorata*) is applied for dyeing pharmaceuticals and to detect acid and alkali in water. Imported logwood (*Haematoxylum campechianum*), a tree native to the Central America (*arbor Indiae occidentalis*), gives a violet hue on cloths but mainly serves as a base for black. The juice of the berries of the Malabar spinach (*Basella alba*), which grows in tropical Asia, dyes an elegant violet color, but due to its poor colorfastness it is only suitable for cosmetics, tinctures and clothlets (*bezetta*). The flowers of the black vanilla orchid (*Nigritella nigra*) add a violet shade to the spirit of corn.

Table 12. Dyeing materials for violet.

Group	Jörlin-No.	Name in Jörlin *Linnaean Name*	Material	English Name *Swedish Name*	*Current Scientific Name* Family
A	75 74 *	VIOLA odorata *Viola odorata* Linnaeus	Flowers	Common violet *Fioler, (luktviol)*	*Viola odorata* L. Violaceae
B	34 34 *	HAEMATOXYLON campechianum *Haematoxylum campechianum* Linnaeus	Wood	Logwood, Campeche wood *Blauholtz, Campecheträd*	*Haematoxylum campechianum* L. Fabaceae, subfamily Caesalpinioideae
B	26 26 *	BASELLA rubra (1) *Basella rubra* Linnaeus	Berries	Malabar spinach *(Malabarspenat)*	*Basella alba* L. Basellaceae
C	75 75 *	SATYRIUM nigrum *Satyrium nigrum* Linnaeus	Flowers	Black vanilla orchid *Brunkulla*	*Nigritella nigra* (L.) Rchb. Orchidaceae

Swedish names between brackets are from other sources than Jörlin; * Number occurring in the index sorted by color in Jörlin [3] (p. 342); (1) Jörlin mentions that this plant provides a fugitive violet, but in the index, it is only placed for dyeing red (rubri); A = native plant, used in Sweden; B = imported trade product; C = native plant with potential use for dyeing.

12. Blacks—*Nigri*

For dyeing black, ten materials are listed (Table 13). Barks, leaves, fruit cups and galls contain mainly tannins, gypsywort and berries of foreign plants possess unknown dyes. The cups of the valonia oak were imported from the Mediterranean region.

Jörlin mentions that the leaves of the bearberry (*Arctostaphylos uva-ursi*) are often used for dyeing, and Linnaeus described this plant growing in Lapland, Småland (Brånsmåla, Villeköl) and Gotland (Martebo) [31] (pp. 122–125), [19] (pp. 21, 32, 182), [20] (pp. 33, 39, 119). In a cloth factory in Norrköping, Linnaeus was told that a black was dyed with the bearberry twigs and vitriol instead of foreign sumac (*Rhus*) [19] (p. 10), [20] (p. 28). The branches and leaves of the bearberry, known as mjölon or 'Swedish sumac', dyed alum-mordanted wool yellow, and an iron-based mordant was used to obtain dull yellow, green, brown and grey tints. Farmers from all parts of Sweden sold this product to the cities, where it was applied by tanners and dyers for green, grey and 'castor black'. Mjölon was exported to Finland and known by dyers in Norway and Denmark [38].

The alder bark (*Alnus incana*) provides a red color, but in particular fishermen dye their nets black using this bark with *martialia* (iron-containing agents). Bark, galls and fruit cups of oaks (*Quercus* sp.) are other sources. Oak galls, rich in tannins, form on the underside of oak leaves after the female gall wasps (*Cynips quercusfolii*) have laid their eggs in the leaves. The common oak (*Quercus robur*) is known as the tree of iron-black (*arbor nigrum Martiale*). The imported cups of the valonia oak (*Quercus ithaburensis*), native to the Mediterranean region, are more common among tanners than among dyers. The juice of baneberries (*Actaea spicata*) boiled with alum provides a black ink. The 'Cingali' dye their faces brown to black with the juice of gipsywort (*Lycopus europaeus*), which cannot be washed away. Two other plant species also dye the skin. When eaten, the berries of various *Melastoma* species, native to Asia, dye the mouth and lips black, which lasts for a fortnight and the same is true for the unripe berries of *Genipa americana.* Hands washed in this juice get a color that cannot be removed for fourteen days. American Indians apply these berries in two ways, to dye their clothes and to paint their faces with the juice to deter their enemies.

Table 13. Dyeing materials for black.

Group	**Jörlin-No.**	**Name in Jörlin** ***Linnaean Name***	**Material**	**English Name** ***Swedish Name***	***Current Scientific Name*** **Family**
A	39 39 *	ARBUTUS Uva ursi *Arbutus uva-ursi* Linnaeus	Leaves	Bearberry *Mjölonris, (mjölon)*	*Arctostaphylos uva-ursi* (L.) Spreng. Ericaceae
A	78 -	BETULA Alnus *Betula alnus* Linnaeus	Bark	Black alder and grey alder *Al*	*Alnus glutinosa* (L.) Gaertn. and *Alnus incana* (L.) Moench; Betulaceae
A	82 82 *	QUERCUS robur *Quercus robur* Linnaeus	Fruits	Common oak *Ek*	*Quercus robur* L. Fagaceae
A	82 82 *	QUERCUS robur *Quercus robur* Linnaeus	Bark	Common oak *Ek*	*Quercus robur* L. Fagaceae
A	100 100 *	CYNIPS Qvercus folii *Cynips quercusfolii* Linnaeus, 1758	Galls	Oak galls *Galläple*	*Cynips quercusfolii* Linnaeus, 1758 Cynipidae
B	83 83 *	QUERCUS Aegilops *Quercus aegilops* Linnaeus	Fruits	Valonia oak (*Valonia-ek*)	*Quercus ithaburensis* Decne. ssp. macrolepis (Kotschy) Hedge & Yalt. Fagaceae
C	3 3 *	LYCOPUS europaeus *Lycopus europaeus* Linnaeus	Herb	Gipsywort (*Strandklo*)	*Lycopus europaeus* L. Lamiaceae
C	48 48 *	ACTAEA spicata *Actaea spicata* Linnaeus	Berries	Baneberry *Trollbar, (trolldruva)*	*Actaea spicata* L. Ranunculaceae
D	17 17 *	GENIPA americana *Genipa americana* Linnaeus	Berries	- -	*Genipa americana* L. Rubiaceae
D	40 40 *	MELASTOMA variarum specierum -	Berries	- -	*Melastoma malabathricum* L. and other species of Melastomaceae

Swedish names between brackets are from other sources than Jörlin; * Number occurring in the index sorted by color in Jörlin [3] (p. 342); A = native plant, used in Sweden; B = imported trade product; C = native plant with potential use for dyeing; D = non-native plant, used abroad.

13. Lichens

Seven lichen species are listed for dyeing purple and yellow (Table 14). Lichens that contain depsides and depsidones provide the purple dye orcein. The yellow colors are due to anthraquinone or xanthone dyes.

Lichens played an important role in the Swedish dye history especially during the Age of Utility (1719–1771), when the use of domestic manufactured products was encouraged. Their application has been subject of investigation by Linder, Linnaeus and two of his students, Pehr Kalm and Johan Peter Westring.

An article written by Kalm [27], and the dissertation of his student Carl Fridric Leopold *Korta frågor angående nyttan af inländska water*, 1753) (*Short questions concerning the use of our domestic plants*) [39] mention native dye lichens, stating that "no realm has more of these [lichens] than Sweden" [40] (p. 299). The Swedish physician and naturalist Johan Peter Westring (1753–1833) investigated the dyeing properties of numerous lichens and published his studies in Swedish in 1805 [41]. It was also his idea to replace expensive imports of dyeing materials with native species to benefit the Swedish economy.

Jörlin writes that *byttelet* (*Ochrolechia tartarea*) gives a purple color and is often used by the inhabitants of Västergötland [32] (pp. 146–147). This lichen species was gathered by coastal dwellers and fishermen along the west coast of Sweden and Norway. Especially after rainfall, it was scraped off the cliffs with the help of a sharp bent knife or a special tool. Linnaeus was told that the inhabitants of the town Borås travelled annually to the Hisingen archipelago north of Gothenburg to collect these lichens. They prepared *Böttelet*, also named *Boråsfärg* (Borås dye), which peddlers traded all over the country. Merchants in Gothenburg bought large quantities of this product and exported it to Scotland for dyeing tweed [40] (p. 301), [21] (p. 158). Kalm described the harvesting and dyeing of *Ochrolechia tartarea* (*Lichen leprosus candidus*) in Bohuslän, a province on the west coast of Sweden: The lichens were scraped off the rocks immediately after rainfall. Then they were put into water and stirred up to remove small stones and impurities, which sank to the bottom of the vessel. Next, the lichens were dried in the sun, ground and washed again. The clean powder was dried, put into a jug with urine and left for one month. When the dye was needed, a spoonful or more was taken and put into a vessel with water. After quickly boiling the cloth was dyed, taken out and finally hung up to dry [27] (pp. 245–246), [40] (p. 298).

Another source is crottle (*Parmelia saxatilis*), which is popular for dyeing wool and clothes in rural areas, as Linnaeus observed in Småland, on Öland and Gotland [19] (pp. 30, 101, 209), [20] (pp. 38, 75, 132). In Sandby on Öland, he saw the dyeing process of wool with 'stone moss' (*Parmelia saxatilis*): The lichens and unmordanted yarns were placed layer by layer in a pot and then boiled in water with lye, a strong alkaline solution made by soaking wood ash in water [19] (p. 101), [20] (p. 75). Without additives, the lichens gave the yarns beautiful brown ('moss brown') to brownish-red colors, which was practiced all over the country [40] (p. 103), [21] (p. 157). It seems that only native lichens were applied to dye textiles. Interestingly, orchil (*Roccella tinctoria*), growing mainly on rocks in the Mediterranean area, is not imported to Sweden for textile dyeing, but Jörlin mentions its use to make the wine brighter in color.

Four lichen species are the sources for yellow dyes. Swedish women take *Xanthoria parietina* and Swedish countrymen dye woolen clothes with *Vulpicida juniperinus*, while *Xanthoria candelaria* and *Trentepohlia jolithus* are of less importance.

Table 14. Lichens for purple and yellow.

Group	**Jörlin-No.**	**Name in Jörlin** ***Linnaean Name***	**Color**	**English Name** ***Swedish Name***	***Current Scientific Name*** **Family**
A	92 -	LICHEN tartareus *Lichen tartareus* Linnaeus	Purple	Viking dye-moss *Byttelet*	*Ochrolechia tartarea* (L.) A.Massal. Ochrolechiaceae
A	93 93 *	LICHEN saxatilis *Lichen saxatilis* Linnaeus	Purple	Crottle *Stenmoßa*	*Parmelia saxatilis* (L.) Ach. Parmeliaceae
B	92 92 *	LICHEN Roccella *Lichen roccella* Linnaeus	Purple	Orchil lichen *Orseille*	*Roccella tinctoria* DC. Roccellaceae
A	94 94 *	LICHEN Juniperinus (1) *Lichen juniperinus* Linnaeus	Yellow	- *Enmoßa* (*enlav*)	*Vulpicida juniperinus* (L.) J.-E. Mattsson & M. J. Lai Parmeliaceae
A	95 -	LICHEN parietinus *Lichen parietinus* Linnaeus	Yellow	Yellow wall lichen *Wäggmåssa*	*Xanthoria parietina* (L.) Th. Fr. Teloschistaceae
A	96 -	LICHEN candelarius *Lichen candelarius* Linnaeus	Yellow	- *Liusmåssa, (ljus-laf)*	*Xanthoria candelaria* (L.) Th.Fr. Teloschistaceae
A	97 97 *	BYSSUS Jolithus *Byssus jolithus* Linnaeus	Yellow	- *Violmåssa*	*Trentepohlia jolithus* (L.) Wallr. Trentepohliaceae

Swedish names between brackets are from other sources than Jörlin; * Number occurring in the index sorted by color in Jörlin [3] (p. 342); (1) Jörlin mentions this lichen only for dyeing yellow, but in the index, it is also noted for dyeing purple (*purpurei*); A = native plant, used in Sweden; B = imported trade product.

14. Conclusions

The hitherto hardly known dissertation *Plantae tinctoriae* by Engelbert Jörlin can be regarded as an historical document on dyeing materials from the mid-18th century. The thesis is successfully studied by applying the 'Noscemus General Model' from Transkribus to transcribe the Latin text, creating a Microsoft Access database and consulting several websites for the information on dye plants and dye insects.

40% of the used dye materials are of native origin (A), 20% are imported (B), 28% of the materials are native to Sweden having a potential to be used in dyeing (C), and 12% concern non-native species that are used abroad (D). During the Age of Utility (1719–1771), the use of domestic manufactured products was encouraged to replace expensive imported trade goods. Native lichens played an important role in that period. One aim of the dissertation was to find new indigenous dyeing materials as substitutes.

The materials were mainly applied for dyeing textile materials and textiles, like wool, silk, woolen cloths, clothes and garments but also for other applications, such as coloring pharmaceuticals, cosmetics (make-up), tinctures and spirit of corn. Red and violet clothlets (*bezetta*), inks and the artist's pigments *Schutgelb* (Stil de grain jaune) and *Sutgrön* (Stil de grain vert) were used for art purposes. The fruits of dyer's croton (*Chrozophora tinctoria*) and the petals of the common violet (*Viola odorata*) served for testing the water quality because their dyes are sensitive to acid and alkali. Jörlin is aware that some dyes have a poor lightfastness, such as the green from ragwort (*Jacobaea vulgaris*), the red from dyer's alkanet (*Alkanna matthioli*), the violet from berries of the Malabar spinach (*Basella alba*) and the pink of inkberries (*Phytolacca americana*).

He performed dyeing experiments to test the dyeing properties of certain plants but he does not go into detail. Without knowing it, Jörlin describes the anthocyanins in an indirect way. He mentions the characteristic color change of the blue dyes from flowers and fruits into red with acid and green with alkali (*colores caerulei, ab acido rubri, ab alcali virides evadunt*). However, it was not until 1835 that the German pharmacist Ludwig Clamor Marquart (1804–1881) gave the name *Anthokyan* to a chemical compound from blue flowers in his treatise *Die Farben der Blüthen*. The knowledge derived from Jörlin's research is now accessible to the scientific community and maybe there are more secrets hidden in his dissertation.

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Article

Woaded Blue: A Colorful Approach to the Dialectic between Written Historical Sources, Experimental Archaeology, Chromatographic Analyses, and Biochemical Research

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Abstract: Research into the sustainability of natural, potentially renewable, resources is one of the major issues of our time. It naturally includes the quest for sustainable sources of colorants for textiles, cosmetics, and food. In industrialized countries, natural dyeing with plants and a few species of coccid insects was practiced on a large scale for centuries before synthetic colorants were developed. Therefore, historical documents on the growing of dye plants and dyeing processes offer a relevant basis from which to start reconsidering the potential of natural colorants in our time. However, written sources need to be completed by experimental archaeologists to allow a scientific understanding of the biochemical reactions at work in the historical processes described. The results of such interdisciplinary research can then inspire contemporary programs to revive the production of natural dyes. The long history of dyeing blue with woad, *Isatis tinctoria* L., is revisited here as an illustration of the fruitful complementarity of sources and approaches. This article presents a step-by-step reassessment of the production chain of woad as described in historical texts, from the growing of the plant to its use as a source of indigo in the woad and indigo vats. The experimental reconstitution of the processing of woad leaves into couched woad allowed us to follow the evolution of the composition and proportions of indigoid colorants in the leaves by HPLC analyses. Additionally, HPLC analyses allowed a comparison of the respective indigoid contents of couched woad and *sukumo*, the form of indigo dye resulting from another couching process, traditionally used in Japan for dyers' knotweed, *Persicaria tinctoria* (Ait.) H. Gross. The reconstitution of the 18th century woad and indigo vat process allowed investigations into the bacterial flora associated with the use of couched woad in vat liquors, which were found to contain different indigo-reducing bacteria, including two distinct strains of a new indigo-reducing species.

Keywords: natural dyes; indigo; woad; *Isatis tinctoria*; woad balls; couched woad; woad and indigo vat; HPLC; indigoid colorants; indigo-reducing bacteria; Etienne Ferrières's Register; Antoine Janot; Paul Gout; 18th century memoirs on dyeing; reconstitution of dyeing processes

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1. Introduction—Context and Purpose

In the present global state of the world, it should appear evident that, with the accelerated depletion of fossil energies and resources, the survival of humankind requires better knowledge and hence, intensified research into the sustainability of natural, potentially renewable, resources. The production and uses of natural colorants are a part of this major issue of our time, particularly as obvious sources of colorants for textiles, cosmetics, and food. In industrialized countries, natural dyeing was practiced on a large scale for centuries before the first synthetic colorants were developed. Therefore, historical documents on the growing of dye plants and dyeing offer a relevant basis from which to start reconsidering the potential of natural colorants in our time.

In Europe, historical archives, both public and private, abound in documents on the cultivation of dye plants and dyeing processes. However, these seldom give all the necessary information and even when precise quantitative data are provided, they need to be converted into modern metrological systems and put into proper economic and technological contexts to become meaningful. Further, it is often not obvious to fully grasp the scale of the technical processes described and assess their relevance to present conditions. In such a situation, experimental archaeology provides a most useful complementary approach to check the accuracy and usefulness of historical sources, and to better understand the biochemical reactions at work in the described processes. In addition, experimental archaeology can reveal gaps in historical technical descriptions and inspire contemporary programs to revive the production of natural dyes. To that effect, woad was grown, collected, and processed into couched woad in France by the first author and then sent to Japan to the third author who used it to set a biological woad and indigo vat according to 18th century French dyers' recipes, as part of her experimental studies of a range of biological indigo vats.

This paper presents a case study illustrating the complementarity of these sources and approaches concerning the production of blues via vat dyeing. The focus of this paper is on a particularly important part of the history of the production of blue dyes, by presenting a step-by-step re-assessment of the production of woad and its remarkably long-lasting contribution to indigo vats for wool in Europe.

2. Woad for Blue for Wool

Woad, *Isatis tinctoria* L., is well known as the only indigo-producing plant indigenous to Europe and the Middle East. It is, therefore, the probable source of the indigo detected in the fast-growing number of analyzed prehistoric textiles from the Bronze Age and Iron Age, discovered in archaeological sites scattered from Ukraine to Scandinavia [1] (pp. 70–71). These findings reveal the prehistoric antiquity of the "gesamteuropäischen Kultur der Waidherstellung" (meaning "pan-European culture of woad production") already highlighted by the German historian Stephen Selzer for the Medieval Period [2] (p. 341).

Fragments of information scattered in written historical documents of different types, from business accounts to guild regulations from 14th to 16th c. France and Italy, have allowed to reconstitute the whole production process and, at the same time, to collect a growing—albeit heteroclite—corpus of quantitative data [3] (pp. 52–61), [4] (pp. 210–305).

Current knowledge can be summarized as follows. Woad seeds sewn in the spring would give four to five successive crops of fresh leaves, from early summer to the middle of autumn. In the south of France and Italy, a fifth harvest could be collected in autumn but it was usually considered of lesser quality as a source for a blue colorant. Leaves were crushed in horse mills, as soon as possible after having been picked, and the resulting mash was shaped into fist-sized balls, dried in sheds, and stored for local consumption or collected by woad merchants and shipped to other regions and foreign countries.

The form in which woad was finally used as a source of indigo in the blue vats was called couched woad in English and *pastel agranat* in French. It was prepared by specialized artisans, either in the regions of important woad cultivation or in the textile centers of wool broadcloth production, where it was used in large quantities. It was obtained by crushing the dry woad balls on paved ground in special buildings [5] (p. 327). Water was added in successive stages during the following days, and the crumbling mass of woad started fermenting and had to be regularly turned over, until after about three weeks. The mass had turned into small dry lumps (hence the expression *agranat*, meaning agglomerated into grains, in Occitan language). The word "couch" dates in English to about AD 1300, and is derived from the French verb *coucher* which means "to lay down, to spread or lay on a surface, to overlay," from Old French *couchier*, which also has a similar meaning to "to lay down, place" as in "go to bed, put to bed". The crushed woad was spread in a thick bed to allow an even distribution of the water and even fermentation—hence, "couching". Interestingly, they have the same imagery in Japanese concerning *sukumo*, meaning "couching". The dry leaves are laid in an even mass (like a straw mattress) to make *sukumo* by watering and letting it ferment. They call that "to put the *ai*, indigo, to bed" and the place they make it is called "the indigo's bedroom".

Couched woad was the only source of indigo, i.e., of a fast blue colorant, available and used on a large scale in Europe in the wool broadcloth industry and tapestry weaving until the first part of the 17th century. Even after the 17th c., when the indigo pigment from India or the West Indies began being imported and used in increasingly bigger quantities in the European blue vats for wool, woad went on being the major ingredient in the setting of the vats until the end of the 19th century [6] (p. 42).

3. Re-Examining Key Information from the Account Book of a Woad Merchant in Light of Experimental Archaeology

3.1. *Etienne Ferrières's Registre*

The register of Etienne Ferrières (Figure 1), preserved in the Municipal Archives of Toulouse under the reference HH 61, describes Ferrières's business transactions for the years AD 1559 to 1561.

Etienne Ferrières lived in Toulouse, where he was one of the very rich and powerful merchants dealing in woad from Languedoc (the south of France) in the 16th century, at the apex of the international importance of this commodity [7]. In this account book, at folio 25 verso, he provides an important piece of quantitative information that was nowhere else to be found until recently: the weight of couched woad obtained from the processing of a number of woad balls.

The circumstances in which he writes are exceptional; in Languedoc, the summer of 1559 has been the driest in living memory. Consequently, the woad crop is going to be much reduced in quantities, in comparison with normal years, but the quality will be excellent. The Flemish clients rush to come and buy woad balls directly from the producers. The competition to buy woad gets so fierce in the region that farmers, for once, can demand to be paid cash and in the best currencies of the time [8] (p. 68).

On the fourth of October 1559, at a time when Etienne Ferrières thinks that with all the cash he has managed to gather together, he will only be able to buy 1,200,000 to 1,300,000 woad balls ("*douze ou treze cent milliers de coquaignes*"); he reckons this will produce 2000 loads of couched woad ("*pour en avoir deux mil charges agranat*"). However, his associates in Lyons soon manage to send him a convoy of mules that travel through the mountains of the Massif Central, loaded with bags of gold and silver coins, so that in the end, the quantity of woad their company has been able to buy that year amounts to the staggering number of 2,400,000 woad balls.

According to Gilles Caster, the historian who first studied the *Registre* extensively, the *charge* mentioned by Etienne Ferrières in connection with his woad transactions weighed 157 kg. Therefore, the 2000 *charges* of couched woad he was expecting to obtain from 1,200,000 to 1,300,000 woad balls would correspond to 314 metric tons. According to this reckoning, the 2,400,000 woad balls that he and his associates eventually managed to buy in 1559 may have produced from 3692 to 4000 *charges*, that is, about 580 to 628 metric tons of couched woad.

It is now possible to compare Ferrières's notes with similar data recently found by Mathieu Harsch in an earlier account book, written from 1362 to 1396, preserved in the Archivio di Stato (State Archive) of Florence. The *Librio in proprio* was a book written by Giovacchino Pinciardi, a woad merchant from Sansepolcro, in Tuscany, who had moved to Florence [4,9]. From Pinciardi's book, it appears that in 1362, the 104,482 woad balls he had imported to Florence from Sansepolcro and the towns of Mercatello and Sant'Angelo in Vado, further east in the hills of the Marches, allowed him to produce 33,653 kg of couched wood (= 33.653 metric tons) [4] (p. 425). Although his business obviously was not of the same magnitude as Ferrières's, the massive quantities of woad balls and couched wood mentioned in these historical documents immediately raise the issues of the huge amounts of fresh leaves needed and of the area of land that must have been cultivated in woad to obtain them. Interestingly, this is still the first issue that is raised in all discussions concerning the possibility and desirability of a revival of the production of natural dyes at a larger scale today.

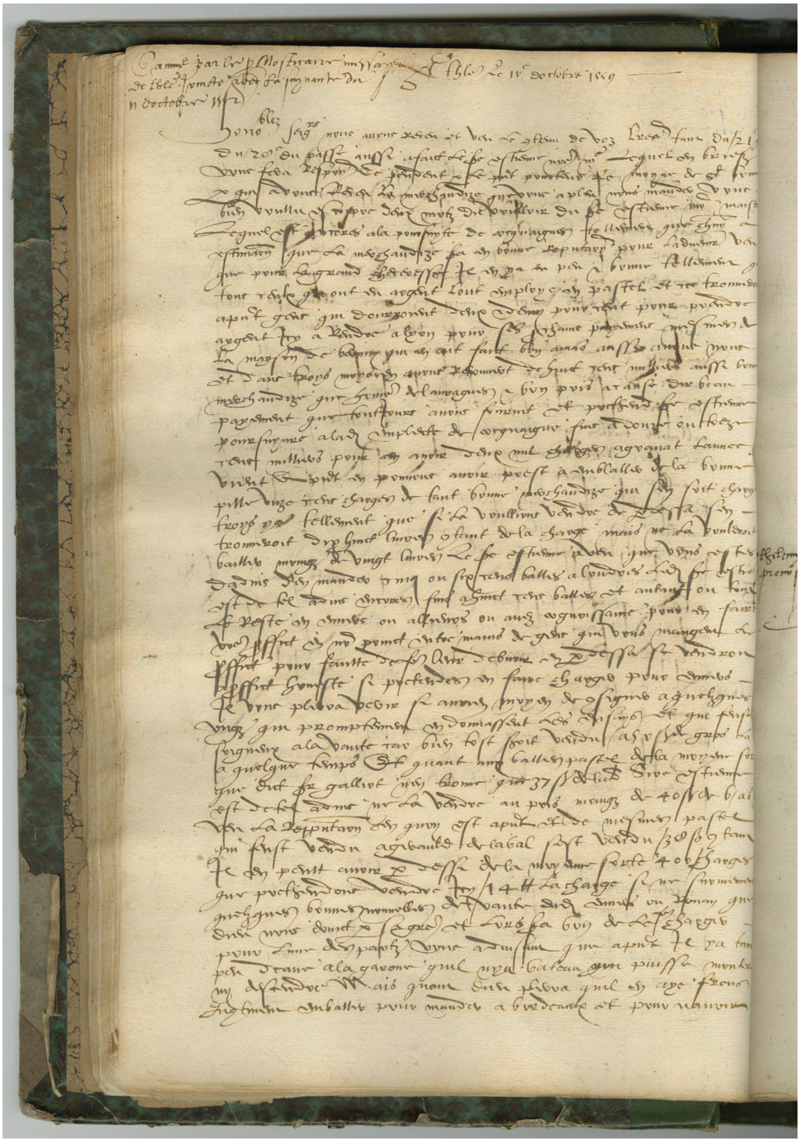

Figure 1. A page from Etienne Ferrières's Registre. Credit: Archives municipals de Toulouse—Archives anciennes, ref. HH 61, folio 25 verso.

3.2. The Expected Contribution of Experimental Archaeology

The approach of experimental archaeology is a way to obtain plausible answers to the questions raised by the data found in historical documents and to fill the remaining gaps in their descriptions of the production process. The goal is to try and reproduce the whole line of woad production, such as growing woad plants in a certain area and defined conditions; picking and weighing the fresh leaves, whose weight will serve as reference weight (= 100%) in all further calculations; making woad balls and weighing first the fresh and then the dry balls; and lastly, couching the crushed woad balls and weighing the dry weight of dye product obtained.

The aims of this study are to obtain, firstly, quantitative data to establish the weight losses at each successive stage of woad processing and, secondly, propose statistically significant weight proportions of woad at each of these stages, in relation to the weight of fresh leaves produced on a given land area. Finally, to assess the land area required to obtain the production volumes mentioned in Ferrières's *Registre* or Giovacchino Pinciardi's *Librio*. These experiments are the only way to obtain samples of woad at different stages to allow qualitative and quantitative analyses of their indigoid content via HPLC analyses, and to produce enough couched woad to test its coloring power and quality as a source of indigo. This information is necessary to scale up laboratory experiments of the historical vat process to its commercial proportions.

3.3. Description of Experiments and Results

Starting in the summer of 1999, the first author already performed a series of experiments in growing woad and making woad balls and couched woad, in preparation for an international exhibition and catalog dedicated to the "Precious Dyes of the Mediterranean: Purple, Kermes, Woad" [10] (pp. 156–159), [11] (p. 370). Additional new experiments were conducted from the spring of 2021 to the autumn of 2022 in order to collect more data and check and complete the first results.

During the two springs, woad was sewn in a row in the first author's garden in the south of France, at an altitude of 650 m above sea level, in granitic, sandy, well-manured soil. Sewing in April allowed for the first harvest of leaves in June and four more pickings to be performed until the end of October. The plants continued to produce beautiful leaves through the winter but these were not collected because it was assumed that the lack of heat and sunlight made them very poor in indigoid precursors. This would still be needed to be studied. The densely sewn plants were thinned down to 6 cm apart in May, as soon as the leaves started forming fairly large rosettes (Figure 2).

Figure 2. Row of woad plants, June 2022 (credit: D. Cardon).

The average yield of fresh leaves per harvest was 1.5 kg per 2.5 m of a row of woad plants. This would correspond to a yield of 6 kg of fresh woad leaves per row that is 10 m long. Assuming plants were cultivated on bigger plots of land, arranged in rows spaced 40 cm apart, this corresponds to a yield of 150 kg per are (= 100 $m^{2)}$. Scaling this up to 1 hectare (10,000 m^2), the amount would be 15,000 kg of fresh leaves per harvest (250 rows, 100 m long). The yield from four harvests could, therefore, amount to 600 kg of fresh leaves per are ar per year. Thus, the total yield per year would be 60 tonnes per hectare.

After each picking, the fresh leaves were crushed in a mortar, shaped by hand into big balls, and put to dry in the shade (Figures 3 and 4). By weighing the products of 31 successive pickings, it was possible to calculate that the average weight of the dry woad balls corresponds to 19% of the weight of the fresh leaves from which they were obtained.

In December 2021, all the woad balls produced during the former summer season were crushed with a hand-held wooden mallet and the mass of crumbles was sprinkled with just enough warm water to keep it damp. This was turned over each day for one week (Figures 5–7). From then on, no more water was added, and turning of the mass was only performed every two and then four days for two more weeks during which lumps were formed and gradually became completely dry and hard (Figures 8 and 9). The weight of couched woad obtained amounted to 76.5% of the weight of dry woad balls that were processed.

From these results, it can be calculated that 1 hectare of woad can produce 11,400 kg of dry woad balls and hence, 8721 kg of couched woad per year. This quantity would have allowed the setting of 39 woad and indigo vats in 18th century Languedoc [6] (p. 42).

Figure 3. Fresh woad ball (credit: D. Cardon).

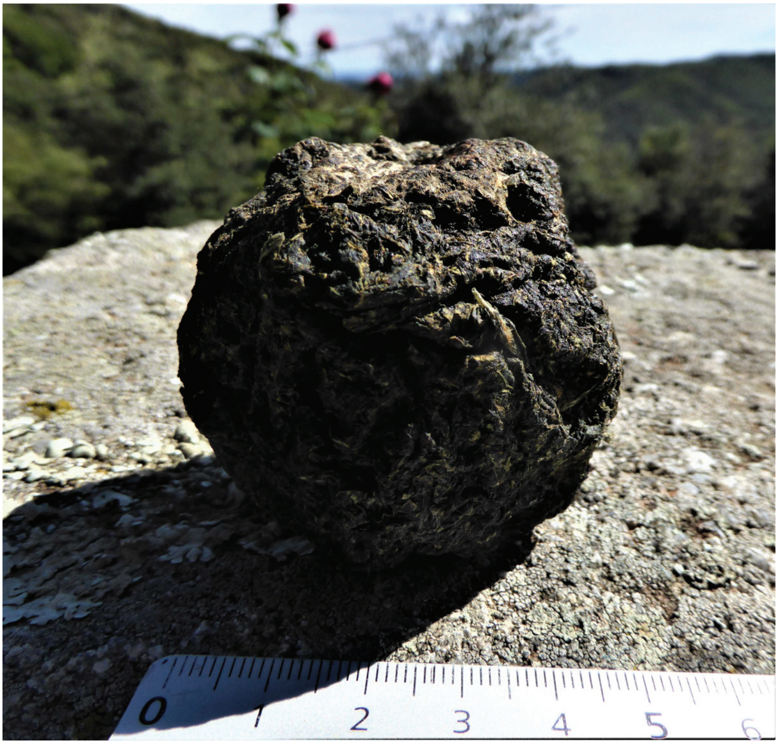

Figure 4. Same woad ball as in Figure 3, dry (credit: D. Cardon).

Figure 5. Crushing of dry woad balls to make couched woad. Day 1 (credit: D. Cardon).

Figure 6. Adding enough warm water to thoroughly wet the mass of crushed woad balls. Day 1 (credit: D. Cardon).

Figure 7. The fermenting crushed woad. Day 1 + 5 (credit: D. Cardon).

Figure 8. Couched woad agglomerating into lumps and drying. Day 1 + 13 (credit: D. Cardon).

Figure 9. Couched woad, final state (credit: D. Cardon).

3.4. Discussion on Experimental Results in Relation to Etienne Ferrières's Registre

According to these results, the 580 to 628 metric tons of couched woad collected by Ferrières in 1559 would have required the processing of 758 to 821 metric tons of dry woad balls. To obtain 758 to 821 tons of dry woad balls, 3990 to 4321 tons of fresh leaves would have had to be collected, crushed, and made into woad balls. These amounts, of 3990 to 4321 tons of fresh leaves, could be obtained from 66.5 hectares (= 0.665 km^2) to 72 hectares (= 0.72 km^2) cultivated in woad, in four harvests per summer.

The somewhat surprisingly high yield of couched woad per area of woad cultivation, based on these experiments, is in agreement with the results of recent historical research and contributes to explaining some newly collected data from historical primary sources by the French historians Marie-Claude Marandet and Mathieu Harsch. The latter found that in 1362–1363, in his *Librio in proprio*, Giovacchino Pinciardi recorded that he could obtain 36,122 pounds (in Florence) of couched woad from 49,300 pounds of dry woad balls, which corresponds to a proportion of 73.26%—quite close, interestingly, to the 76.5% obtained in the course of the first author's experiments [4] (pp. 238–239). Marandet, studying local notaries' books, observed that in the region of Lauragais, famous for its woad production, in the first half of the 15th century woad was cultivated around many villages, mostly on comparatively small plots of land of sizes commonly between 3000 and 6000 m^2, with one mention of a bigger parcel of 2.4 hectares. These could be worked by the members of one family who would also bring the leaves to the nearest mill—if they did not own one—shape the woad balls and put them to dry in sheds. Growing woad in this way, almost like a garden crop, proved highly profitable, as highlighted by a contemporary chronicler, Guillaume de Catel, who wrote that "the profit gained from woad in Lauragois is so great that it often happens that in a fertile year, the product of a woad field is worth as much as, or even more than, the price of the field in which it has been sewn". This assertion has been confirmed by Marandet's calculations, based on data mentioning the selling prices of land and of woad balls that she could find in local contemporary sources [3] (pp. 52, 57).

4. Re-Assessing the Efficiency of the Woad and Indigo Vat in Light of Biochemical Research

4.1. Antoine Janot's and Paul Gout's Memoirs on Dyeing

Antoine Janot, in 1744, and Paul Gout, in 1763, wrote *Memoirs* on piece dyeing of wool broadcloth with fast dyes, illustrated with dozens of cloth samples dyed in colors corresponding to the processes described (Figures 10 and 11). Both manuscripts have been recently published as critical editions and the descriptions of their dye recipes have been translated into English [12–15]. Their accounts allow woad production to be followed down the line to the use of couched woad in the woad and indigo vat. Since the 17th century, when the addition of imported indigo pigment to the woad vat was allowed in European countries, this came to be the process generally used to obtain the various degrees of fast indigo blues on wool and woolen textiles.

Antoine Janot was a master dyer, and owner of a dye workshop in Saint-Chinian, a small town but an important center of wool broadcloth production, north of Béziers, in Languedoc. Paul Gout was the manager of two Royal Manufactures of fine broadcloth in succession, first in Saint-Chinian from 1754 to the end of 1756, and then in Bize, not far to the south of Saint-Chinian, from 1756 to the first years of the French Revolution. In both places, he also acted as a master dyer, supervising all dyeing operations. In Antoine Janot's dye workshop, an average of 3000 pieces of cloth, produced by the local clothiers of Saint-Chinian and its surroundings, were dyed per year. Paul Gout's Royal Manufacture of Bize was producing between 600 and 800 pieces of cloth annually. As in all the textile centers of Languedoc at the time, mostly Londrin Second broadcloth, the best-selling quality in the Levant, was produced and all pieces were exported to different parts of the Ottoman Empire. Each cloth piece had to measure from 18 to 20 m in length, be at least 1.40 m in width, and weigh no less than 10.35 kg. Nearly half of them had to be dyed in the woad and indigo vat into various shades of blue. Depending on the Oriental customers' orders, some pieces were kept blue but a majority of blue-dyed pieces were further mordanted and top-dyed in red or yellow dye baths to produce beautiful ranges of purples and greens. Blue grounds of different degrees were also used to create numerous shades of greys and browns. In addition, dark blue grounds were key prerequisites to obtaining fast black dyes. All the above helps us understand at what considerable scale couched woad was routinely used in the dye workshops of these broadcloth production centers.

2

Rend malade, de façon a Rebuter le —
travail que le teinturier peut hazardér —
dela ce meme travail se trouve si imparfait
quil faut Recourir au faux pour couvrir —
ces deffauts.

On trouve quun teinturier qui a beaucoup
dexperiance ne tombe que Rarement dans
de pareils cas, Et sil y tombe Cest tres —
souvent la faute du pastel qui se trouve
falsiffié par le fabriquant ou mal —
preparé.

Labus qui sest glissé jusquaujourdhuy
Et qui se pratique journellement de —
faire plusieurs cuillettes du pastel au
dela de lordre des Reglemens fait tombér
le teinturier dans de pareils cas ou il se —
trouve trompé.

Couleurs que la Cuve produit
Lorsquelle Est En etat de travail

La Cuve Etant assize avec quatre Balles
pastel Et 4l. Indigo par Balle Produit
Les Couleurs cy apres.

4 Pces aile de Courbeau.
4 Pces bleu turquin.
4 Pces bleu de Roy.
4 Pces bleu Celeste.
4 Pces bleu Dazur.
4 Pces bleu de Ciel.
4 Pces bleu mignon.
12 Pces bleu de blanchy de trois differentes
nuances.

jl y a de plusieurs qualittés de bleus —
Compris dans les Reglemens Genneraux
Et particuliers. qui ne sont differents de ceux
cy que par leur degré de couleur.

Figure 10. Antoine Janot's scale of blues from the woad and indigo vat. Memoir on dyeing, 1744. Archives départementales de l'Hérault, ref. C/5569, folio 2 recto (credit: D. Cardon/P.-N. Granier).

Bleu Pers
La faux

Fonds de pastel d'un Bleu de Roy foncé
1 bois de Campeche
2 bois de Bresil } Par pièce dans un Bleu frais
Bouilli une heure, avant de mettre dedans [illegible] pris tempérez tenez dedans jusque à la nuance que vous souhaitez

Bleu Pers

Passé sur un Cochenillage de Violets

Bleu turq.

Lavé au foulon seulement et passé sur l'eau chaude

Bleu de Roy

Lavé au foulon seulement et passé sur l'eau chaude

Bleu lavé

Lavé sur la suite d'un Bouillon de Couleur de fer ou de jujube, on y ajoute un peu de pastel quand le bain est trop tiré

Bleu D'azur

Lavé au foulon et passé sur l'eau chaude

Bleu Celeste

Lavé au foulon et passé sur l'eau chaude

Bleu mignon

Idem

Bleu de lait

Idem

Bleu de Blanchy

Idem

Figure 11. Paul Gout's scale of blues from the woad and indigo vat. Memoirs on dyeing, 1763. Priv. Coll., p. 41 (credit: D. Cardon).

In his description of the setting of a vat, Gout mentions that three bales (about 223.56 kg) of couched woad are used [6] (p. 42). Indigo pigment, imported from the French West Indies, is only added later, when "the vat is ready and that it bears some blue [. . .]

imperceptible veins can then be seen: in such a state, the vat can receive such quantity of indigo as one judges appropriate to put into it" [15] (p. 52). Antoine Janot gives the more precise proportion of 4 pounds of indigo powder to be added, per each bale of woad (= 2.2% of the weight of couched woad used). Both Gout and Janot are clearly aware of the double function of couched woad in the process; firstly, as the main fermenting agent giving the dye bath its reducing power, essential in every vat-dyeing process (Figure 12), and secondly, as a source of blue colorant.

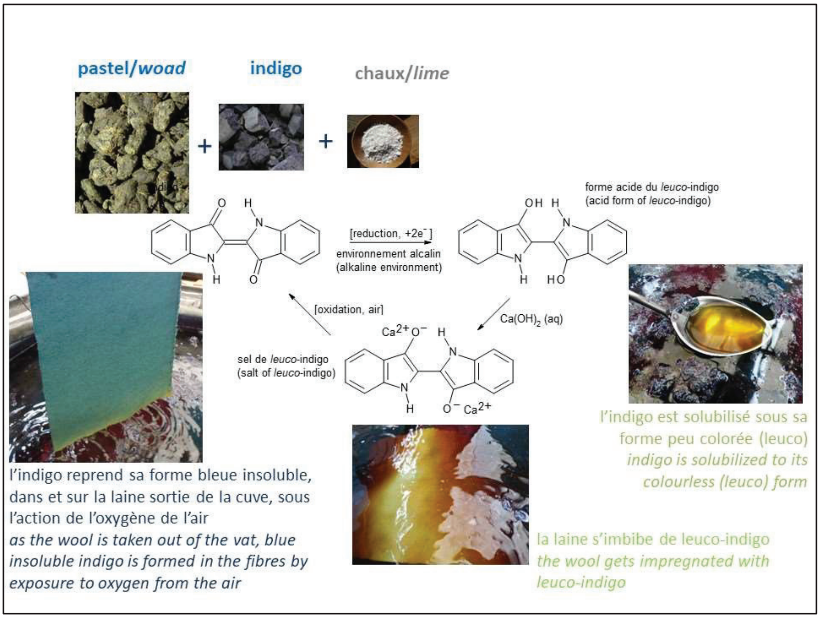

Figure 12. Chemical reaction of indigo in the woad and indigo vat of 18th c. dyers. Indigo is solubilized and reduced in the vat, imbibes the textile, and is regenerated in it by the oxygen from the air (credits: photo D. Cardon, D. Santandreu; diagram D. Cardon, C. Higgitt).

Consequently, our research and experiments focused on better understanding the scientific basis of the two distinct contributions of couched woad: the satisfactory evolution and the coloring efficiency of the vat. Hisako Sumi included the couched woad produced by Dominique Cardon in her research, pursued in collaboration with bacteriologists in Japan. They studied the bacteriological environment that gives a woad and indigo vat its power to reduce the insoluble blue indigo pigment to its soluble form, to impregnate the textile fibers. Zvi Koren's chemical analyses explored the contents and proportions of indigoids in the woad leaves from the moment they are collected to their reduction into dry-couched woad.

4.2. Bacteriological Environment and Its Reducing Role in the Fermentation Liquor of a Woad and Indigo Vat

Hisako Sumi's experiments with woad and indigo vats were parts of a wider research, aimed at comparing four types of indigo-fermented vats, their reducing power, and the colors obtained [16–18].

In the first experiment at a reduced scale, a 20-L vat was set (Figure 13), using 1275.5 g of couched woad and 41.4 g of crushed woad balls (total weight 1316.9 g) produced by D. Cardon, as described above. Then, 3 L of wood ash lye (measured pH 10.87), heated to 35 °C, were added. After 2.5 h, the pH decreased to 9.59 and 5 g of slaked lime was added to obtain the necessary higher degree of alkalinity mentioned in reports on previous experiments to reproduce the medieval woad vat [19]. The next day, the pH decreased to 8.94, and 15 L of wood ash lye and 35 g of slaked lime were added, as well as 90 g of wheat bran boiled in water for 15 min. After stirring, the pH of the liquor was checked again and had gone up to 10.33. On the morning of the third day, the alkalinity of the liquid was measured again and found to be at pH 9.29; a purple film was forming on the surface of the vat (Figure 14). Slaked lime was added to keep the pH close to 10 and the temperature of the bath was maintained at about 30 °C. One hour later, the first dyeing test produced a good medium blue, but after a rather long oxidation time (Figure 15). The reason for this was thought to be a combination of the high reduction performance of the microflora of the woad fermentation liquid and its low indigo content. In this experiment, natural indigo pigment from India was added 8 days after setting. "As per the dyer's judgement", following Gout's approach, the first addition consisted of 65 g of indigo cakes reduced to powder (5% in relation to the weight of couched woad used). A purple layer and fine bubbles started forming on the liquid surface (Figure 16). An additional quantity of 5% indigo powder was added later. From then on, dyeing could be performed repeatedly for several months (Figure 17). The temperature of the vat was kept as constant as possible, as well as the optimum alkalinity, maintained by successive additions of slaked lime.

In later experiments, the volume of the vat was first increased to 50 L and then to 100 L, re-using the same indigo fermentation liquor and adding new woad balls produced in Hokkaido, wood ash lye, wheat bran, and indigo pigment. Details of all experiments have already been published elsewhere [16,17,20]. These experiments have shown that woad and indigo vat-related microorganisms are particularly active at pH 9.8–10.3, with temperatures of the vat liquor kept between 25 and 30 °C, which is lower (less energy-consuming) than in other organic vats.

The bacteriological environments of the vat liquors from these experimental reconstitutions of the woad and indigo vat were studied in Hokkaido, Japan, by a team of bacteriologists. This study was part of more general research into the bacterial flora of various indigo fermentation vats set by H. Sumi with diverse indigo plant sources, processed in different forms. An indigo-reducing bacterium, *Clostridium isatidis*, had already been identified by a scientific team in England, in the fluid of a couched woad vat prepared following a medieval Italian recipe published by D. Cardon [19,21]. The woad and indigo vats set by Hisako Sumi were found to contain a particularly rich bacterial flora. A complete list of the species identified has been published elsewhere [22] (p. 283, Figure 2). They include two different indigo-reducing species: *Alkalibacterium indicireducens*, and, in the fermentation liquor of Sumi's second experiment, two distinct strains of a new species of indigo-reducing bacteria were isolated and described as *Fundicoccus fermenti* sp. nov. [23]. The presence of these indigo-reducing bacteria in the liquors of woad and indigo vats contribute to explaining why these vats could become ready for dyeing in such a short time and retain their reducing power for such a long time, provided the right environmental conditions for the proliferation of the useful bacteria were maintained.

Figure 13. Setting of a woad and indigo vat in Hisako Sumi's Studio in Otaru, Hokkaido, Japan, the first day (photo H. Sumi).

Figure 14. The third day, morning. Patches of reduced indigo from woad reoxidizing at the surface of the vat (photo H. Sumi).

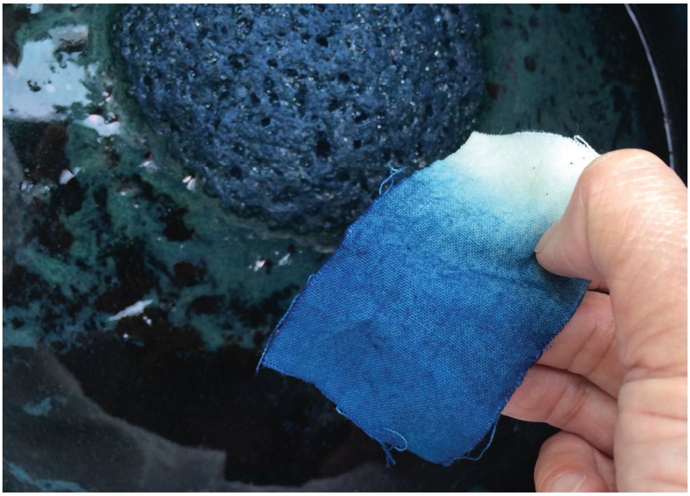

Figure 15. The third day, later. Testing of the coloring power of the vat with a sample of cotton cloth (photo H. Sumi).

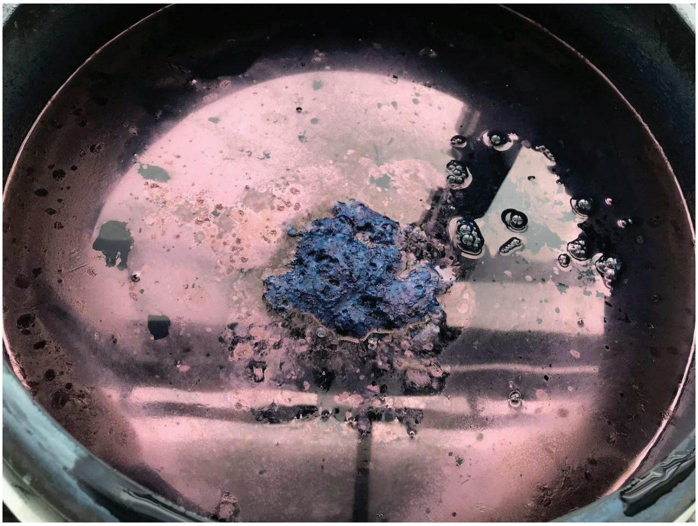

Figure 16. Appearance of the top of the woad and indigo vat after additions of indigo pigment (photo H. Sumi).

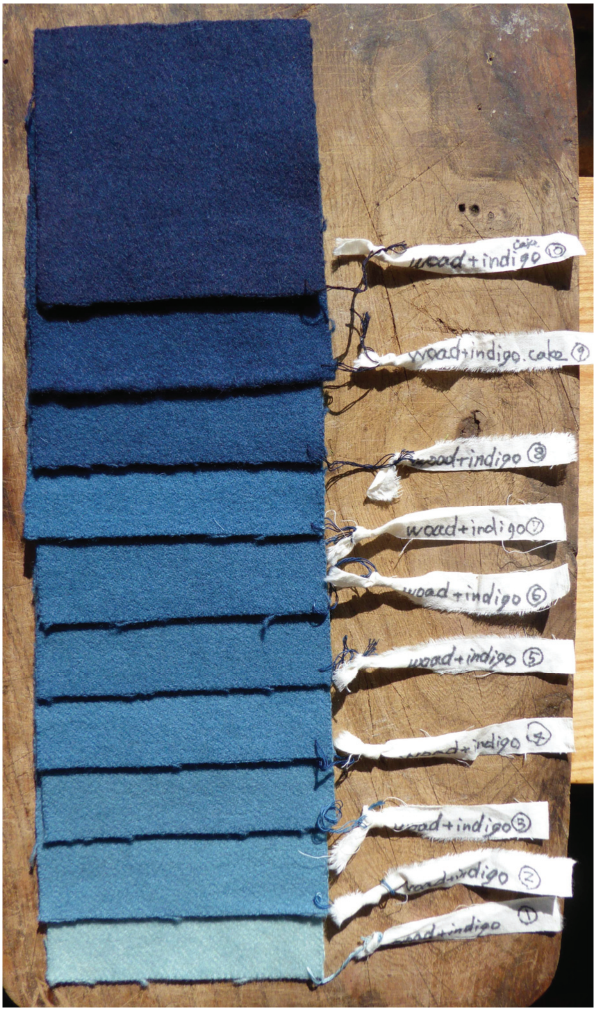

Figure 17. Hisako Sumi's scale of blues from the wood and indigo vat (photo D. Cardon/H. Sumi).

4.3. *Woad as a Source of Indigo Blues: An assessment via HPLC Analyses*

The following results were obtained as part of a more general study [24] aimed at quantifying the dye components in indigo-producing plants. This report focuses on the leaves of *Isatis tinctoria* L. (woad), and for comparison purposes, on *Persicaria tinctoria* (Aiton) H.Gross whose leaves, like those of woad, were traditionally processed into a compost (Japanese *sukumo*). Woad was cultivated in Dominique Cardon's garden in the mountains of Cévennes, south of France. The couched leaves of *P. tinctoria* were provided by artist dyer Hisako Sumi from Hokkaido, Japan.

Prior to the dye extraction, each dried plant sample was pulverized in a mortar and pestle in order to produce a relatively uniform powdered mass for the analyses, and fresh leaf samples were cut into smaller pieces. Each sample analyzed consisted of an exactly weighed quantity (usually a few milligrams). The dyes from these samples were extracted via repeated additions of measured volumes (usually a few milliliters) of dimethyl sulfoxide (DMSO) at 100 °C for 5 min at a time until no visible color in the last extracted solution was visible. The multiple extractions from each sample were combined and highly concentrated extracted solutions were diluted when necessary. Prior to the HPLC analysis, the dye solution was filtered in a centrifuge tube assembly consisting of a 0.2-μ nylon filter.

The ambient-temperature reverse-phase Waters chromatographic system used consisted of a 600E Controller pump and a 996 PDA detector, each controlled by the Milleniu m-32 software. The stationary phase was composed of a Waters 3.0 × 150 mm C-18 Symmetry column with 5 mm and 100 Å particle and pore diameters, respectively. The ternary mobile phase eluents passed through a 20 μL sample loop and consisted of the following: methanol, water, and phosphoric acid (H_3PO_4, 5% aqueous). The HPLC elution method for the separation of indigoids and related dyes consisted of a constant flow rate of 0.8 mL/min. In addition, a constant 10% volume of acid was used, and thus water decreased inversely with the following increasing % volumes of methanol:

0–3 min: 30–60%; 3–14 min: 60%; 14–21 min: 60–90%; and 21–40 min: 90%.

5. Results of the HPLC Analyses

A typical HPLC chromatogram showing the three main dye components investigated in this study—indigo (IND), indirubin (INR), and isatin (IS)—is shown in Figure 18. The peaks eluting from 4–12 min are non-colorants extracted from the leaves and are thus not discussed in the paper, which focuses on the three main dyes investigated in this study.

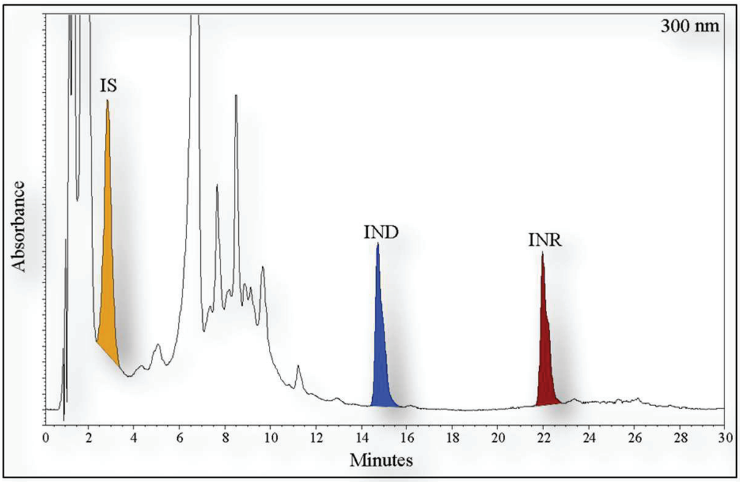

Figure 18. Typical HPLC chromatogram (at 300 nm) displaying the separation of the three dyes: isatin (IS), indigo (IND), and indirubin (INR).

The UV/visible spectra and molecular structures of these dyes are given in Figure 19.

The results of the HPLC analyses are based on the PDA-derived integrated peak areas (in PDA units) in the chromatograms calculated at a specific wavelength. The wavelength chosen for the quantification of the presence of IS, IND, and INR was the near-UV value of 300 nm because at this wavelength all three dyes have appreciable light absorptions. These dyes also have appreciable absorptions at wavelengths below 300 nm, for example at about 240 nm; however, at these low UV values, a significant number of co-eluting colorless components in the leaves have relatively high absorptions, which may mask that of the dyes.

In order to prevent the inclusion of any co-eluting components in the peak area calculations of the dyes, the contour diagrams were first checked to determine whether there are any co-eluting components. Secondly, the peak areas were calculated in the chromatogram displayed at their respective visible λ_{max} values and then converted to the standard UV wavelength value, which was the method previously used [25]. Thus, for indirubin, the wavelength of 540 nm was chosen for the calculation of the integrated peak area because it is the only colorant extracted from the leaves that has a maximum absorption at that wavelength, and any possible co-eluting non-colorants at the same or similar retention time are invisible at that wavelength. Similarly, for indigo, the peak area was first calculated at 615 nm. The peak area values at 300 nm for both dyes were then calculated based on the absorbance ratios for each dye at their visible λ_{max} relative to their absorbance at 300 nm. These relative absorbance ratios are obtained from the UV–Vis absorption spectrum of each dye. For isatin, its peak area was evaluated with the chromatogram displayed at 241 nm, as at this value, its absorbance is extremely high, as can be seen in its UV–Vis absorption spectrum, and then was scaled down to the standard 300 nm as with the other dyes.

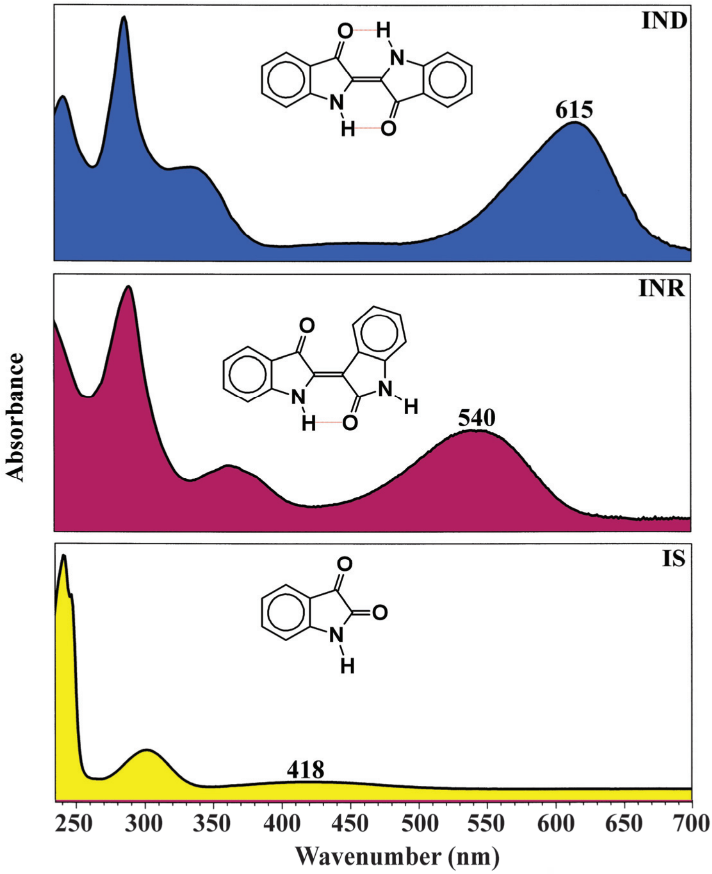

Figure 19. UV/Vis spectra and molecular structures of the three dissolved dyes as obtained by the PDA detector, showing the prominently visible wavelengths with maximum absorption, λ_{max}.

These peak area values were normalized with regard to the constitution of the injected dye solution by dividing the area values by the composition. The composition of the injected dye solution is represented by the mass of the leaf sample divided by the total volume of DMSO used (including all dilutions). The resulting scores given for each dye in the figures below are thus these normalized peak areas (measured at 300 nm) and scaled to represent convenient values typically greater than 1. Thus, the compositional value for each dye i can be expressed as:

$$\text{composition of dye } i = 10^{-11} \times \text{Area}_{i,300}/(\text{g of material}/\mu\text{L}),$$

where the 10^{-11} factor is to down-scale the values to represent more practical numbers.

It should be noted that these peak areas are not percentage values, nor actual compositions of the dyes in the leaves, but are related to them and can, nevertheless, be used as semi-quantitative comparative properties indicative of relative compositions, as discussed below.

5.1. Fresh and Aged Woad Leaves

The following triplicate analyses of each sample assess the indigoid contents of different woad materials: fresh leaves, dry leaves, dry woad balls, and couched woad.

Figure 20 shows the quantitative HPLC results of woad leaves stored in paper and allowed to age up to 67 days after cutting. Comparing the dark and green areas of relatively fresh leaves, 3 days after cutting and storing in paper (labeled as 3 d and 3 g, respectively) shows that the indigo content in the dark area was about 10 times that of the green area, which was also accompanied by nearly 25 times more isatin. An appreciable amount of indirubin was also detected in the dark area and was absent in the green part of the leaf. Allowing the leaves in paper to age for 17 days after cutting showed a respective increase in all the dyes. Indigo increased by about 25%, a nearly threefold increase in indirubin content, and there was 70% more isatin. After 67 days of aging, the indigo content in the dark dry leaves essentially did not change with only a slight increase in indirubin, while the quantity of isatin decreased to about a third of its previous level.

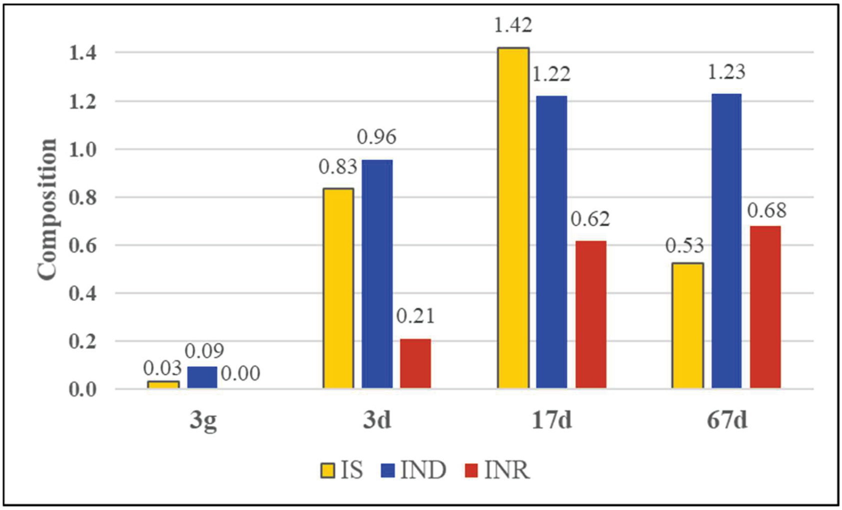

Figure 20. Indigo content in woad leaves stored in paper 3 days after cutting in the green part of the leaf (3 g) and in the dark part (3 d), and the dark part of the leaf after 17 days (17 d) and 67 days after cutting (67 d). (See text for explanation of "composition").

The effect of the way woad leaves are stored also has an effect on the dye compositions in the leaves. This can be seen from the first two sets of Figure 21, which compare the green parts of woad leaves stored in paper vs. those stored in plastic, both 3 days after cutting. Although, in both cases, the quantity of indigo in the green leaves is, as expected, very low, the indigo content in the paper-stored leaf is almost twice that of storing the leaf in plastic. This phenomenon may be due to the availability of oxygen in the air in the case of paper as opposed to that of hermetically sealed plastic, which effectively does not allow atmospheric oxygen to enter the plastic bag. Thus, there is more oxidation of the precursors in the leaves to indigo in the paper case than in the plastic one.

Processing of woad can increase the formation of indigo in the leaves, as shown in Figure 21, which shows the comparison for woad leaves that were processed into a ball vs. woad that has been couched. Figure 19 shows that couching has a markedly strong effect on the indigo content in the processed woad by more than 6-fold. Couching is very efficient in concentrating indigo. Although isatin and indirubin contents also show significant increases, their overall quantities are very small.

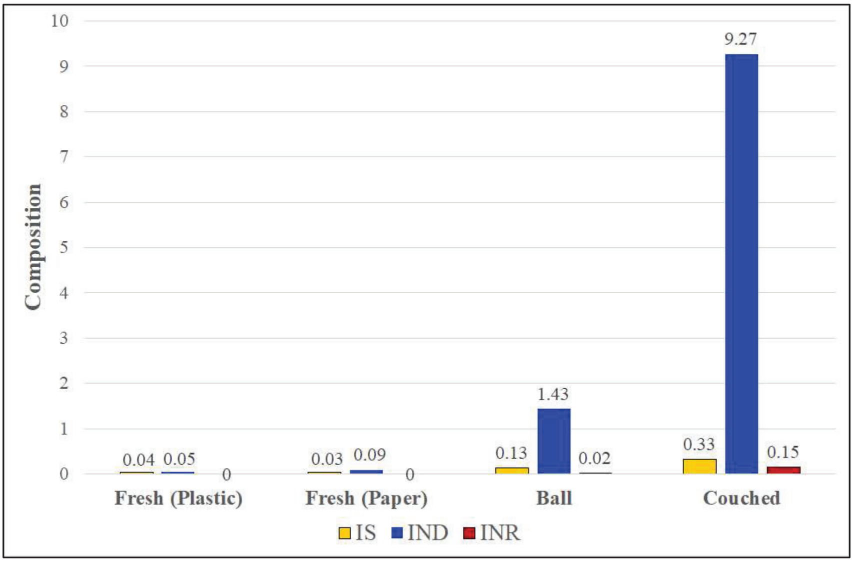

Figure 21. Indigo content in green woad leaves stored in paper compared with those stored in plastic 3 days after cutting (first two sets in the graph) and dye content in woad material formed into a ball vs. couched (last two sets in the graph).

5.2. Comparison of Couched Woad and *Sukumo*

A comparison between the indigo concentrations in couched woad with another processed plant material, *Persicaria tinctoria* compost (*sukumo*), is shown in Figure 22.

Although couching of woad increases the indigo content in that plant material, as shown above, the couched woad is a less concentrated source of indigo than, for example, *sukumo*. Thus, assuming that after the crushing and couching of these plant leaves all the precursors in the leaves have undergone enzymatic hydrolysis (as a result of these actions) and subsequent oxidation to form indigo, in the plant material used in this study, there is about 2.5 times more indigo in the crushed *P. tinctoria* than in couched woad.

On the other hand, H. Sumi's experiments with both the traditional Japanese *sukumo* vat and the woad and indigo vat have shown that in a 100 L vat, 6 kg of *sukumo* is needed, while 2 kg of couched woad with the later addition of 640 g of indigo powder are enough to obtain both a good reducing power and a stronger coloring power. An additional advantage is the lesser volume of plant colorant mass at the bottom of the vat, leaving more space for the textiles to dye evenly.

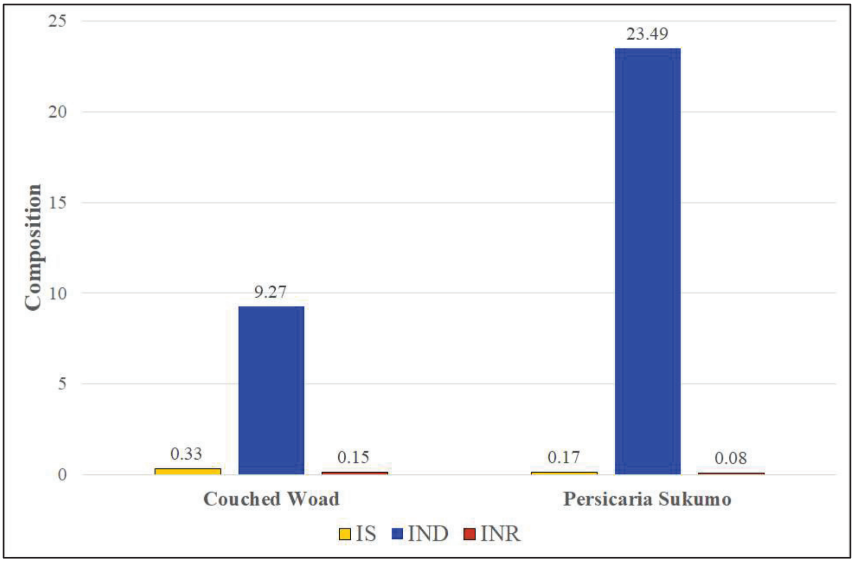

Figure 22. Indigo content in couched woad vs. in *Persicaria tinctoria* compost (*sukumo*).

6. Conclusions

Growing woad plants as a garden or small plot crop was found to give higher yields of fresh leaves per year than recorded from large-scale mechanized farming, as performed from the latter part of the 19th c. to the recent experiments at reviving woad cultivation in order to produce woad indigo pigment.

The processing of woad leaves into couched woad, as opposed to the maceration process leading to the production of woad indigo pigment, appears an efficient way of obtaining a good yield of indigoid colorants from woad. Moreover, couched woad has been found to significantly contribute to the reducing power of the woad and indigo vats. The woad and indigo vat process was found to be a cost-efficient and environmentally friendly process only requiring warm water and the addition of wheat bran, wood ash lye, and slaked lime to the two sources of indigo.

In the conclusions drawn from the HPLC analyses, it is important to note that in this study, the quantities of all the precursors in the leaves were not investigated. The analytical HPLC study focused on the spontaneous formation of three detectable dyes—indigo, indirubin, and isatin—in the leaves of these plants. The analytical results lead to the following conclusions:

1. Spontaneous indigo formation begins even in the green part of the leaf as soon as the leaf is cut off from the plant.
2. With time, further oxidation significantly increases the indigo content in the dry parts of the cut leaves with an eventual decrease in isatin as more of it is converted to indirubin.
3. Couching of woad significantly increases the indigo content in the dried leaves.
4. However, couched woad does not yield the maximum amount of indigo, which is the case with other plant species.

Our experiments and their corresponding scientific analyses validate the efficiency of the whole technological line of woad production and use as practiced in Europe since the Middle Ages.

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Traditional Natural Dyeing Materials Used in Greece from the 19th Century Onwards

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Abstract: Textiles and clothing were and still are an important source of culture as well as an indicator of a robust economy and social status. Textile household goods and clothing are important heirlooms, providing valuable information about the standard of living, socio-political events, and cultural influences of the regions from which they originate. This paper presents the preliminary results of a research project dealing with the traditional natural dyes used in Greece for the decoration of garments from the 19th century onwards (from the 19th until the mid-20th century). The research aims to identify and record all the different plants and dyeing techniques used in Greece during this period and also to propose a non-destructive methodology for the study of dyed textiles in order to facilitate their preservation. In this paper, the focus is on the presentation of the classification and identification data of the plants used as the dyeing sources, according to recipes collected in various areas in Greece, as well as the description of their botanical characteristics. The research was based on the study of more than 2000 manuscripts and many interviews with older people who have used these materials. Thus, more than 140 plants have been documented, together with their recipes. The data produced include the phytological characteristics of the plants, as well as the parts of the plant used, the period collected and the areas they were used, together with images of the plants and various details regarding the recipes used in many places around Greece, along with the related documentation. The study also refers to ethics and traditions related to the dyes, the color, or the dyeing procedures used. Woolen samples were prepared based on the data collected in order to investigate how the differences recorded from place to place are reflected in the final result. Through this research, it was possible to identify and replicate some of the non-common recipes which use the Mediterranean strawflower, *Helichrysum stoechas* (L.) Moench, red algae, *Rytiphloea tinctoria* (Clemente) C.Agardh, and the common poppy *Papaver rhoeas* L as dyestuffs.

Keywords: natural dyes; dyeing procedure; old traditional recipes; natural dyes tradition; color superstitions; Greek manuscripts; *Cupressus sempervirens* L.; *Helichrysum stoechas* (L.) Moench; *Rytiphloea tinctoria* (Clemente) C.Agardh

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1. Introduction

This paper is a preliminary report of a PhD thesis dealing with the traditional natural dyes used from the 19th century until the first half of the 20th century in Greece for the decoration of garments. The aim of the research is to record all the different plants, insects, and dyeing techniques used in the past all over Greece for the decoration of traditional costumes, so that in the future it will be possible to build a totally non-destructive methodology based on hyperspectral imaging, fiber optics reflectance spectroscopy, infrared spectroscopy and chromatometry in order to identify natural dyes found in traditional clothing without sampling the objects.

The research is based on the study of written historical sources such as the documenting manuscripts of the National and Kapodistrian University of Athens, henceforth

NKUA (Figure 1) and manuscripts of the Research Center of Greek Folklore of The Athens Academy, henceforth RCGF. These manuscripts are written documentations which were produced from the beginning of the 20th century onwards, and which record practices performed from the 19th century. Each of them refers to a certain place or village of Greece and contains data regarding the ethics, the way of living, and the beliefs of people who lived in the past. The research is also based on interviews taken during fieldwork in various areas of Greece such as Crete, Macedonia, Thrace, and the Ionian islands. The data regarding the dyeing materials used since 19th century, as well as the dyeing techniques, are of outmost importance for preserving this knowledge for the future generations and assisting the preservation of these objects. It is worthy to mention that most previous research concentrates on a few famous dyes used in the Greek region. This is an effort to find all the possible dyestuffs and the authentic recipes used.

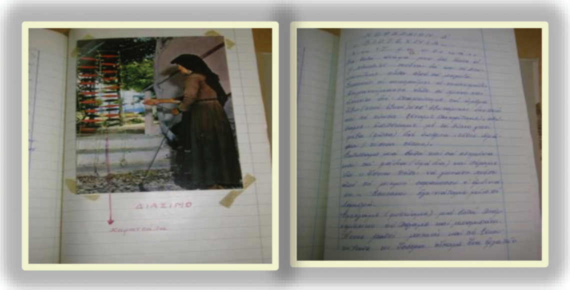


Figure 1. Photos of the NKUA manuscripts (photos taken by the authors in the National and Kapodistrian University of Athens, at 2010).

Furthermore, woolen samples were prepared using the dyeing materials and according to the documented recipes to serve the purposes of the research (to examine the result of the dyeing procedure, to create a database of dyed samples, and to create a non-destructive protocol of identification).

Textiles and clothing were and still are an important source of culture as well as an indicator of a robust economy and social status. Textile household goods and clothing are important heirlooms, providing valuable information about the standard of living, socio-political events, and cultural influences of the regions from which they originate.

Clothes were not only used to protect against the weather and external hazards, but it was also a mean of demonstrating power, wealth, and authority [1]. Clothing is influenced by the social conditions of each era, the ways and customs of each place, its geophysical characteristics and trade contacts with other cultures. In the dress code developed in every historical era and in every region, the colors used have a special meaning. Color is an integral part of the clothing of every historical period and every culture [2].

In addition to semiotics, the customs that developed around the color of clothing significantly influenced commerce and science. Human camaraderie was the springboard to develop production and commercial arrangements around clothing and furthermore to develop every scientific field related to clothing-dyeing procedures. Textile dyes/color are among the most important cultural indicators [3].

The development of the art of dyeing is reflected through written manuscripts and historical relics. In Egypt, preserved Greek papyri, the *Papyrus Graecus Holmiensis* and the *Papyrus Leidensis X*, along with methods for converting common stones and metals into precious stones and noble metals, include recipes for dyeing clothes. They emphasize too the importance of dyes, referring to their value as equal to that of precious metals [4,5]. The know-how around the dyeing processes, the dyes and pigments used and their quality, and the semiotics around the dyed garment are some of the factors reflecting the economic-social development of each region.

In Greece, the dyeing techniques in combination with weaving are for the researcher a source that reflects, perhaps more than any other folk art, the self and ethnic awareness of craftsmen. All the important situations of human life such as birth, death, love, passion, and sickness, all the sad or happy moments, are reflected in the color of the garments [6]. Natural awareness is depicted in the motifs and in the combination of the colors used, and through them, influences can be traced from ancient Greek, Roman, and Byzantine cultures [7].

In the past, each discovery was made through much experimentation and many "accidents". The accidental events, as well as the mistakes, were exploited, providing valuable knowledge [8]. The oldest dyeing techniques were performed with natural pigments. The use of dyes dates to the same period (prehistoric) as the use of mineral pigments. [9]. However, due to the sensitivity of textile fibers, very few archaeological findings have survived until today but modern analytical methods allow the identification of the most important dyeing materials used in antiquity. The dyers' craft evolved and reached a high level in ancient times, as evidenced by several historical documents [10]. In the most developed ancient Greek cities, this craft possessed a prominent position. The enormous development of the craft in antiquity is evidenced by the great variety in the tones and shades of the ancient fabrics' colors. In Greece, natural dyes have been replaced by modern synthetic dyes from the middle of the 20th century. The importance of natural dyes in the past can be proved through the way dyers treated the secrets of the dyeing processes [11].

Dyeing was mostly the prerogative of the priesthood or performed by craftsmen who belonged to the king's social circle. In many cases, the secrets of centuries were lost because craftsmen did not bequeath the secrets of their craft to subsequent generations, either because they did not find successors to pass on their knowledge, or because they did not want to give away their secrets for fear of competition. Information is scattered; some is recorded in manuscripts, while some is possessed by elderly people only, who are dwindling dramatically. Another difficulty is the local dialect, which makes it difficult to identify plant and invertebrate dyes [12].

In recent years, there has been a rising international trend in the utilization of natural dyeing materials in the garment industry [12]. Ecological consciousness has boosted this tendency to turn to natural dyes. This trend is observed internationally in the scientific literature, raw material supply companies, and schools for learning basic dyeing methods and materials [13]. This fact brings to the fore once again forgotten dyeing techniques and materials that modern people could not think of.

2. Materials and Methods

2.1. Gathering Information

As mentioned above, the information related the natural dyes and the dyeing processes in the Greek region was not centralized. Several sources have been used for the collection of all this scattered information. Some of them were found in old books [14,15], others in the manuscripts[1] of the NKUA [16], and the RCGF [17], and the rest from the interviews during the field research.

Within these manuscripts, information and specific details related to dyeing processing and traditions have been found. All this priceless information was processed and classified with respect to the local idioms. More than 2000 different manuscripts were studied and analyzed, containing valuable information from various places in Greece. The major difficulties of this endeavor were the handwriting, the physical condition of some manuscripts and the local idioms of the language.

Botanical dictionaries at this phase proved to be extremely helpful bringing the pieces of the puzzle together [18]. In Greece, different vernacular names (local names) are used for the same plant species in different regions. It is therefore the first time that such a detailed dyeing identification of dye plants and their classification by their botanical name and plant characteristics has been undertaken in Greece.

There are vast levels of latent knowledge amongst the elders, the people who lived in times were natural dyeing was a common procedure, and those who possess the materials and secrets of their collection and application get fewer and fewer every day. Thus, field research was a necessity. during the last decade, visits took place to towns or villages either famous for their natural dyes or because there was information about people who knew the local dyeing stuffs and procedures. Different regions of Greece representing "traditions" of dyeing methodologies such as Athens, Crete, Nauplio, Thessaloniki, Serres, Skyros, Ampelakia, the Ionian islands, Hermioni, Parga, Kavala, Larissa, Kranidi, Euboea, Feneos, Kalavryta, and Cyprus[2] have been visited. The main objective was to record and classify the different natural dyes and dyeing processes that were used from region to region in order to gather and preserve the know-how of these people [19–22]. Sometimes the older people who were interviewed were extremely cautious and hesitant to give up the information they possessed. It was a time-consuming procedure to visit them, make them feel comfortable, and persuade them to share their precious knowledge. On the other hand, it was like travelling back to time, since they were letting the researcher enter their world. Some of them were willing to give all their knowledge and most of them enjoyed the whole procedure. A total of 30 interviews were performed during the last decade.

2.2. *Materials and Dyeing Procedure*

After harvesting and processing the raw information, the research focused on specific dyeing materials and the replication of the recipes related to them. This was thought to be necessary for several reasons. One of these is to check the shades mentioned in the recipe. Another is to create a database of dyeing materials, recipes, and samples in order to create a non-destructive method of identification. The replication of specific recipes demands to find all the appropriate dyeing plants and auxiliaries. The first step was to locate and collect the appropriate plants from the countryside or from related shops. Most of them, such as the almond, *Prunus amygdalus* (L.) *Batsch*, the common myrtle, *Myrtus* L., the sweet chestnut, *Castanea sativa*, *Mill* plants of the genus *Hibiscus* L., the oriental plane, *Platanus orientalis* L., and the southern blue gum, *Eucalyptus globulus* Labill., were collected from the fields. Others, such as the tea plant, *Camellia sinensis* (L.) Kuntze, the red algae *Rytiphloea tinctoria* (Clemente) C.Agardh, *Quercus* L., and kermes *Kermes vermilio* Planchon, 1864, were bought. The plants, based on the recipes used, should be used either dried or fresh. The textile material used was woolen fabric in its natural form, because this was the material most used in the past for clothing. The instructions given in the recipe were followed in every detail, especially when pre-mordanting or other preparatory procedures were mentioned. For example, different dyeing techniques were performed for the same dyestuff, while an effort was made to replicate recipes using rare and unknown dyestuffs, such as Mediterranean strawflower, *Helichrysum stoechas* (L.) Moench (Figure 2) [23,24]. The result of this experimental procedure is more than 60 dyed samples.

Figure 2. Woolen sample dyed with the Mediterranean strawflower, *Helichrysum stoechas* (L.) Moench (photo taken by the authors).

2.2.1. Sample Preparation

The dyed samples were from wool fabrics. The samples measure 5 cm × 5 cm and were thoroughly cleaned with a scouring agent in order to ensure they were clean of dirt, chemicals, or any other substances. During the cleaning procedure, the woolen samples were not stirred and the temperature was kept below 60 °C. After washing for about 30 min, the samples were rinsed thoroughly. Following this, the wet samples were dyed by following the procedure.

2.2.2. Dyeing Method

Depending on the recipe, the samples could be either mordanted or not. Temperature, dyeing time, saturation time, and rinsing were also performed according to each recipe. Table 1 summarizes the plants, the concentration by weight, and other auxiliaries used for the sample preparation and dye.

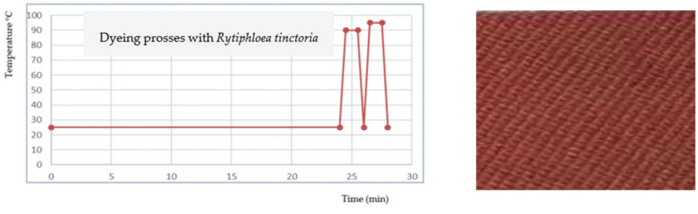
Table 1. Dyestuffs, mordants, and auxiliaries used for dyeing. C = collected in the field, M = bought on the market.

Color	Scientific Name English and Greek Name	Sources C/M	Used Part	% by Weight	Mordants and Auxiliaries	% by Weight
Brown	*Allium cepa* L. Onion, κρεμμύδι	C	brown onion skins	60%	Potassium alum Tartaric acid	25% 6%
Brown				60%	$K_2Cr_2O_7$	3%
Brown				100%	$K_2Cr_2O_7$	3%
Brown				60%	$K_2Cr_2O_7$ Tartaric acid	3% 6%
Brown				60%	Lye	10%
Brown				100%	Lye	10%
Brown	*Amygdalus communis* L. Almond, αμυγδαλιά	C	Fresh leaves	60%	$K_2Cr_2O_7$	3%
Brown			Fresh leaves	60%	CH_3COOH	3%
Green			Fresh leaves	60%	Lye	10%
Yellow	*Calendula officinalis* L. Common marigold, καλέντουλα	C	Flowers	100%	CH_3CCOH	3%
Brown	*Camellia sinensis* (L.) Kuntze Tea plant, Τσάι	M	Leaves	60%	-	-
Brown	*Castanea sativa* Mill. Sweet chestnut, καστανιά	C	Fruits	10%	Potassium alum Tartaric acid	25% 6%
Brown				10%	-	-
Brown	*Cercis siliquastrum* L. Judas tree, κουτσουπιά	C	Leaves	100%	-	-
Yellow	*Cota tinctoria* (L.) J.Gay (syn. Anthemis tinctoria L.) *Dyer's chamomile*, χαμομήλι	C	Flowers	200%	-	-
Brown	*Cupressus sempervirens* L. Mediterranean cypress, κυπαρίσσι	C	Cones	60%	Potassium alum Tartaric acid	25% 6%
Brown	*Eucalyptus globulus* Labill. Southern blue gum, ευκάλυπτος	C	Leaves	200%	-	-
Green	*Ficus carica* L. Fig, συκιά	C	Leaves	200%	CH_3CCOH	3%
Yellow	*Freesia* Eckl. ex Klatt Freesia, φρέζες	C	Flowers	100%	CH_3CCOH	3%
Brown	*Hedera* L. Ivy, Κισσός	C	Leaves	150%	-	-
Brown		C	Fruits	200%	-	-
Yellow	*Helichrysum stoechas* (L.) Moench Mediterranean strawflower, Ελίχρυσο	C	Flowers	100%	-	-
Brown	*Hibiscus* L. Hibiscus, Ιβίσκος	C	Flowers	40%	-	-
Brown	*Humulus lupulus* L. Common hop, Λυκίσκος	M	Fruits	200%	Potassium alum Tartaric acid	25% 6%
Brown	*Hypericum perforatum* L. St. John's wort, Υπέρικο	C	Flowers	60%	Potassium alum Tartaric acid	25% 6%

Table 1. *Cont.*

Color	Scientific Name English and Greek Name	Sources C/M	Used Part	% by Weight	Mordants and Auxiliaries	% by Weight
Red	*Kermes vermilio* Planchon, 1864 Kermes, Κρεμέζι	M	Female insects	70%	Potassium alum Tartaric acid	25% 6%
Red				2.5%	SnCl2 Tartaric acid	3% 1 g/L
Red				10%	-	-
Red				10%	Potassium alum Tartaric acid	25% 6%
Red				10%	$K_2Cr_2O_7$	3%
Brown	*Mentha spicata* L. Common mint, Δυόσμος	C	???	200%	-	-
Brown	*Myrtus communis* L. Common myrtle, Μύρτιλο	C	Leaves	200%	Potassium alum Tartaric acid	25% 6%
Brown	*Papaver rhoeas* L. Common poppy, παπαρούνα	C	Petals flower	60%	-	-
Brown	*Persea americana* Mill. Avocado, Αβοκάντο	M	Fruit skin	200%	-	-
Brown	*Pinus* L. Pine, Πεύκο	C	Bark	300%	-	-
Brown	*Platanus orientalis* L. Oriental plane, πλάτανος	C	Leaves	100%	-	-
Brown		C	Fruits	200%	-	-
Dark brown	*Punica granatum* L., pomegranate, ρόδι	C	Fruits skin	300%	$FeSO_4$	2%
		C	Fruits skin	300%	-	-
Brown	*Quercus coccifera* L., Oak, Πουρνάρι	C	Acorns	100%	Lye	25%
Brown		C	Acorns	100%	-	-
Red	Rubia tinctoria L. madder, ριζάρι	M	Rhizomes	60%	H_2SO_4	10%
Red			Rhizomes	60%	-	-
Red	*Rytiphloea tinctoria* (Clemente) C.Agardh, red algae, φύκι	M	Algae	60%	H_2SO_4	10%
Red			Algae	60%	CH_3COOH	10%
Brown	*Taraxacum officinale* F.H. Wigg. Dandelion, Ραδίκι του βουνού	C		200%	-	-
Green	*Vitex agnus-castus* L., Vitex, λυγαριά	C		200%	-	-

Two dyeing circles were performed for each material. The first was undertaken according to the recipe and the second was performed by changing variables such as the mordant procedure and the amount of the dyestuff, the dyeing temperature, and the kind of fabric used in order to produce different shades, providing a valuable database and reference point for further research. An example of dyeing procedures regarding time and temperature is given in Figure 3.



(a) **(b)**

Figure 3. (**a**) Dyeing prosses with *Rytiphloea tinctoria* (Clemente) C.Agardh, (**b**) Dyed woolen sample.

3. Results and Discussion

The branched asphodel, *Asphodelus microcarpus* Rchb., *Berberis cretica* L., the oriental plane, *Platanus orientalis* L., (Figure 4) the pink rock-rose, *Cistus creticus* L., the orchil lichen, *Roccella tinctoria* DC, the red algae, *Rytiphloea tinctoria* (Clemente) C.Agardh, and the dyer's alkanet, *Alkanna tinctoria* (L.) Tausch, are plants used in the past for garment dyeing in Greece. It is remarkable that some of the dyeing plants, such as *Cistus creticus* L., were mentioned by Pliny and Aristotle [25] and continued to be used until recently. All the abovementioned dyestuffs are only a few of the plants recorded through the research.

Figure 4. *Platanus orientalis* L. Oriental plane, (Greek: πλάτανος) fruits and leaves (photo taken by the authors 2013 at Abelakia Greece).

3.1. Classification and Dyeing

The classification and identification of the dye plants and the description of their botanical characteristics is necessary in order to gather knowledge. Usually, every researcher refers to the dyeing procedure of one area. In the results of such research, the plants used for dyeing are documented by their local name. For this research gathering, all this information was crucial since, although some plants have a similar use, in several cases some plants were known in different places within the Greek region by different names and used in different ways. Sometimes, the same plant was used with many different procedures, consequently resulting different shades.

Thus, more than 140 plants used in Greece have been identified. Their use is described in manuscripts such as those of NKUA, while others reached us through oral testimonies.

A large portion of the people interviewed insisted that many of the natural dyes, depending on the dyeing process, had excellent durability and did not fade. They proved their opinion by showing garments, some even dyed more than 100 years ago. The color depth varied depending on the water, pH, and the amount of dye used, which, as is recorded, the dyers were very conscious about. From the data collected, it was proved that the dyeing process affected the quality of the dyed material. Other factors that affect the quality of the dyed garment are the climate conditions, the sunshine, the soil, the water, and the rainfall rates of each region, in relation to plant development. The color tone is mentioned as being modified according to the season of the plant's collection.

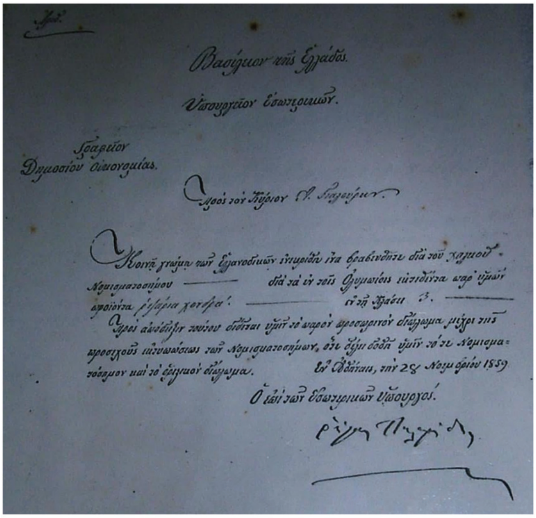
Existing documentation indicates that exactly the same materials and similar dyeing techniques were used in various areas of Greece, even in other countries [16]. In the island of Nisiros, for example, *Rytiphloea tinctoria* (Clemente) C.Agardh, a kind of algae (Figure 5a), was used to achieve shades of red. In Cyprus[3], hundreds of miles away, it was mentioned as being used for the same purpose. The use of the same algae in Kefalonia for egg decoration (Figure 5b) is a matter of common knowledge even to the present.

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

Figure 5. (**a**) The morphology of the algae[4]. (**b**) Traditional dyed eggs using the algae *Rytiphloea tinctoria* (Clemente) C.Agardh (photo taken by the authors in Kephalonia, during Easter 2015).

Another dye, widely used from Thrace to Crete, is made of *Vitis vinifera* L., commonly known as grape vine. The color variation depends on the part of the plant used. It also depends on the dyeing process. All the testimonies from the bibliography or from manuscripts indicate that they were of excellent quality [26].

The plant *Dittrichia viscosa* (L.) Greuter, also known as Koniza, Akonizia, konizo, nerokonizo, nerokollisia, psilithra, psilithro, and psilistra, is a common plant of the Mediterranean area, which, according to the testimonies, was widely used in Greece as a dyestuff. Kefalonia, Arachova, and Crete are some of the places (all far away from each other) where this specific plant was used for obtaining green shades. However, in some places, there are records for using this specific plant for achieving yellow shades. A more remarkable fact is that in Crete, the false yellowhead, *Dittrichia viscosa* (L.) Greuter was used in combination with other plants in order to dye in different shades [27,28]. Similar to this is the use of parts (leaves, barks, or acorn) of the oak, *Quercus* L. (), which was also a widely known dyestuff. However, by using different procedures, it could produce variations in shades. It is worth mentioning that dyestuffs from oaks, *Quercus* L., dyer's madder, Rubia tinctorum L., and dye insects were just a few examples of substances which the trade and consequently the prosperity of places (Figure 6) depended on [29–31].



Ἀρ.

Βασίλειον τῆς Ἑλλάδος.

Ὑπουργεῖον Ἐσωτερικῶν.

Γραφεῖον
Δημοσίου Οἰκονομίας.

Πρὸς τὸν Κύριον Α. [illegible]

Κοινῇ γνώμῃ τῶν Ἑλλανοδικῶν ἐνεκρίθη ἵνα βραβευθῆτε διὰ τοῦ χαλκοῦ Νομισματοσήμου — διὰ τὰ ἐν τοῖς Ὀλυμπίοις ἐκτεθέντα παρ' ὑμῶν προϊόντα ῥιζάρια χονδρά. — ἐν τῇ Τάξει 3. —
Πρὸς ἀπόδειξιν τούτου δίδεται ὑμῖν τὸ παρὸν προσωρινὸν δίπλωμα μέχρι τῆς προσεχοῦς κατασκευάσεως τῶν Νομισματοσήμων, ὅτε θέλει δοθῇ ὑμῖν τό τε Νομισματόσημον καὶ τὸ ἐπίσημον δίπλωμα. Ἐν Ἀθήναις, τὴν 28 Νοεμβρίου 1859

Ὁ ἐπὶ τῶν Ἐσωτερικῶν Ὑπουργός.

Figure 6. Document found in an old house in the island of Skyros. It refers to a price awarded for the excellent quality of the madder cultivated in the area. The cultivation of madder was a source of wealth and prosperity (photo taken by the authors, Skyros 2007).

3.2. Anthropological Aspects

It is particularly important to mention that many of the dyes were an exportable good for several regions of Greece, and played an important role as a source of enrichment. Examples, such as the partnership of Ampelakia, which was the first partnership to be established, demonstrate the unique role that natural dyes have played and can play in local prosperity [32,33]. The city of Ampelakia experienced days of wealth and spiritual and material prosperity due to the trade of red-madder-dyed fabrics. They safeguarded the secrets they possessed, which gave unique properties to their dye. Part of those secrets include the use of special tools (Figure 7) or secret ingredients, such as pork blood.[5] From the above, it can be realized that the dyeing was a particularly complex process with many factors that had to be considered to achieve the desired result and the requested repeatability. The method of cultivation, together with the dyeing and mordanting procedure, proved to be of major importance, since they affected the final quality. These, indeed, are the reasons why the madder red of Ampelakia was so famous [34,35].

Figure 7. Stone mortar for pulverizing the dyestuff. Used in Ampelakia [34].

The mores and the customs concerning the color of clothing and fabrics are many. The color combinations of the threads and the decorative patterns reveal the aesthetics and the soul of the folk craftsmen, as well as their beliefs, religious, artistic, and cosmological concerns [36].

In disastrous situations for the local society, the semiology, but also the properties of color, deeply connected to the expression of the inner state of the individual person, were charged with supernatural powers. This is how many beliefs were born around the preparation and use of a clothing color. Through these elements, the importance of natural dyes can be seen [36–38]. For example, it was believed that if one were dyeing while an ill person was present, the dye quality would be poor [39]. The same applied to the presence of strangers while dyeing, because of their bad energy, which would affect dyeing. Such superstitions are recorded in several places in Greece. The supernatural protective powers of the blue and red color are very common. In Crete, a blue thread was used on a baby's legs in order to protect the baby from any bad energy [40,41]. Similar superstitions existed about the day of dyeing; thus, Tuesdays and Sundays were avoided. It was also believed that if someone were to see one dyeing or one's dyed hand, this could affect the strength and the quality of the dye. A large number of such testimonies from various areas of Greece have been recorded during field work, indicating the great importance of dyed garments in the local society [42,43].

4. Conclusions

In conclusion, this is the first time that the natural dyes used in Greece for the decoration of traditional clothes have been studied systematically, allowing us to preserve all this knowledge for future generations. During this first stage of the project, it was possible to record about 140 different plants, and their local names, and a large number of dyeing secrets used for producing vivid and durable colors. The anthropological records reveal the importance of the dyeing materials in dyers' lives. It is important to approach their way of thinking in order to approach their way of acting. The collected data, on one hand, is an extremely useful tool which can be used in a creative way for our modern needs, and on the other hand, can provide useful information for conservators and researchers regarding the materials used for the decoration of textile objects during the 19th and early 20th century in Greece.

More than 2000 manuscripts have been studied so far and many interviews have been undertaken with older people who have used these materials. By gathering and saving as much information as possible, it came to the researchers' attention that an enormous number of plants were used in more than one city or region. These plants were known most of the time by a local name (sometimes quite similar to the one widely used).

The data produced include all the phytological characteristics of the plants, as well as the parts of the plant used, the period collected, and the areas where they were applied, together with images of the plants and various details regarding the recipes used in many places around Greece with the related documentation. It also refers to ethics and traditions related to the dye, the color, or the dyeing procedure.

The replication of old recipes resulted in dyed samples in shades quite similar to those documented and expected. Some divergences are to be expected. The application of the most commonly used plants on woolen samples on one hand helps in examining how these data could be used for the current needs and also provided samples for the next and final step of this research, the non-destructive investigation of colored fabrics. Hopefully, these techniques will provide data on special characteristics which will be used for dye identification, without the need to sample the objects.

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Notes

[1] These manuscripts were created since 1965, when researchers used to visit a place and were gathering raw information about the ethics, the tradition, the way of living, etc. All this amount of information was recorded in the manuscripts, to preserve the knowledge for the next generations. In the NKUA, are gathered more than 3000 different manuscripts from several places of Greece.

[2] Today Cyprus is a different country; however, both countries share common traditions and customs.

[3] Cyprus is referred, since historically and traditionally is united to Greece.

[4] The photo of the algae is taken from the following site: https://www.blue-ecosystems.com/racheliSeaWeed/English/Rytiphlaea-tinctoria-%28Clemente%29-C.-Agardh-, last accessed on 20 December 2023.

[5] Pork blood has a high iron content. Iron binds to the dye molecule and the fiber molecule, forming a metal complex. Due to its large size, it is supposed to reflect the light giving a bright shade.

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Article

Transition from Natural to Early Synthetic Dyes in the Romanian Traditional Shirts Decoration

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Abstract: The traditional shirt ("*ie*") is the most well-known element of Romanian anonymous textile art. Apart from aesthetic and utilitarian roles, it has strong symbolic significance, mainly through the colours used for decoration. Very recently, the traditional shirt with decoration over the shoulder ("*ia cu altiță*") was introduced as a Romanian identity element as part of UNESCO heritage. Depending on the ethnographic area, the traditional shirt with decoration over the shoulder has acquired special expressive particularities over time. Particularly relevant is that from Valea Hârtibaciului, an area of Transylvania in the very centre of Romania. Although sober in appearance with large fields of white plain weave, it is discreetly decorated with elaborated embroidery on the sleeve bracelets, over the shoulders and neck. Even the colour range and decoration motifs remain unchanged in time, evolution in the materials used and a subtle transition from natural hues to more strident alternatives were observed in the late 19th and early 20th centuries. For the present study, samples were taken from representative objects in the collections of the ASTRA Museum, Sibiu and Ethnographical Museum, Brasov, documented as belonging to the area of Valea Hârtibaciului and dated in the museum archives as from the late 19th and early 20th century. The textile materials and the dyes used in the shirts' embroidery were monitored. Fibre identification was made by optical microscopy and infrared spectroscopy (FTIR-ATR). Dye analysis was performed by liquid chromatography coupled with UV-Vis (diode array) detection, while some of the samples were also analysed by liquid chromatography coupled with mass spectrometric detection (LC-DAD-MS). Dyes were extracted from the fibres by acid hydrolysis. Identification was based on data collected on standards, dyes and dyed fibres. For the early synthetic dyes, a dedicated library of references was built, which includes information relative to the most relevant representatives used between 1850 and 1900, the 'Helmut Schweppe list'. According to the study, in the last decades of the 19th century, natural dye sources such as dyer's broom, madder, Mexican cochineal and indigoid dyes were gradually replaced by early synthetic dyes: fuchsine (1856), methyl violet (1861), synthetic alizarin (1871), brilliant green (1879), azo flavine 3R (1880), rhodamine B (1887) and others.

Keywords: natural dyes; early synthetic dyes; textiles; liquid chromatography; identification; shirts; Romania

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1. Introduction

The shirt is the most significant part of the Romanian traditional costume and therefore receives particular attention, reflected in cut, decoration, chromatics, materials and techniques [1]. On special occasions, it acquires even a stronger symbolic significance, becoming a vestmental code to express provenience, appurtenance to age and ethnic groups, or civil status [1,2]. At the end of the 19th century, this traditional shirt elegance attracted the attention of the Romanian Queen Elizabeth (1843–1916), who started to wear shirts at Court events and international meetings. Her aim was to evidence that Romanian spirituality has deep roots in the history of the nation and that it is also witnessed the refinement and artistic diversity of traditional clothing. Noblewomen followed the Queen's model in her effort to promote the traditional costume, while later on Queen Mary of Romania (1875–1938) and her daughters also became ambassadors of the traditional costume [3]. Nowadays, traditional shirts dating back to the 19th and 20th centuries are preserved in museum collections, as material testimonies of the peasants' skillfulness and artistic taste. An increasing interest in their examination has materialized in recent years in several studies and exhibitions [1,2]. Moreover, the traditional shirt with decoration over the shoulder, the so called "*ia cu altiță*"—still widespread nowadays on both sides of the Carpathian mountains—was recently accepted as part of the UNESCO National Inventory of Active Intangible Cultural Heritage Elements [2]. Since 2012, the concern to conserve the traditional shirt as an element of cultural identity was also reflected in the spontaneous organisation of several sewing groups, in different areas of Romania, who produce their own shirts by following models of traditional items. In order to reproduce them as faithfully as possible, special attention is given to the materials—textile fabrics, sewing and decoration yarns, as well as to the dyes used.

Natural dyes were the only source of colour for textile dyeing since antiquity and until synthetic alternatives became available. The first successful efforts to develop new colouring compounds date from 1740 to 1771, when indigo carmine and picric acid were first synthesized [4]. Nevertheless, the triumph of synthetic dyes started in 1856, when the first synthetic dye, mauveine, was accidentally discovered [4,5]. In the following years, a large number of synthetic dyes with different structures came on the market, about 400 being in use before 1900, which resulted in the rapid decline of the natural dyes [4]. Regarding the period between 1850 and 1900, the literature mentions that in the three Romanian provinces (Wallachia, Moldavia and Transylvania) a large number of local plants were employed for dyeing purposes [6–9]. An invaluable treasure for documentation of rural life at the end of the 19th century is a collection of dyeing recipes edited by the Romanian Academy in 1914, which includes about 300 descriptions. Beside the large number of natural local sources discussed, the book makes reference to imported natural dyes and early synthetic alternatives [10].

The use of natural and synthetic dyes in historic textiles is nowadays revealed by analytical investigation. Since its first use in 1985 [11], liquid chromatography with UV-Vis (diode-array) detection became the standard method for dye identification and characterisation [12–17], while more recently mass spectrometers were added to the configuration due to their increased sensitivity, which results in lower detection limits, more accurate identifications and smaller sample consuming [18–25]. Report describing historic textiles research based on natural dye detection remain of major interest; however, an increasing number of publications refer to the early synthetic dyes' characterization and identification [4,5,26–32].

Since 1997, a project aiming to enrich the existing information on textiles in the Romanian collection based on the analytical investigation of dyes has been developed. A particular attention was given to traditional textiles through studies on representative items from several museum collections in Romania (see Acknowledgements) [33–38]. Research brought analytical evidence that natural local and imported dyes and synthetic colours coexisted in villages in the three Romanian provinces in the 19th and 20th century. A collection of shirts dated between 1850 and 1930 are catalogued within the cultural project *Saving the others' culture*. Research on home-made shirts with decoration over the shoulder, from Valea Hârtibaciului [39] seemed the ideal opportunity to better understand the transition from natural to early synthetic alternatives. Although sober in appearance due to the large fields of white plain weave, the shirts from Valea Hârtibaciului (an area of Transylvania, in the very center of Romania) are discreetly decorated on the sleeve bracelets, over the shoulders and the neck, with elaborated embroidery (Figure 1). The case study selection was based on the observation that, depending on the ethnographic area, the shirt with decoration over the shoulder has acquired special expressive particularities over time, which is also reflected by the textile materials and dyes used.

Figure 1. Image of shirt inv. 3816 (Muzeul ASTRA Sibiu) to illustrate the overall look of a traditional shirt from Valea Hârtibaciului and details of neck and shoulder decorations.

This article analytically documents the use of natural and early synthetic dyes in hand-made shirts with decoration over the shoulder from Valea Hârtibaciului. A total of 50 samples from 12 shirts belonging to collections of the Ethnographical Museum, Brasov, and the ASTRA Museum, Sibiu, were available for study. One more shirt which was part of a previous survey [35] but typologically belonging to the same group was also included in the discussion.

2. Materials & Methods

2.1. Sample Description, Documentation and Pretreatment

Samples about 0.5–1 cm long were taken from the back of the shirts' decoration during the conservation procedures. Fibers were first observed under the optical microscope at 10–80× magnification and yarns about 0.5 cm (~3 mg) were cut from the original samples and non-destructively analyzed by attenuated total reflectance infrared spectroscopy (FTIR-ATR). Some of the samples were also analyzed by X-ray fluorescence spectrometry (XRF) for mordants or inorganic colorant identification.

Dyes were extracted from the yarns by the standard acid hydrolysis method [11]. This was preferred to the mild extraction alternatives due to a database of natural dyes which was already in use, and contains information on dyes extracted from standard dyed yarns (yarns dyed in the laboratory with well-documented biological sources) by acid hydrolysis. This was the decision assumed and its limits, caused by the decomposition of glycosides to their parent aglycons, in the case of (natural) flavonoid dyes, were known [40–43]. To each yarn, 200 µL mixture 37% $HCl/CH_3OH/H_2O$ 2:1:1 ($v/v/v$) were added and the mixtures were kept at 100 °C for 10 min. The solutions were evaporated to dryness in a vacuum desiccator. Each sample was redissolved in 100 µL solution CH_3OH/H_2O 1:1 (v/v) and centrifuged at 12,000 rpm for 10 min. The supernatants were transferred into chromatographical vials and injected into the chromatographical system. When the presence of indigo based dyes was suspected, as in the cases of visual blue, green, violet 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 merged and thus analyzed.

2.2. Fiber Identification

Fiber documentation and image collection were made with a Nikon SMZ 1000 stereomicroscope coupled with a Nikon DSLR camera, model D3100 Kit AF-s 18–55 mm VR DX. 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 dedicated software, Opus 7.0.

2.3. Dye Analysis by Liquid Chromatography, Instrumentation and Parameters

All the samples were analyzed by liquid chromatography with UV-Vis (diode-array) detection, LC-DAD on System 1, while selected samples were also investigated by liquid chromatography with UV-Vis and mass spectrometric detection, LC-DAD-MS on System 2.

2.3.1. System 1 (LC-DAD)

An Agilent 1260 Infinity II series liquid chromatograph (Agilent Technology, Santa Clara, CA, USA) consisting of a quaternary pump (G7129A), a standard autosampler (G7111B), a column thermostat (G7116A) and 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, 150 mm length, 4.6 mm i.d. and 5 µm particle size, was thermostated at 40 °C. The mobile phase consists of a mixture of aqueous 0.2% (v/v) formic acid (solvent A) and methanol/acetonitrile (1:1, v/v) plus 0.2% formic acid (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.

2.3.2. System 2 (LC-DAD-MS)

An Agilent 1260 LC system was used, composed of the following modules: quaternary pump (Model G1311C), automatic injector (G1367E) and column thermostat (G1316C). The diode array detector (G4212A) and the triple quadrupole mass spectrometer (G6410B) were serially connected. The latter used an ESI ionization source (ESI, Model G1948B), operated under negative and positive ion monitoring modes. Chromatographic separation was the same as for System 1, except for Solvent B which was methanol/acetonitrile 1:1 (v/v) with no formic acid content. No extra samples were prepared for LC-DAD-MS analysis, 10 µL from the samples already prepared for LC-DAD being injected in the chromatographic system. UV–Vis spectra were acquired with a DAD detector which was placed between the column and the MS ion source. Spectra were collected over the 190–640 nm range, with a resolution of 2 nm. For the MS detector, the following ESI operation parameters were used: drying gas temperature 350 °C; drying gas flow 8 L/min; pressure of the nebulising gas 40 psi; Vcap 2500 (−) in negative ion mode and 2500 (+) in positive ion mode. The triple quadrupole used MS2 type scan when used as a single MS instrument; the data storage was set on profile and the peak width at 0.07; fragmentor 135 V; ΔEMV 400 V. The scanning interval for the mass to charge ratio (m/z) was between 100 and 600 a.m.u., and acceleration voltage on the collision cell: 7 V; Dwell Time 500 ms. In order to control the chromatographic system, as well as for data acquisition and processing, Agilent MassHunter Quantitative Analysis B.06.00 software was used. The analytical procedure was described in detail in an earlier publication, where an ion trap mass spectrometer was used instead of the triple quadrupole [44]. The selected samples were first analyzed with single MS detection in the Full Scan mode and the resulting data was processed by extracting chromatograms, according to the molecular ions of the dyes in the database.

2.4. Dyes 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 [35], biological source attribution was based on data collected on yarns dyed in the laboratory, by following traditional dyeing recipes. The existing database which mainly contained natural dyes was enriched with information on synthetic products, in order to correspond to actual needs. Experiments were thus performed on dyes and dyed yarns (prepared in the laboratory with contemporary products acquired from various providers), as well as on the Schweppe collection of early synthetic dyed yarns. The latter is a collection of yarns dyed with a selection of 65 synthetic dyes, considered by Helmut Schweppe as the most commonly used between 1850 and 1900 [26,45]. It was offered by the chemist to European and worldwide museums in the 1960–1970, during a series of dyeing workshops with these well-documented products. The collection used in the present study was prepared by Ronnee Barnett, textile restorer at the Metropolitan Museum of New York (MET) and offered by Florica Zaharia, Muzeul Textilelor Băița Romania (see Section Acknowledgements). Analytical information from the in-house built database was supplemented with literature data on early synthetic dyes [4,5,26–29]. Retention and UV–Vis data on the natural dyes and biological sources discussed is given in Table 1, while similar information on the early synthetic alternatives can be found in Table 2. When mass spectrometric data was used for dye attribution (samples analyzed with System 2), it was added in a separate column in each of the two tables.

2.5. X-ray Fluorescence Spectrometry (XRF)

Elemental analysis of selected samples was performed with a portable XRF spectrometer Bruker S1 TITAN Model 600, with the following specifications: rhodium (Rh) tube, silicon drift chamber detector (SDD), 5 mm spot size. The system used was air-path, elemental range Z > 12 (Mg). It was set to 45 kV/10 µA for heavy elements and to 15 kV/27 µA for the easy.

Table 1. The biological sources discussed, the corresponding dyes and their retention and UV–Vis data. MS data for the dyes identified by LC-DAD-MS were also included.

Biological Source Common and Latin Name(s)	Dye	Abbreviation	Retention (min.)		UV_Vis Data	MS Data
Madder (Mad) (*Rubia tinctorum* L.)	Alizarin	al	15.4		202; 248; 278; 430	-
	Purpurin	pu	16.4		204; 256; 294; 480	-
Indigo based (see text) (Ind) Woad (*Isatis tinctoria)* or Indigo (*Indigofera* sp.)	Indigotin	ind	16.2		238; 285; 330; 610	-
Dyer's broom (DB) (*Genista tinctoria* L.)	Luteolin	lu	13.0		208; 254; 266; 348	-
	Genistein	ge	13.7		208; 260	-
	Apigenin	ap	13.9		210; 268; 336	-
Sawwort (Saw) (*Serratula tinctoria* L.)	Luteolin	lu	13.0	12.7	208; 254; 266; 348	MS− 285
	Apigenin	ap	13.9	13.7	210; 268; 336	MS− 269
	3-O-methyl-quercetin	3-O-methyl-qu	-	12.9	-	MS− 315
Carminic acid based Mexican cochineal (*Dactylopius coccus* C.) (ca) (see text)	Carminic acid	ca	8.8	9.0	226; 276; 310; 494	MS− 491
Tannins (tan)	Ellagic acid	ea	9.9	10.0	254; 366	MS− 301

Table 2. Early synthetic dyes detected, their retention and UV–Vis data. MS data for the dyes identified by LC-DAD-MS were also included.

Dye	Color Index	Retention (min.)		UV-Vis Data	MS Data
		System 1 (LC-DAD)	System 2 (LC-DAD-MS)		
Alizarin (synthetic) (1871) (Al) anthrapurpurin, flavopurpurin, alizarin	Mordant Red II CI 58,000	13.6	-	274; 338; 428	-
		13.8	-	272; 406	-
		15.2	-	248; 278; 430	-
Alkali blue (1864)	Acid Blue 110 CI 42,750	14.4	-	596	-
		16.6	-	596	-
Auramine (1883) (Aur)	Basic Yellow 2 CI 41,000	14.2	-	360	-
		15.7	-	366; 486	-
		16.9	-	368	
Azo Flavine 3R (1880) (AzoFl)	Acid Orange 1 CI 13090	16.2	15.9	410	MS− 258
Brilliant green (1879) (Bri Gr)	Basic Green 1 CI 42,040	15.4	15.9	428; 626	MS+ 385
Fuchsine (magenta) (1856) (Fuch) pararosaniline, fuchsine (rosaniline), methylrosaniline, dimethylrosaniline	Basic Violet 14 CI 42510	10.6		544	-
		11.2		546	-
		11.9		548	MS+ 316
		12.5		550	MS+ 330
Methyl Violet (1861) (Me-Vio)	Basic Violet 1 CI 42,535	13.9		568	-
		14.2	14.5	574	MS+ 344
		14.6	15	582	MS+ 358
		15.0	15.4	590	MS+ 372
Cristal Violet (1883)	Basic Violet 3 CI 42,555	15.0	15.4	590	MS+ 372
Orange GG (1878) (Ora GG)	Acid Orange 10 CI 16,230	12.2		480	-
Picric acid (1771) (Pic Ac)	Acid Dye CI 10,305	12.5		360	-
Safranin T (1859) (Saf T)	Basic Red 2 CI 50,240	11.7		530	-
		12.1		526	-
Rhodamine B (1887) (Rhod)	Basic Violet 10 CI 45,170	15.1	15.2	557	MS+ 443
Uranine A (1871) (Uran)	Acid Yellow 73 CI 45,350 (20)	14.0		482	-
					-
Victoria Blue B (1883) (Vic B)	Basic Blue 26 CI 44,045	-	15.3	-	MS+ 442
		15.4	15.8	306; 346; 604	MS+ 456
		15.7	16.1	308; 350; 616	MS+ 470

3. Results

Results are presented in Table 3 and will be discussed in the following sections according to the visual colours of the yarns examined and the dyes identified.

Table 3. Objects, samples and the results obtained by dye analysis. See Table 1 for the natural dyes abbreviations.

No.	Sample Code Colour (Fibre)	Sample Location	Dye	Dye Source (Common Name)
Shirt, inv. 1252, Ethnographical Museum, Brasov (end 19th century)				
1	1252_P1 Red (wool)	Shoulder decoration, left	al, pu	Madder
2	1252_P2 Orange (cotton)	Sleeve bracelet, right	-	Lead chromate (PbCrO4) (Pb and Cr confirmed by XRF)
3	1252_P3 Blue (wool)	Sleeve bracelet, right	ind	Indigo based
4	1252_P4 Green (wool)	Sleeve	lu, ge, ap	Dyer’s broom (with copper mordant) (Cu confirmed by XRF)
Shirt, inv. 1415, Ethnographical Museum, Brasov (end 19th century)				
5	1415_P1 Red (wool)	Neck decoration	al, pu	Madder
6	1415_P2 Orange (wool) Analizat MS	Neck decoration	9.2 min (max 273, 482) MS− 330 The dye do not match any of the dyes in the database	
7	1415_P3 Blue (wool)	Neck decoration	ind	Indigo based
8	1415_P4 Green (wool)	Neck decoration	lu, ge, ap, ind	Dyer’s broom + Indigo based
Shirt with lines over the elbow, inv. 1422, Ethnographical Museum, Brasov (end 19th–early 20th century)				
10	1422_P1 Red (wool)	Sleeve bracelet, left	al, pu, ea	Madder and tannins
11	1422_P2 Red (cotton)	Sleeve bracelet, left	anthrapurpurin flavopurpurin al	Synthetic alizarin (1871)
12	1422_P3 Red-pink (silk)	Sleeve bracelet, left	Rhodamine B (1887)	
13	1422_P4 Yellow (wool)	Sleeve bracelet, left	lu, ge, ap	Dyer’s broom
14	1422_P5 Blue (wool)	Sleeve bracelet, right	ind	Indigo based
Shirt, inv. 1429, Ethnographical Museum, Brasov (early 20th century)				
15	1429_P1 Red (silk)	Neck decoration	anthrapurpurin flavopurpurin al ca	Synthetic alizarin (1871) Carminic acid based
16	1429_P2 Violet (silk)	Neck decoration	Fuchsine (magenta) (1856)	
17	1429_P3 Violet (wool)	Neck decoration	Rhodamine B (1887)	
18	1429_P4 Yellow (silk)	Neck decoration	Azo Flavine 3R (1880)	
19	1429_P5 Blue (silk)	Shoulder decoration	Victoria Blue B (1883)	

Table 3. *Cont.*

No.	Sample Code Colour (Fibre)	Sample Location	Dye	Dye Source (Common Name)
Shirt, inv. 6847, Ethnographical Museum, Brasov (second half 19th century)				
20	6847_P1 Orange (cotton)	Shoulder decoration, right	-	Lead chromate (PbCrO4) (Pb and Cr confirmed by XRF)
21	6847_P2 Red (wool)	Shoulder decoration, right	al, pu	Madder
22	6847_P3 Blue (wool)	Shoulder decoration	ind	Indigo based
23	6847_P4 Yellow (cotton)	Shoulder decoration	-	Lead chromate (PbCrO4) (Pb and Cr confirmed by XRF)
Shirt, inv. 194P, ASTRA Museum, Sibiu (second half 19th century)				
24	194_P1 Red (wool)	Neck decoration	al, pu	Madder
25	194_P2 Green (wool)	Shoulder decoration, right	lu, ge, ap, ind	Dyer's broom Indigo based
26	194_P5 Violet (silk)	Shoulder decoration	ca MS− 491	Carminic acid based
27	194_P6 Brown (silk)	Shoulder decoration	ea MS− 301	Tannins
28	194_P7 Blue (wool)	Shoulder decoration	ind	Indigo based
Shirt, inv. 177P, ASTRA Museum, Sibiu (end 19th–early 20th century)				
29	177_P1 Pink (silk)	Shoulder decoration	Rhodamine B (1887)	
30	177_P2 Violet (wool)	Shoulder decoration	Methyl Violet (1861)	
Shirt, inv. 169P, ASTRA Museum, Sibiu (second half 19th century)				
31	169_P1 Pink (silk)	Shoulder decoration	ca	Carminic acid based (with tin mordant) (Sn confirmed by XRF)
32	169_P2 Blue (pale) (silk)	Shoulder decoration, right	ind	Indigo based
33	169_P3 Blue (dark) (silk)	Neck decoration	ind	Indigo based
34	169_P4 Brown (silk)	Shoulder decoration, right	ea MS− 301	Tannin based with iron mordant (Fe confirmed by XRF)
Shirt, inv. 3728, ASTRA Museum, Sibiu (last decade 19th–early 20th century)				
35	3728_P1 Red (silk)	Shoulder decoration	Orange GG (1878) and Methyl Violet (1861) (contamination, see coments in the text)	
36	3728_P2 Green (silk)	Shoulder decoration	Brilliant Green (1879)	
37	3728_P3 Violet (silk)	Shoulder decoration	Fuchsin (1856) and Methyl Violet (1861)	
38	3728_P4 Blue (silk)	Shoulder decoration	Victoria Blue B (1883)	

Table 3. *Cont.*

No.	Sample Code Colour (Fibre)	Sample Location	Dye	Dye Source (Common Name)
Shirt, inv. 3816, ASTRA Museum, Sibiu 1885				
39	3816_P1 Red (silk)	Shoulder decoration	ca	Carminic acid based
40	3816_P2 Green (silk)	Shoulder decoration	Picric acid (1771)	
41	3816_P3 Blue (silk)	Shoulder decoration	Alkali Blue (1864)	
42	3816_P5 Green (wool)	Neck decoration	Brilliant Green (1879)	
43	3816_P6 Blue (lână)	Neck decoration	Victoria Blue B (1883)	
44	3816_P7 Yellow (silk)	Shoulder decoration	Auramine (1883)	
Shirt, inv. 6464, ASTRA Museum, Sibiu (last decade 19th–early 20th century)				
45	6464_P1 Red (silk)	Shoulder decoration	Rhodamine B (1887)	
46	6464_P2 Pink (silk)	Shoulder decoration	Rhodamine B (1887)	
47	6464_P3 Blue (silk)	Shoulder decoration	Victoria Blue B (1883)	
48	6464_P4 Yellow (silk)	Shoulder decoration	Uranine A (1871)	
Shirt, inv. 210, ASTRA Museum, Sibiu (second half 19th century)				
49	210_P1 Pink-violet (silk)	Shoulder decoration	ca	Carminic acid based
50	210_P2 Violet (silk)	Neck decoration	Methyl Violet (1861)	
Shirt, inv. 20P, ASTRA Museum, Sibiu (end 19th century) (samples analysed by LC-DAD-MS [35]				
51	20_P1 Pink (silk)	Neck decoration	ca, fk, ka	Carminic acid based
52	20_P2 Pink (pale) (silk)	Neck decoration	ca	Carminic acid based
53	20_P3 Black (silk)	Shoulder decoration	ca	Carminic acid based and Prussian Blue (Pr Blue) * (Fe confirmed by XRF)
54	20_P4 Blue-green (silk)	Shoulder decoration	ind, lu	Indigo based Luteolin based
55	20_P5 Blue (silk)	Neck decoration	ind	Indigo based
56	20_P6 Brown (wool)	Neck decoration	-	Natural dyed wool
57	20_P7 Ochre yellow (silk)	Neck decoration	lu, ge, ap, 3-O-methyl qu	Dyer's broom and sawwort

* Identified by FTIR/ATR b (signal at 2074 cm^{-1}) and confirmed by the presence of Fe in XRF.

3.1. Red and Violet

21 samples from the 50 studied have a visual red or violet colour. About half of these samples (9/21) turned out to be naturally dyed while in one other case a combination of natural and synthetic dyes was used. Madder and carminic acid based dyes were the only natural sources of red and violet. Madder was responsible for the colour in half of the red samples (5/10), in all cases being used on wool. Carminic acid based dyes were revealed as single dye source in one red and four violet (or pink–violet) hues, always on silk. Carminic acid was also detected in two more pink silk samples in the shirt previously studied as well as in another red silk sample from the present group, in a dyeing combination with synthetic alizarin.

Identification of madder (*Rubia tinctorum* L.) was based on the presence of the two main anthraquinones in the plant roots, alizarin and purpurin, attributed according to retention and UV-Vis data. The absence of the other anthraquinones in the roots, munjistin, anthragallol, xantho-purpurin and rubiadin, could be explained by their low amount in the acid hydrolyzed samples, under the detection limit of the UV-Vis detector. This observation is supported by previous studies performed in the same research group where the above-mentioned anthraquinones were identified in samples prepared in the same conditions but investigated by using a sensitive mass spectrometer detector [46]. Identification of madder in traditional Romanian textiles is in perfect correlation with the literature, as a Romanian plant encyclopedia dated 1906 refers to madder as local spontaneous plant (*roibă*, *brociu* etc.) sometimes also cultivated for dyeing [6], and a study on Transylvanian traditional textiles with a remark to technology and aesthetics also mentions madder as main source of red [9].

Carminic acid is the main dye component in various insects, with *Porphyrophora species* and *Dactylopius coccus* as the most well-known representatives. Identification of species in historical textiles dyeing is based on the relative calculation regarding carminic acid and minor components, such as dcII (flavokermesic acid C glycoside), kermesic and flavokermesic acids. However, in the present study such interpretation is not possible, due to the reasons explained above when the absence of the minor components in madder roots was discussed. It is very probable that *Dactylopius coccus* (Mexican Cochineal) was used, according to previous studies on traditional Romanian textiles and correlating with the literature [10,33–35]. This supposition is also supported by the use of tin chloride as mordant, as suggested by the presence of tin according to elemental analysis in one of the samples where carminic acid was detected (169_P1).

Synthetic dyes were detected in 11/21 samples, including one where a synthetic dye was detected in a dyeing combination with a natural source (synthetic alizarin and carminic acid based). Apart from synthetic alizarin mentioned above, three other synthetic dyes were detected: fuchsine (in two cases, once together with methylviolet), methyl violet (four, including the one mentioned before) and rhodamine B (five cases). Fuchsine (magenta) (1856) and methyl violet (1861) are representatives of the first class of synthetic dyes, triarylmethane, usually composed by several chromophores which could be evidenced based on the UV-Vis data or the molecular cations (M+) when analyzed in positive ESI mode. In the present study, fuchsine was identified as the unique dye source in one violet silk sample (analized by LC-DAD) and in a dyeing combination with methyl violet, in a red silk one (additionally examined by LC-DAD-MS). For the former (1429_P2), the four dyes described in the literature as pararosaniline (λmax = 544 nm), rosaniline (λmax = 546 nm), methylrosaniline (λmax = 548 nm) and dimethylrosaniline (λmax = 550 nm) [5,26,27] were present while, in the latter (3728_P3), only methylrosaniline (λmax = 548 nm, MS+ 316) and dimethylrosaniline (λmax = 550 nm, MS+ 330) were detected. According to the literature [27], this could be explained by the differences in the synthesis, two production processes being reported, which would result in the so called "early fuchsine" and "late fuchsine", respectively. "Early fuchsine" is characterized by a mixture of the four compounds mentioned above and was obtained in the late 19th century by heating an oxidant with a coal tar distillate containing a mixture of aniline and toluidine in various ratios, either with or without further inclusion of carbon tetrachloride. "Late fuchsine" would be the result of a later process that involved reaction of 4,4′methylene-di-o-toluidine and o-toluidine with an oxidant, to give mainly methylrosaniline (also called magenta II) and dimethylrosaniline (new fuchsine). Consequently, sample 1429_P2 is more likely to have been dyed with "early fuchsine" and 3728_P3 with "late fuchsine" and methyl violet. Both versions of fuchsine were previously identified in other traditional textiles in Romanian collections, mainly on wool but also on silk [33,37]. The other representative of the triarylmethane group, methyl violet, was detected based on the presence of the three chromophores: λmax = 568 nm, λmax = 574 nm (MS+ 344), λmax = 582 nm (MS+ 358) and crystal violet λmax = 590 nm (MS+ 372). It was evidenced in three samples: a wool violet, a silk violet (in a dyeing combination with fuchsine) and a red silk (in a dyeing combination with Orange GG 3728_P1). However, the putting together of an acid dye (Orange GG) and a basic one (methyl violet) is unlikely, which means that the latter, which was present in another sample from the same shirt, should be considered as contamination. Both methyl violet and fuchsine were also detected in Saxon sheepskin coats' silk decoration, dated between 1892 and 1908, examined in a previous study [38].

Identification of synthetic alizarin was based on the detection of alizarin and the two marker compounds, anthrapurpurin (λmax = 430 nm) and flavopurpurin (λmax = 408 nm). Synthetic alizarin was introduced in 1868, when Graebe and Liebermann made the first artificial synthesis of a natural organic dye, and became available in 1871 [47,48]. It was one of the first synthetic dyes to be used extensively in Romanian traditional textiles, which may be explained by its qualities, as it was considered exceptionally fast against light and washing [47]. It was frequently detected, mainly on cotton, either as an individual dye to achieve a red hue or together with chrome yellow for orange [37]. Its identification, in the present study, in a dyeing combination with carminic acid based dye in a red silk yarn (1429_P1) is illustrative of the experiments performed in the synthetic dyes' debut period.

Rhodamine B (1887), which belongs to the class of xanthene, is detected based on information available in the literature and confirmed by examination of the standard dyed wool samples, λmax = 558 nm and MS+ 443 (Figure 2). These characteristic features were observed in one violet wool and two pink silk samples, as individual dye, and in a red silk sample together with a red dye, which did not match any of the dyes in the existing database but presents UV-Vis data related to safranin T. Unfortunately, no mass spectrometric data was available for the respective sample. Rhodamine B was also identified in Saxon sheepskin coats' silk decoration, dated between 1900 and 1908, in a previous study [38].

3.2. Yellow and Orange

Yellow dyes were detected in seven samples described as yellow and green. Dyer's broom, a natural dye, was responsible for the colour in all the samples where wool was implied (4/7), while synthetic dyes were used on silk (3/7). The presence of dyer's broom was suggested by the detection of luteolin (λmax = 348 nm), genistein (λmax = 260 nm) and apigenin (λmax = 336 nm), as compared with data collected on standards. Where a green hue was intended, either copper sulphate as mordant (1252_P4) or indigo based dyes were used (1415_P4 and 194_P2). According to previous studies [33,34,49], dyer's broom was the most commonly preferred biological source in Romanian traditional textiles, which is also supported by its frequent mention in the collection of dyeing recipes edited by the Romanian Academy in 1914, cited above (see Introduction section) [10]. Uranine A (1871) from the class of xanthenes, azo flavine 3R (1880) and the diphenilmethane auramine O (1883) are the three synthetic dyes identified based on the UV-Vis data (λmax = 482 nm for uranine A, λmax = 410 nm for azo flavine 3R and λmax = 366, 486 nm for auramine O), each correlating with retention, as resulted for the analysis of dyes in the Schweppe collection.

A dye which elutes at 15.9 min, with λmax = 410 nm and a molecular weight M = 259 (MS− 258) was present on an orange wool sample but cannot be identified, as these characteristics did not match those of dyes in the database. In three cotton samples, orange and yellow, an inorganic pigment, lead chromate ($PbCrO4$) was responsible for the colour. In these cases attribution was based on the results of elemental analysis performed by X-ray fluorescence spectroscopy, which revealed the presence of chrome and lead.

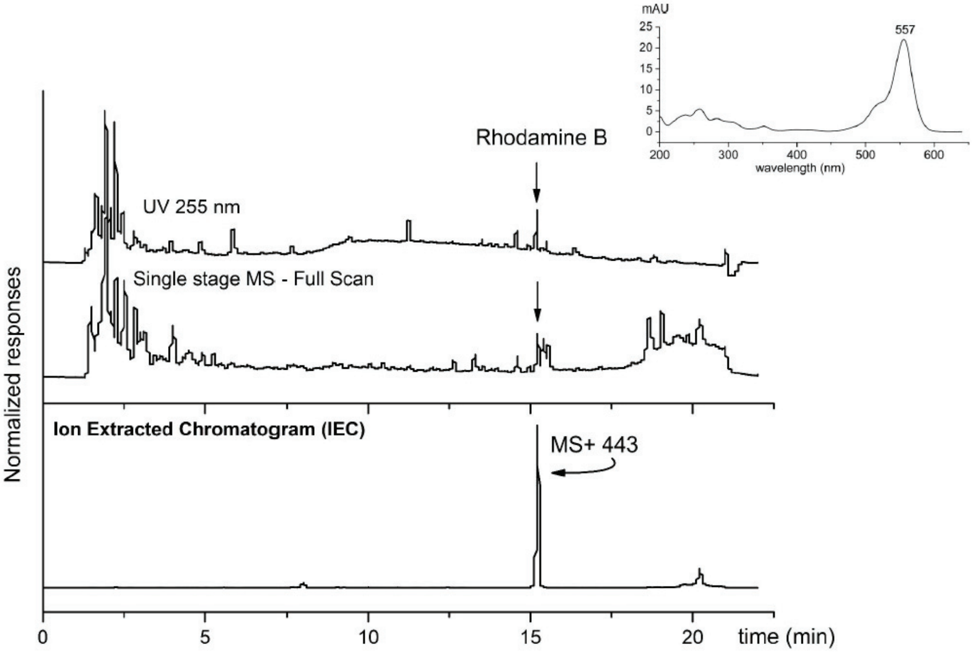

Figure 2. Image to support identification of Rhodamine B (1887) by LC-DAD-MS, in shirt inv. 1422 red-pink silk sleeve bracelet decoration (late 19th–early 20th century, Ethnographical Museum, Brasov, Romania).

3.3. Green

Apart from the three cases mentioned above, where dyer's broom with a copper mordant or with indigo based dyes were used, synthetic dyes were responsible for the colour. Picric acid (1771), obtained by nitration of phenol and considered one of the first semi-synthetic dyes, was identified in a silk sample which presents a green-yellow hue in a shirt dated 1885 (inv. 3816). As for the other synthetic dyes, detection was based on the UV-Vis spectra (λmax = 360 nm) correlated with retention, according to information acquired by examination of standards. Picric acid was previously identified in a silk sample from a flag used at a celebration in 1871 [50,51]. Brilliant green (1879), a representative of the triarylmethane group, was detected in two samples, on wool and on silk respectively, based on UV-Vis and mass spectrometric data (λmax = 428, 626 nm and M+ 385), associated with retention (Figure 3). According to previous studies, brilliant green was enthusiastically adopted, as proved by its identification in shirts and sheepskin coats from the end of the 19th and beginning of the 20th century [38].

3.4. Blue

Twelve samples were described as blue, indigo based dyes being responsible for the colour in more than half (7/12), as well as in the two green samples mentioned above (see Sections 3.2 and 3.3), when they were used together with dyer's broom. Although in most cases (5/7) indigo based dyes were found on wool, they were also used on silk. In all the cases, attribution was based on the detection of indigotin according to UV-Vis spectra (λmax = 238; 285; 330; 610 nm), associated with retention. Indigo based dyes were also the main source of blue in all previous studies dedicated to traditional textiles in Romanian collections [33–38]. Several plants are mentioned in the literature to contain indigotin precursors [52], *Indigofera species* and *Isatis tinctoria* (woad) being the most frequently discussed in relation to European textiles. According to the existing literature [53], with the instrumentation and knowledge available nowadays it is not possible to distinguish between these species, and neither between natural and synthetic indigo, which became available in 1882. However, as woad was cultivated in Europe for a long time and, under the name *drobșor*, was mentioned in the Romanian literature as dye source at the end of the 19th century, this remains the most likely indigo source.

Synthetic dyes from the triarylmethane group were used in almost half of the total number of samples to achieve a blue hue (5/12), in all but one being used on silk. Victoria Blue B (1883) was responsible for the colour in almost all cases (four/five), on wool and silk while alkali blue (1864) in the remaining silk item. Identification of Victoria Blue B was made based on the UV-Vis and MS data, λmax = 604 nm (MS+ 456), λmax = 616 nm (MS+ 470), correlated with retention, for the chromophores mentioned in the literature (Figure 4) [26]. This dye was also detected on rayon, in the decoration of a Saxon accessory, dated 1935 [36]. The other triarylmethane dye detected, alkali blue, was revealed according to the UV-Vis data, λmax = 596 nm, correlated with retention, as resulted from the analysis of reference dyes in the Schweppe collection.

3.5. Brown

Ellagic acid was identified in the two brown silk samples available for analysis, which suggests the use of tannins. Detection of ellagic acid was based on the UV-Vis and mass spectrometric data, λmax = 254, 366 nm, MS− 301. Iron was also present in these samples as revealed by XRF (Figure 5), which is in perfect correlation with the literature which mentions the use of iron salts and tannin-containing plants to dye brown and black. Tannins are polyphenols of vegetal origin, galls on *Quercus species*, *Alnus* barks *and Cotinus coggygria* leaves being among the most popular sources. Recipes to describe the use of tannin sources and iron represent 80% of the formulae for dyeing black and brown in a collection of dyeing recipes edited by the Romanian Academy in 1914 [10]. Alnus bark and green walnut husks and leaves are the most frequent tannin sources used.

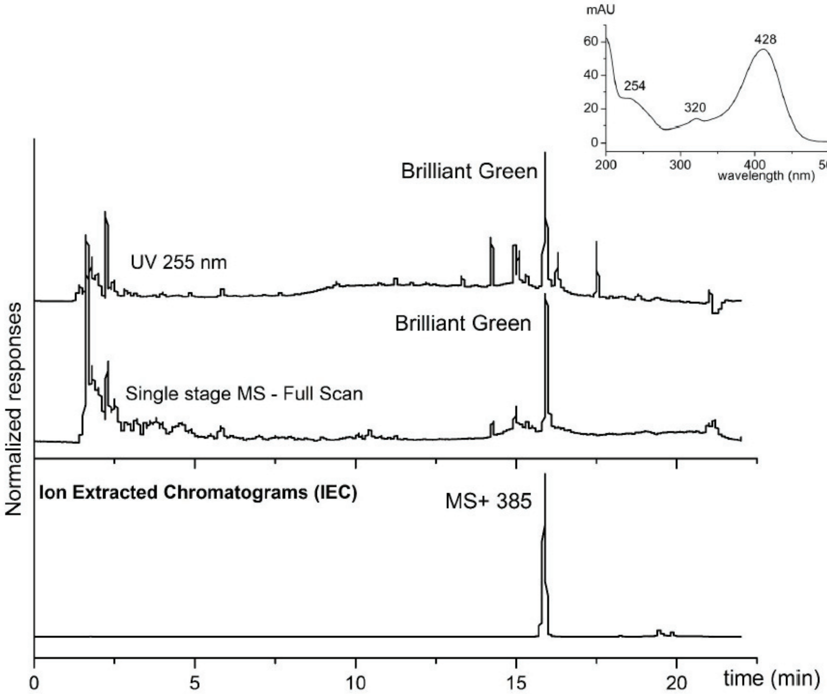

Figure 3. Image to support identification of Brilliant Green (1879) by LC-DAD-MS, in shirt inv. 3728 green silk shoulder decoration (last decade 19th–early 20th century, ASTRA Museum, Sibiu, Romania).

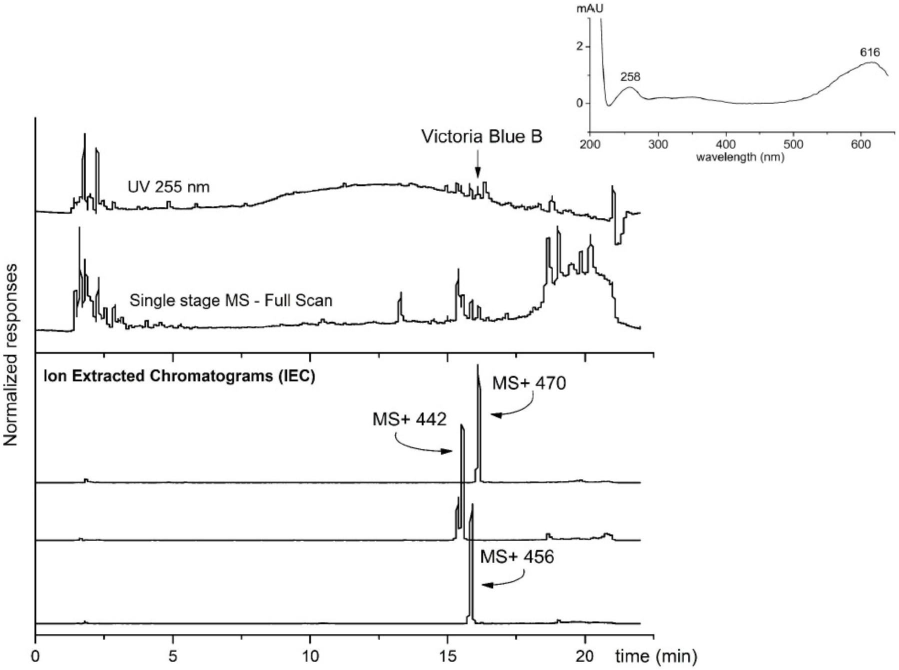

Figure 4. Image to support identification of Victoria Blue B (1883) by LC-DAD-MS, in shirt inv. 1429 blue silk shoulder decoration (early 20th century, Ethnographical Museum, Brasov, Romania).

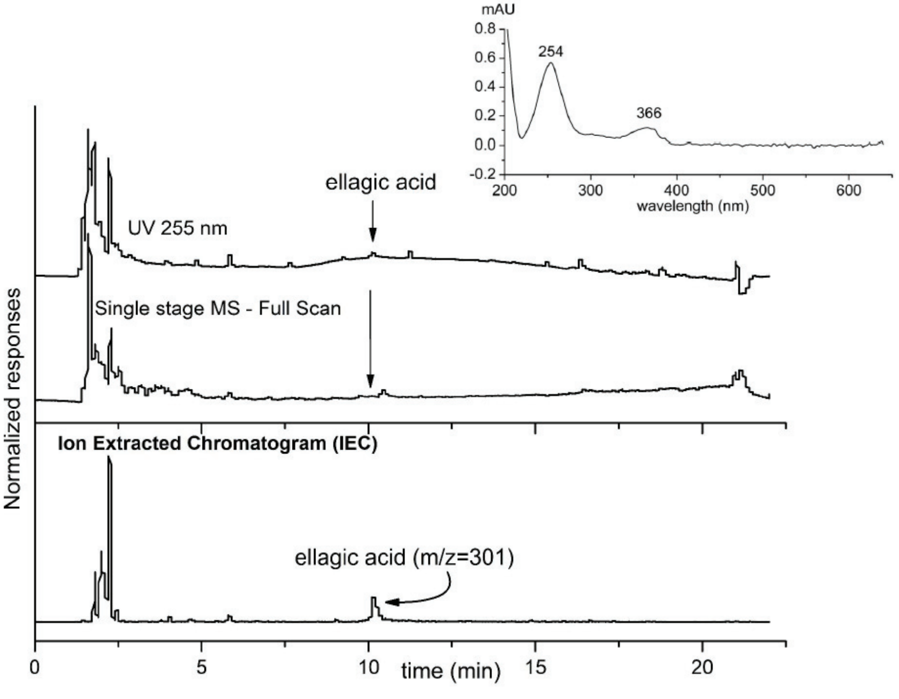

Figure 5. Image to support identification of tannins, based on the detection of ellagic acid by LC-DAD-MS, in shirt inv. 194 brown silk shoulder decoration (second half 19th century, ASTRA Museum, Sibiu, Romania).

4. Discussion and Conclusions

In total, 50 samples from 13 shirts dated between 1850 and 1930 from the same area in the very center of Romania were studied, in order to monitor transition from natural to the early synthetic dyes. The shirts are hand-made, produced in a small rural area of less than 50 km. A general view of the results, presented for each visual colour of the decoration yarn and correlated to the fiber (Table 4), illustrate the progressive change from natural dyes on wool to synthetic dyes on silk. Although this transition is fast, some phases are worth document, as these observations could be further used in the characterization of undocumented items. The oldest shirts studied, dated in the museum archives as end or late 19th century (inv. 1252, 1415, 6847, 194P, 169P and 20P), are decorated with natural dye sources such as madder, carminic acid based dyes, dyer's broom, sawwort, tannins and indigo dyes. Mineral pigments lead chromate and Prussian blue were added to enlarge the palette of colours with orange or black hues. However, if in the cases of shirts inv. 1252 and 1415, which should be considered the oldest in the study group, dyes are applied on wool (with the exception of lead chromate which is always on cotton), for inv. 169P and inv. 20P natural dyes are used on silk, and should be thus regarded as later. Shirts inv. 194P and inv. 6847, where natural dyes are applied either on wool or on silk, would be placed in between the two groups mentioned. The following step would be represented by shirts decorated with both natural and early synthetic dyes, such as inv. 210 and inv. 1422, applied on wool or on silk. Shirt inv. 3816, which in the museum archives is dated 1885, is worth particular attention, due to its very precise date and the large number of synthetic dyes detected, including two, auramine and Victoria Blue B, introduced (in 1883), two years before the given date. If we consider that, in the absence of written sources, museum dating is usually based on interviews at the moment objects enter the collections, it becomes debatable if 1885 is the correct date for shirt inv. 3816, and whether synthetic dyes (either as dyes or dyed yarns) were available in Transylvanian villages so quickly or, in another scenario, if the date of 1885 should be refined based on literature data regarding the exact moment when each of the dyes detected was traded (not available at the moment of the present study). A last step in the adoption of the early synthetic dyes would be represented by shirts inv. 177P, 3728, 6464 and 1429, dated 19th to 20th century or early 20th century, where a large number of early synthetic dyes are exclusively used, mostly on silk. The use of a natural dye source, carminic acid based dye, in combination with synthetic alizarin in a red silk decoration (shirt inv. 1429) would be seen as an exception, representative of the experiments which characterize the transition period. Apart for documentation and criteria for undocumented objects' characterization, the results obtained represent a valuable resource for the new movement of sewing-groups, interested in reproducing the old shirts as faithfully as possible, including the textile materials and dyes used.

LC-DAD and LC-DAD-MS were used to successfully notify the use of six natural dye sources and to identify 13 early synthetic dyes, many of them for the first time, in textiles from Romanian collections. With reference to the latter detections, their recognition comes to certify the procedure followed and the in-house database used, especially concerning what the analytical experiments collected from samples from the Helmut Schweppe collection. LC-DAD was proved as a useful tool for dye identification in most cases. However, information provided by the mass spectrometer detector, placed in line with the diode array, significantly improves dyes and biological source attribution. These benefits come, on the one hand, from the mass spectrometer's high sensitivity, and on the other from the complementarity of the two detectors. The first attribute will have consequences in better detection of minor compounds and the second provides more identification criteria and confident recognition of the dyes used.

Based on the case study presented, transition from natural to the early synthetic dyes in the second half of the 19th century is for the first time documented, based on analytical arguments. Adoption of the early synthetic dyes was very fast, the high enthusiasm for brighter colours and the larger variety of hues resulting in the complete replacement of the natural sources by the first decades of the 20th century.

Table 4. General view on the results obtained to illustrate, for each color, the chronology of the dyes used from the end of the 19th to the early 20th century. For abbreviation, see Tables 1 and 2. The fibers used are given in brackets (C—cotton, W—wool, S—silk). Date attribution is based on the museum archives.

	Inv. 1252 (End 19)	**Inv. 1415 (End 19)**	**Inv. 194P (Late 19)**	**Inv. 6847 (Late 19)**	**Inv. 169P (Late 19)**	**Inv. 20P (Late 19)**	**Inv. 210 (Late 19)**	**Inv. 1422 (19–20)**	**Inv. 3816 1885**	**Inv. 177 (19–20)**	**Inv. 3728 (19–20)**	**Inv. 6464 (19–20)**	**Inv. 1429 (Early 20)**
red	Mad (W)	Mad (W)	Mad (W)	Mad (W)	ca (S)	ca (S)	ca (S)	Mad (W) Al (C) (1871)	ca (S)	Me-Vio (W)	Ora GG (1878) (S)	Rhod (1887) + Saf T (1859) (S)	Fuch (1856) (S) Al (1871) + ca (C)
pink/violet			ca (S)			ca (S)	Me-Vio (1861) (S)	Rhod (1887) (S)		Rhod (1887) (S)	Fuch Me-Vio (S)	Rhod (1887) (S)	Rhod (1887) (W)
orange	PbCrO4 (C)			PbCrO4 (C)					Aur (S) (1883)			Uran (S) (1871)	
yellow	-	-		PbCrO4 (C)		DB + Saw (S)		DB (W)	Pic Ac (1771) (S)				Azo Fl (1880) (S)
blue	Ind (W)	Ind (W)	Ind (W)	Ind (W)	Ind (S)	Ind (S)		Ind (W)	Vic B (1883) (S) Alkali Blue (1864)		Vic B (1883) (S)	Vic B (1883) (S)	Vic B (1883) (S)
green	DB Cu (W)	DB Ind (W)	DB Ind (W)			lu + Ind (S)			Bri Gr (1879) (W)		Bri Gr (1879) (S)		
brown/black				tan (S)	tan Fe(S)	ca + Pr Blue (S)							

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Article

A First Approach to the Study of Winsor & Newton's 19th-Century Manufacture of Madder Red Lake Pigments

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Abstract: This paper focuses on the first investigation of the 19th-century manufacture of red lake pigments obtained from madder by Winsor & Newton (W&N), prominent artists' colourman at that time. The first approach to their manufacture was carried out by studying the madder entries of the company's book P1, found in the W&N 19th Century Archive Database. Eleven production records were discovered under names such as Rose Madder, Madder Carmine, Madder Lake and Madder Rose. Three main methods of synthesis were identified and reproduced, revealing three main steps: washing of the madder roots (*Rubia tinctorum* L.); extraction in acid media and complexation with Al^{3+} using alum; and precipitation by the addition of salts such as ammonium carbonate and sodium borate. The syntheses were followed by UV-VIS spectroscopy, and the pigments were further characterised by colourimetry, Energy-Dispersive X-Ray Fluorescence Spectrometry (XRF), Fourier Transform Infrared Spectroscopy (FTIR) and High-Performance Liquid Chromatography-Diode Array Detector (HPLC-DAD). They all exhibited a rose hue in a highly insoluble aluminate matrix. Although the dye extraction was incomplete, alizarin, purpurin and pseudopurpurin were identified. An analytical comparison with a Rose Madder 19th-century oil paint tube was also performed by micro-FTIR and microspectrofluorimetry. This work intends to be foundational to a systematic study of the W&N's 19th-century madder colours aiming to contribute new knowledge towards their identification and preservation in heritage objects.

Keywords: madder; 19th-century manufacture; Winsor & Newton; multi-analytical characterisation; heritage preservation

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1. Introduction

Since antiquity, madder has been one of the most important sources of red colours. Used as dyes and pigments, these colours have been found in treasured artworks [1–4]. The first reference to its use as a dye dates back to the seventh century BC found in a neo-Babylonian tablet kept at the British Museum. The earliest it has been identified as a pigment was also in ancient objects such as Cypriot pottery of the 8th–7th century BC [1,3].

Madder colours are extracted from the roots of plants from the Rubiaceae family, but the most relevant species for dyeing are *Rubia peregrina* L. (wild plants) and *Rubia tinctorum* L. (cultivated plants), the latter being the most used for dyeing in western Europe from the Middle Ages to the 19th century [1–7]. Their composition differs quantitatively but qualitatively is based on anthraquinone compounds in the form of glycosides and respective aglycones (Figure 1). The main anthraquinones responsible for the colour are alizarin (1,2-dihydroxyanthraquinone), followed by purpurin (1,2,4-trihydroxyanthraquinone) and pseudopurpurin (1,3,4-trihydroxyanthraquinone-2-carboxylic acid) (Figure 1) [1–3].

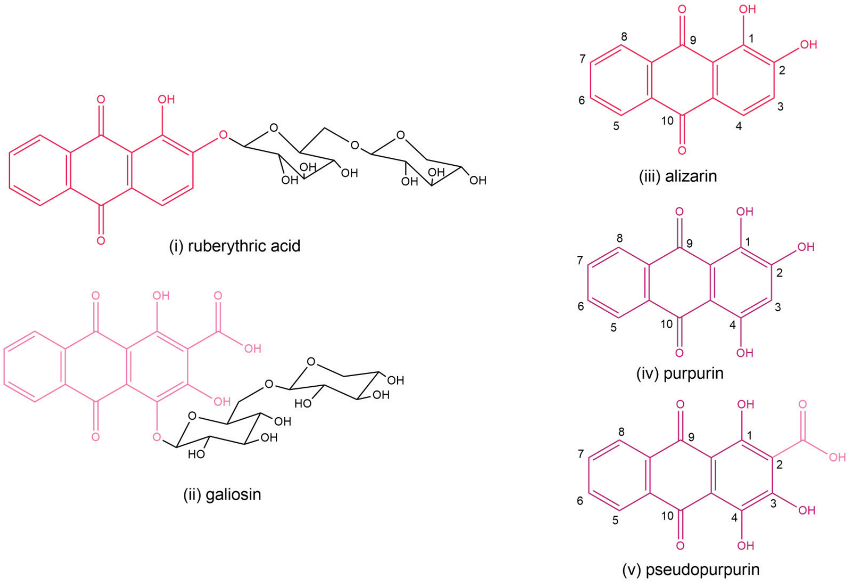

Figure 1. Molecular structures of the principal components found in madder roots.

Madder lake pigments are obtained by precipitation with salts such as alum ($AlK(SO_4)_2 \cdot 12H_2O$), forming aluminium (Al^{3+}) coordination complexes that are yet to be fully identified [8,9]. The proposals follow the model by Kiel and Heertjes, in which Al^{3+} coordinates to two alizarin ligands through the 9-C=O and the 1-OH, and the model by Wunderlich, in which Al^{3+} coordinates to two alizarin ligands through the catechol of hydroxyl groups at positions 1 and 2, and calcium ions (Ca^{2+}) close the structure by coordinating two alizarin ligands through the 9-C=O and the 1-OH [10–12]. Identification of madder lake pigments is a well-known challenge in the field of conservation, not only due to their complex composition but also because of the low dye concentrations in the pigment formulation as well as the degradation mechanisms that may occur. The latter can cause undesirable changes in the heritage objects' original visual appearance [8,13–15]. Nevertheless, great efforts have been made to improve their detection in heritage objects, including by in situ techniques such as Raman Microscopy, Fibre Optics Reflectance Spectroscopy (FORS) and Hyperspectral Imaging and Microspectrofluorimetry [16–21]; however, unequivocal identification is still only possible by fingerprinting techniques using micro-samples such as High-Performance Liquid Chromatography-Diode Array Detector (HPLC-DAD) and Surface-enhanced Raman spectroscopy (SERS) [22–24].

Madder colours can range from orange through different shades of red to purple and brown, depending on the manufacturing conditions, such as the pH of extraction, pH of precipitation and different complexing agents and additives [1,2,5,6,25]. Although much documentary evidence is found for their dyeing processes throughout history, there is a knowledge gap concerning pigment production. Furthermore, it was common to use madder lakes prepared with the dye extracted from shearings of textiles [1,2,5,7,25]. This paradigm changed in the 19th century when remarkable developments in the manufacture of madder lake pigments were accomplished and enabled their industrial production [6,7,26]. However, their production was considered very expensive, which unfortunately led to their adulteration by adding other colourants and/or cheaper materials [26,27]. Nonetheless, even after the discovery of synthetic substitutes, madder colours continued to be manufactured and sold by Winsor & Newton (W&N), a leading paint manufacturer of the 19th century [27]. Table 1 presents the colour names associated with madder red lake pigments, which appeared in W&N's catalogues throughout the 19th century [27].

Table 1. Availability of colours associated with madder red lake pigments in powder and oil paint tubes throughout the 19th century from W&N, adapted from L. Carlyle, 2001 [27].

W&N 19th-c. Madder Red Colours	Oil Paint Tube		Powder	
	First Appearance	Last Appearance	First Appearance	Last Appearance
Pink Madder	1835	-	1835 [1]	-
Rose Madder	1835	-	1835 [1]	-
Madder Carmine	c. 1840	-	c. 1840	-
Madder Lake	c. 1840 [2]	-	not in powder	
Extra Madder Carmine Deep	c. 1861	c. 1861	not in powder	
Extra Madder Carmine Bright	c. 1861	-	1864	-
Extra Madder Carmine	1864	-	1864	-
Scarlet Madder	1886	-	1892	-
Crimson Madder	1886	-	not in powder	
Rose Madder (pink shade)	1900	-	not in powder	
Pink Madder Lake	not in oil		c. 1840	c. 1849
Rose Madder Lake	not in oil		c. 1840	c. 1849

[1] Not listed again until 1851. [2] Not listed again until 1861.

This work resulted from the first investigation of the madder records found on the W&N 19th century Archive Database, enabling a unique insight into the company's workshop practices using madder. The W&N 19th century Archive Database is a fundamental primary source of information on the commercial availability and preparation of 19th-century artists' materials. Its study has demonstrated that W&N was committed to supplying the most durable products possible [28–32]. This investigation is being carried out in the framework of two funded projects, namely "REDiscovering madder colours: Science & Art for the preservation and creation of cultural heritage" (2022.02909.PTDC) and "Magic Lantern—Study, Safeguard, Uses and Reuses in 19th-Century Portugal" (PTDC/ART-PER/1702/2021). Their joint objective is to improve the identification of madder colours in complex matrices as those found in heritage objects such as historical hand-painted magic lantern glass slides. Another goal is to establish a correlation between the manufacturing conditions (e.g., pH of precipitation, different complexing agents and additives) and the stability of madder colours towards their preservation.

2. Materials and Methods

2.1. Materials

Madder roots and gum arabic were purchased from Kremer Pigmente®. Potassium aluminium sulfate ($AlK(SO_4)_2 \cdot 12H_2O$) and sulfuric acid (H_2SO_4) were purchased from Fluka®, ammonium carbonate ($(NH_4)_2CO_3$) from Alfa Aesar® and sodium borate ($Na_2B_4O_7 \cdot 10H_2O$) from Sigma-Aldrich®. Alizarin and purpurin analytical standards were purchased from Merck® and Aldrich®, respectively. Pseudopurpurin was isolated following the protocol described by V. Daniels [33]; the analysed final product presented a purity of 80–87%, with purpurin also being detected. HPLC-DAD analyses of the latter compounds may be seen in Figure A1.

For the HPLC-DAD extractions and analyses, all solvents were HPLC grade. Millipore ultrapure water was used.

2.2. Synthesis Methods for Madder Lake Pigments

Investigation of the W&N 19th century Archive Database was focused on the sub-topic madder on the manuscript book P1 as further detailed below. Eleven production records pertaining to the manufacture of madder red lake pigments were discovered; see Table A1. It was possible to organise eight production records in three main representative formulations: Rose Madder, Madder Lake and Madder Rose, whose synthesis methods are described in Table 2.

Table 2. Formulation name and code of the synthesis methods of madder red lake pigments.

Formulation Name | Code	Synthesis Methods
Madder Rose | MR	1. Wash 5 g of madder powder with 100 mL of water (repeat 5 times); 2. Dissolve 8.57 g of alum in 30 mL of hot water (near boiling); 3. Pour the above solution into the madder roots; 4. Decant the supernatant liquor into 88 mL of distilled water; 5. Slowly add an aqueous solution of carbonate of ammonia (1.2 M) and stir occasionally; 6. Filter the precipitate.
Madder Lake | ML	1. Let 5 g of madder powder rest in 100 mL of water for 1 h; 2. Decant the supernatant and let the madder rest in 100 mL of water for 30 min; 3. Decant the supernatant and wash the madder 3 times; 4. Dissolve 10.48 g of alum in 30 mL of hot water (80 °C); 5. Run through the above solution into the madder roots placed in a cotton filter bag and collect the red extract; 6. To the red extract, add immediately, one at a time, three solutions of sodium borate: 1.9 g in 10 mL, 0.24 g in 5 mL and 0.06 g in 2.5 mL; 7. Filter the precipitate.
Rose Madder | RM	1. Prepare a solution of 0.5 mL of sulfuric acid in 4 mL of water; 2. Pour the solution into the madder roots after step 5 of the Madder Lake recipe. 3. After 30 days, add 16 mL of boiling water; 4. Add immediately, one at a time, three solutions of sodium borate: 0.5 g in 2.5 mL, 0.06 g in 1.25 mL and 0.03 g in 1.25 mL; 5. Filter the precipitate.

The above materials were interpreted based on previous works [28–32]. As most production records call for 28 to 42 lbs (12.7 to 19 kg) of madder, all materials were scaled down from industrial to laboratory scale, and quantities in British measures were converted to SI units [27]. All madder red lake pigments produced were thoroughly washed with water, air-dried and then ground to a powder.

pH measurements throughout the syntheses were carried out with a Sartorius Docu-pH Meter. Calibration was performed with pH 4 and 7 buffer solutions from Panreac.

2.3. Analytical Equipment and Experimental Conditions

2.3.1. Colourimetry

For measuring colour, a handheld spectrophotometer Lovibond® TR 520 with a diffused illumination system, 8° viewing angle, and a 48 mm integrating sphere was used. The measuring aperture was 8 mm in diameter. Equipment calibration was performed with white and black references. Colour coordinates were calculated defining the D65 illuminant and the 10° observer. The colour data are presented in the CIE-Lab 1976 system. In the Lab cartesian system, L*, relative brightness, is represented by the z-axis. Variations in relative brightness range from white (L* = 100) to black (L* = 0). The (a*, b*) pair represents the hue of the object. The red/green y-axis plots a* ranging from negative values (green) to positive (red). The yellow/blue x-axis reports b* going from negative (blue) to positive numbers (yellow).

The colour was measured on paint references prepared with gum arabic (10% solution). The lake pigments were first ground with pure water and then ground with the gum arabic solution. The paints were applied on filter paper with a paintbrush and allowed to dry.

2.3.2. Energy-Dispersive X-ray Fluorescence Spectrometry (XRF)

XRF analyses were performed on an ArtTAX spectrometer of Intax GmbH, equipped with a molybdenum (Mo) anode and an Xflash detector refrigerated by the Peltier effect (Sidrift). The primary X-ray beam is focused to a diameter of 70 µm using polycapillary X-ray mini lens. The characteristic X-rays emitted by the sample are detected by a silicon drift electro-thermally cooled detector with a resolution of 160 eV at Mn-Kα. The experimental parameters used were 40 kV of voltage, 300 µA of intensity and 300 s of acquisition time. Measurements were carried out in a helium atmosphere to enable the detection of aluminium (Al).

2.3.3. UV-VIS Absorption Spectroscopy

The UV-VIS absorption spectra were recorded on a Cary 100 Bio UV-VIS Varian spectrophotometer, at room temperature. The spectra were acquired in the range 200–800 nm, with an average scan time of 0.1 s/nm and scan rate of 600 nm/min.

UV-VIS absorption spectra were acquired for the solutions obtained throughout the syntheses in poly(methyl methacrylate) cuvettes.

2.3.4. Fibre Optics Reflectance Spectroscopy (FORS)

Reflectance spectra were acquired with Ocean Optics equipment composed of a single-beam dispersive fibre optic spectrometer (model MAYA 2000 PRO) equipped with 2048 linear silicon CCD array detector (Hamamatsu). MAYA 2000 PRO has a spectral response from 200 nm to 1050 nm. The illumination is an Ocean Optics HL-2000-HP with 20 Watt halogen light source in a single optical path covering the 360–2400 nm range. Spectra were obtained with an integration time of 8 ms and 15 scans to average. The measuring head, in a 45°/45° (illumination/acquisition angles) configuration, gives a diameter of analysis of about 2 mm. As reference, a Spectralon® standard was used. FORS spectra were acquired in reflectance but are presented as apparent absorbance, A′ = Log10(1/R).

FORS analysis was performed on the paint references described above.

2.3.5. High-Performance Liquid Chromatography with a Diode Array Detector (HPLC-DAD)

HPLC-DAD analysis of the madder roots was carried out by placing 0.01 g of the ground material with 1 mL of 1:1 (*v*/*v*) solution of methanol:water and heating in a water bath at 80 °C for 30 min. Then the extract was centrifuged for 10 min, and the supernatant liquid was filtered through a 0.45µm filter [3]. Its chromatographic profile may be seen in Figure A2.

The extraction of the dye molecules from the madder lake pigments was revealed to be very challenging as they are highly insoluble. Several extraction methods were tried. In all experiments, c. 2 mg of pigment powder was used. The one used in this work resulted from adding 300 µL of 1:1 (*v*/*v*) solution of methanol:HCl to the pigment sample and heated in an ultrasonic bath at 60 °C for 1 h. Then the extract was evaporated under nitrogen flow, and the residue was dissolved in 200 µL of methanol. Although this method showed better results until the present moment, the obtained results are far from the desired since the complete extraction of the free dye molecules was not possible, and further optimisation is needed. The other extraction methods experimented with, showing worst results, were (i) 1 mL of solution of oxalic acid (0.2 M):methanol:acetone:water (0.1:3:3:4, *v:v*) added to the pigment sample and heated in a water bath at 60 °C for 30 min [32]; (ii) two consecutive extractions of the pigment sample: a first one with 200 µL of dimethylformamide:methanol (2:1, *v*/*v*) heated in a water bath at 80 °C for 10 min, after which the extract is reserved, followed by a second one with 200 µL of solution of oxalic acid (0.5 M):methanol:acetone:water (0.1:3:3:4, *v:v*) heated in a water bath at 80 °C for 15 min, after which the residue is evaporated under nitrogen flow and dissolved in 200 µL of methanol:water (1:2, *v*/*v*) plus the extract from the prior DMF extraction [3]; and (iii) 300 µL of methanol:HCl (30/1, *v*/*v*) and (iv) 300 µL of methanol:HCl (70/30, *v*/*v*) added to the pigment sample and heated in an ultrasonic bath at 60 °C for 1 h [34].

The HPLC-DAD analysis data were obtained by the Analytical Laboratory LAQV/REQUIMTE—Chemistry Department, FCT | NOVA—Portugal. The analysis was carried out in a Dionex Summit (Sunnyvale, CA, USA) HPLC-DAD system with a DAD Dionex Ultimate 1000, an autosampler and a gradient pump. The sample separations were performed in a reversed-phase column, Phenomenex Luna C18, with a 5 µm particle size column (250 mm × 4.6 mm), with a 1 mL/min flow rate with the column at a constant temperature of 30 °C. The samples were injected with a 20 µL loop. The elution gradient consisted of two solvents, A: 99.9% acetonitrile + 0.1% trifluoroacetic acid (*v*/*v*) and B: 99.9% water + 0.1% trifluoroacetic acid (*v*/*v*). An elution program was used with a linear increase in the ratio of A to B from 5:95 to 30:70 over 25 min, followed by a second linear gradient to 100:0 until 40 min of run and then 10 min of isocratic 100% A (re-equilibration time). The eluted peaks were monitored at 430 nm and 500 nm.

2.3.6. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared analyses were carried out with a Nicolet Nexus spectrophotometer coupled to a Continuμm microscope (15x objective) with an MCT-A detector cooled by liquid nitrogen. The pigments were analysed in transmission mode between 4000 and 650 cm^{-1}, with a resolution of 8 cm^{-1} and 128 scans, using a Thermo diamond anvil compression cell. The spectra are shown here as acquired, without corrections or any further manipulations, except for the removal of the CO_2 absorption at ca. 2300–2400 cm^{-1}.

2.3.7. Microspectrofluorimetry

Fluorescence excitation and emission spectra were recorded on a Jobin-Yvon/Horiba SPEX Fluorog 3-2.2 spectrofluorimeter hyphened to an Olympus BX51 M confocal microscope, with spatial resolution controlled with a multiple-pinhole turret, corresponding to a minimum 2 μm and maximum 60 μm spot, with 50× objective. Fluorescence spectra were corrected for the wavelength response of the system. Beam splitting is obtained with standard dichroic filters mounted at 45°; they are located in a two-place filter holder. Standard dichroic filters of 500 and 600 nm were used to collect the emission and excitation spectra, respectively. Emission spectra were acquired exciting at 490 nm, and excitation spectra were performed collecting the signal at 610 or 620 nm. Both were acquired in a 30 lm spot (pinhole 8) and the following slit set: emission slits = 3/3/3 mm, and excitation slits = 5/3/0.8 mm. The optimisation of the signal, through mirror alignment in the optic pathway of the microscope, was performed for all pinhole apertures following the manufacturer's instructions. Spectra were collected after focusing on the sample (eye view) followed by signal intensity optimisation (detector reading). Emission and excitation spectra were acquired in the same spot whenever possible.

Microspectrofluorimetry analysis was performed on the paint references described above.

3. Results and Discussion

3.1. Research in the W&N 19th Century Archive Database

An initial assessment of the significance given to madder red/purple lakes by W&N in the 19th century can be made by analysing all sub-topics under those terms (Figure 2). As previously reported by Vitorino et al., there are more than eight thousand database records on red/purple lake pigments [29]. From these, 35% pertain to madder. However, it is relevant to note that W&N also had access to the manuscript books by George Field (1777–1854), one of the most important colour chemists in the 19th century, who greatly influenced W&N pigment manufacture, especially of madder red lake pigments [26,27]. Field's books are not included in the W&N archive database.

Its relevance is also evident if we consider that, at the time the W&N Archive Database was created in 2006 [35], the majority of the madder records were restricted due to their commercial sensitivity. Recently, this restriction has been removed, prompting the beginning of this research.

Due to the high number of database records, this first approach to studying W&N's 19th-century manufacture of madder red lake pigments was carried out by analysing the madder entries of the manuscript book P1. This book belonged to Arthur Henry Newton, son of W&N's founder Henry Charles Newton, and it is primarily dedicated to pigment manufacture between 1846 and 1858. It includes several comments on the production records, significantly assisting with their laboratory reproduction, as will be shown below. Furthermore, he was well aware of the potential of madder as he wrote: "*The root of the Rubia Tinctoria or madder plant, so valuable for the solidity of its colours in dying, is invested* *naturally with tingent matter in a series of states, and of colours from the lightest yellow, on the one extreme to the deepest purple (. . .).*" (URC P1P022AL01).

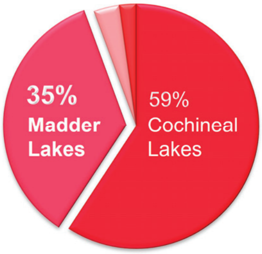

Figure 2. Distribution of the red/pink lakes in the pigment sub-topics from W&N's database; 59% of cochineal lakes [29], 35% of madder lakes, 2% of lac lakes and 4% of other lake pigments, mostly of unidentified dye sources.

In book P1, there are 35 database entries under the sub-topic madder, of which 29 correspond to the pigment manufacture of madder reds (11), browns (10), purples (5) and yellows (3). The 11 database records on the manufacture of madder red lake pigments appear under several names, such as Madder Rose, Madder Lake, Rose Madder and Madder Carmine (Table A1). These can be related to W&N's 19th-century trade names (Table 1).

Eight production records fall into three main representative formulations, hereafter referred to as Rose Madder, Madder Lake and Madder Rose, as shown in Table 2. The other three production records correspond to different synthesis methods and were left out, namely, a recipe for Liquid Madder Lake (P1P030AL03), and the other two are experiments for a Crimson Madder (P1P205AL12) and a Madder with lime water (P1P299AL01).

It is important to emphasise that in this preliminary work, with a limited number of records, it is not possible to establish a correlation between the identified formulations and W&N's 19th-century products. This can only be achieved by a systematic study of all W&N's records on the manufacture of madder colours and an analytical comparison with W&N's historical materials.

3.2. Main Steps for the W&N's 19th-Century Manufacture of Madder Red Lake Pigments

In Figure 3, we present the three essential steps of the three main methods of synthesis identified: (i) washing of the ground madder roots (*Rubia tinctorum* L.); (ii) extraction in acid media and complexation with Al^{3+} using alum ($AlK(SO_4)_2 \cdot 12H_2O$); and (iii) precipitation by the addition of salts such as ammonium carbonate ($(NH_4)_2CO_3$) and sodium borate ($Na_2B_4O_7 \cdot 10H_2O$).

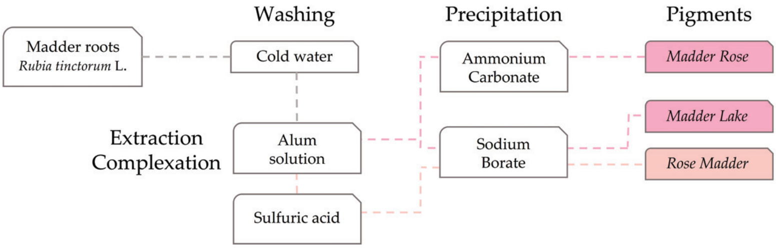

Figure 3. Scheme of the main steps of W&N's 19th-century manufacture of madder red lake pigments.

The importance of washing the madder roots is clear throughout the records, as it is stated: "*Take 7lbs [or any quantity] of the finest Crop Madder powder, infuse and perfectly diffuse it in any quantity of pure, cold water, which decant;—repeat the same with a fresh quantity of water—again and again,—there being no danger of repeating such lavations too often; the first condition* *toward a perfect Rose—color being the entirely removing all the dark brown and yellow-colors soluble in cold water from the root*" (URC P1P025AL01), and "*In fact the washing of the Madder Root with repeated water is simply getting rid of the fine fecula & dirty matter that would otherwise spoil the brilliance of the madder red extract*" (URC P1P114AL13). Two washing methods were found, one for Madder Rose, in which we washed the ground madder roots five times, and another one for Madder Lake and Rose Madder, in which the water is left with the madder for longer periods of time. HPLC-DAD analyses reveal that this process reduces the alizarin content (Figure 4a), and XRF results show that the presence of elements calcium (Ca) and iron (Fe) is also significantly reduced when compared with the final product (Figure 4b). The pH values of the water washings were always between 6 and 7.

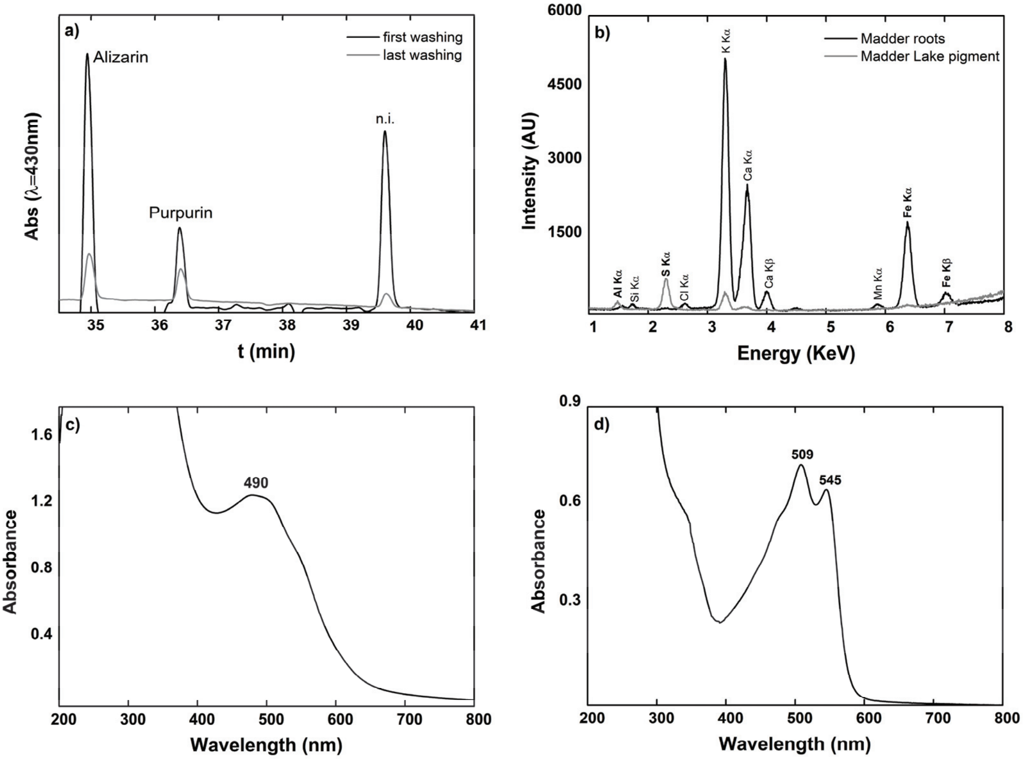

Figure 4. (**a**) Chromatograms at 430 nm of solutions of the first and last washing of the production of Madder Lake pigment (n.i.—non-identified); (**b**) XRF spectra of the madder roots and a Madder Lake pigment (ML3); (**c**) UV-VIS spectrum of the solution of the madder roots washing; and (**d**) UV-VIS spectrum of the madder solution after the addition of alum (madder red extract).

After washing, colour extraction is performed in acid media by adding a concentrated hot solution of alum ($AlK(SO_4)_2 \cdot 12H_2O$), which decreases the pH to 2-3. This favours the extraction of pseudopurpurin [33]. Regarding this step, there is also reference that "*Attention to this is expedient to success, the aluminous salt taking up spontaneously a moderate proportion of color only;—precipitated in which state it affords but a comparatively weak pigment-but as the alum crystallises without color, the color it thus gives up is retained in chemical combination in the tincture affording all the richness of color required, at the same time that the beauty and transparency of the pigment is improved by the spontaneous precipitation of terrene impurities*" (URC P1P025AL01). In Madder Rose, alum is added directly to the madder roots, and the madder red extract is afterwards decanted. In Madder Lake and Rose Madder, the alum solution is poured through a cotton filter bag where the madder roots are, and the red extract is collected in a recipient below the filter. However, for the Rose Madder, this step is still to be better understood as there is the extra addition of sulfuric acid (H_2SO_4), further lowering the pH. In this work, this was done to the madder roots after the alum was run through, but as will be shown below, the resulting pigments do not correspond to what was expected: "*a bright scarlet tinted & transp' madder rose of excellent strenght in oil*" (URC P1P114AL13). Furthermore, precipitation did not always occur, probably due to the low pH. Ingredients such as sulfuric acid are always more challenging to work with when reproducing historical recipes, as their purity and quantity conversion can significantly influence the processes and final products [28,29]. Further experiments must be conducted to determine the role of sulfuric acid in producing W&N's madder reds.

Figure 4c,d show the UV-VIS spectra of the madder roots in water before and after alum extraction, respectively, demonstrating that extraction and complexation with aluminium (Al^{3+}) occur in one single step. The UV-VIS spectrum of the madder red extract is very similar to that of purpurin and/or pseudopurpurin complexes with Al^{3+} presenting maxima at 509 nm and 545 nm [9,36].

The final step is the precipitation of the madder lake pigments by adding salts such as ammonium carbonate ($(NH_4)_2CO_3$) and sodium borate ($Na_2B_4O_7 \cdot 10H_2O$) to the madder red extracts. The first is only used for Madder Rose, and sodium borate is used for Madder Lake and Rose Madder. The final pH, obtained after precipitation, was always around 4, except for one replication of Rose Madder, where a higher quantity of sodium borate had to be used for precipitation to occur, resulting in a final pH of 6.

The records show that the Madder Rose lake pigments were "*of a colour literally as beautiful as the rose, and surpassing in truth and purity of hue all other red pigments*" (URC P1P025AL01). On the other hand, Madder Lake formulations may be revealed to be "*not so strong as might have been expected, but was very bright having a scarlety pink colour*" (URC P1P127AL05).

Interestingly, contrary to what was found for W&N's cochineal formulations, no reference to the use of extenders such as calcium carbonate ($CaCO_3$) or calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) was found [29]. The complete study of all production records in the future will allow us to infer whether this is a characteristic of W&N's 19th-century madder colours.

3.3. Characterisation of the Madder Red Lake Pigments

All formulations were repeated three times to assess reproducibility. Each madder lake pigment produced was analysed by colourimetry, UV-VIS Fibre Optic Reflectance Spectroscopy (FORS), Energy Dispersive X-Ray Fluorescence Spectrometry (XRF), Fourier Transform Infrared Spectroscopy (FTIR) and High-Performance Liquid Chromatography-Diode Array Detector (HPLC-DAD). A summary of the results is presented in Table 3.

Table 3. Summary of the analytical results obtained by colourimetry, FORS, XRF, FTIR and HPLC-DAD for all madder lake pigments produced following the protocols described in Table 2.

Formulation Name	Code	L*	a*	b*	FORS	XRF	FTIR	HPLC-DAD
Madder Rose	MR1	78.80 ± 0.35	32.87 ± 0.25	2.81 ± 0.08	511, 549 (sh)	S, K, Al	Aluminate	1. Pseudopurpurin 2. Alizarin 3. Purpurin
	MR2	78.82 ± 0.61	31.59 ± 0.58	3.00 ± 0.21	512, 546 (sh)			
	MR3	82.81 ± 0.46	24.79 ± 0.28	2.45 ± 0.24	513, 549 (sh)			
Madder Lake	ML1	85.61 ± 0.75	23.38 ± 1.37	5.37 ± 0.24	511, 547 (sh)	S, K, Al		
	ML2	83.48 ± 0.53	23.21 ± 1.31	4.19 ± 0.21	512, 547 (sh)			
	ML3	85.12 ± 1.04	20.60 ± 1.75	3.69 ± 0.06	510, 547 (sh)			
Rose Madder	RM1	92.24 ± 0.07	5.98 ± 0.12	6.86 ± 0.06	508	S, K, Al, Fe		
	RM2	86.96 ± 1.03	16.18 ± 1.38	4.95 ± 0.1	504, 538 (sh)			
	RM3	89.67 ± 0.32	8.97 ± 0.4	7.61 ± 0.1	505, 538 (sh)			

As seen in Table 3 and Figure 5a, all madder lake pigments display a pink hue. Madder Rose and Madder Lake formulations were reproducible as their colour coordinates (a* and b*) tend to cluster (Figure 5a). It is also perceptible that Madder Rose lake pigments are redder, with the highest a* values. On the other hand, as noted before, reproducibility was not verified for the Rose Madder formulations, which are found to be less red (lower a* value) and more yellow (higher b* value), still exhibiting signs of the presence of iron (Fe) from the madder roots.

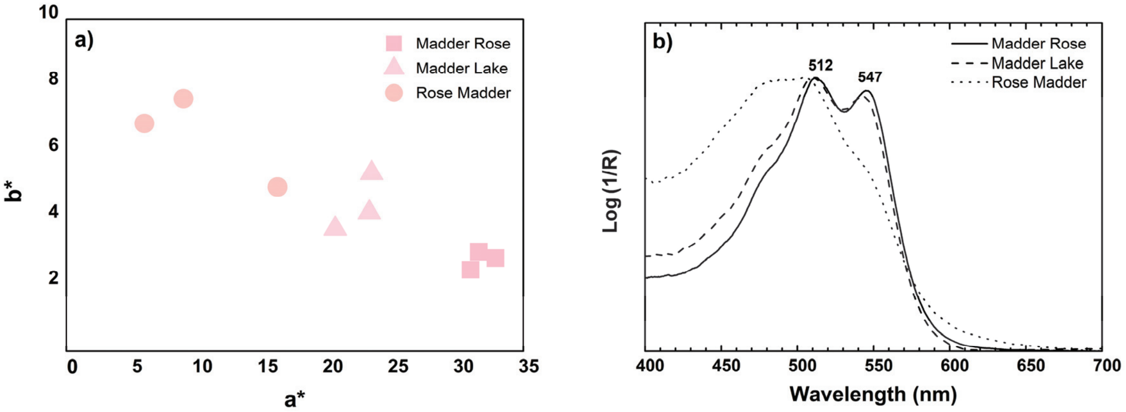

Figure 5. (**a**) Colour coordinates (a* and b*) for the madder lake pigments detailed in Table 3 and (**b**) representative absorbance spectra of the madder lake pigments. These analyses were carried out in samples painted with gum arabic on filter paper.

Figure 5b shows representative FORS spectra of all three formulations. Those of Madder Rose and Madder Lake are similar in shape and maxima around 512 nm and 547 nm, also observed in Al^{3+}-purpurin and pseudopurpurin complexes [9,36]. The FORS spectrum of Rose Madder is shifted to lower wavelengths, with the shape and maxima at 508 nm, similar to that of Al^{3+}-alizarin complexes [9,36].

Infrared analyses of most madder lake pigments (except for the RM2 lake pigment, whose infrared spectrum may be consulted in Figure A3) reveal the presence of an amorphous aluminate polymeric matrix with characteristic bands at 3343 cm^{-1} attributed to the stretching vibration of $-OH$ (broad band), at 1114 cm^{-1} assigned to the bending vibration of Al-OH, at 1644 cm^{-1} corresponding to the bending vibration of coordinated water and at 983 cm^{-1} assigned to the stretching vibration of Al-O-Al. There is also the overlap of the stretching vibration of SO_4^{2-} at 1114 cm^{-1} (Figure 6a) [37]. Additional bands of weak to medium intensities in the region of the asymmetric stretching vibration of CO_3^{2-} between 1500 and 1400 cm^{-1} and of the asymmetric stretching vibration of B-O between 1400 and 1300 cm^{-1} are also observed. These are related to the use of the ingredients ammonium carbonate for the Madder Rose formulations and sodium borate for the Madder Lake and Rose Madder lake pigments. No infrared bands of the Al^{3+}-anthraquinone complexes were detected.

As mentioned above, the madder lake pigments were highly insoluble, making the dye extraction for HPLC-DAD analyses complicated; details can be found in the experimental part. Although it was possible to detect pseudopurpurin, alizarin and purpurin (HPLC-DAD data of the dye molecules in Figure A1), as shown in Figure 6b, a signal at the beginning of the run was observed corresponding to Al^{3+}-anthraquinone complexes exiting the column, indicating that the dye extraction was incomplete. This interferes with any quantitative analysis that could be carried out in this work. Optimisation of the dye extraction method of these madder lake pigments will be pursued in the future.

3.4. Comparison with a W&N 19th-Century Oil Paint Tube

An analytical comparison was made with a late 19th-century W&N oil paint tube labelled "Rose Madder" (dated according to the appearance and data on the label). As shown in Figure 7a, its infrared spectrum presents a direct match with a Madder Rose lake pigment reconstruction, exhibiting the infrared fingerprint of an aluminate polymeric compound, as described above, in an oil binder, identified by its characteristic bands at 2928 cm^{-1} and 2856 cm^{-1} assigned to the stretching vibrations of -CH, at 1740 cm^{-1} attributed to the stretching vibrations of -C=O and at 1464 cm^{-1} corresponding to the bending vibrations of -CH [38]. The presence of an oxalate compound may also be suggested due to the bands at 1608 cm^{-1} and 1377 cm^{-1} assigned to the asymmetric and symmetric stretching vibrations of COO^- [39].

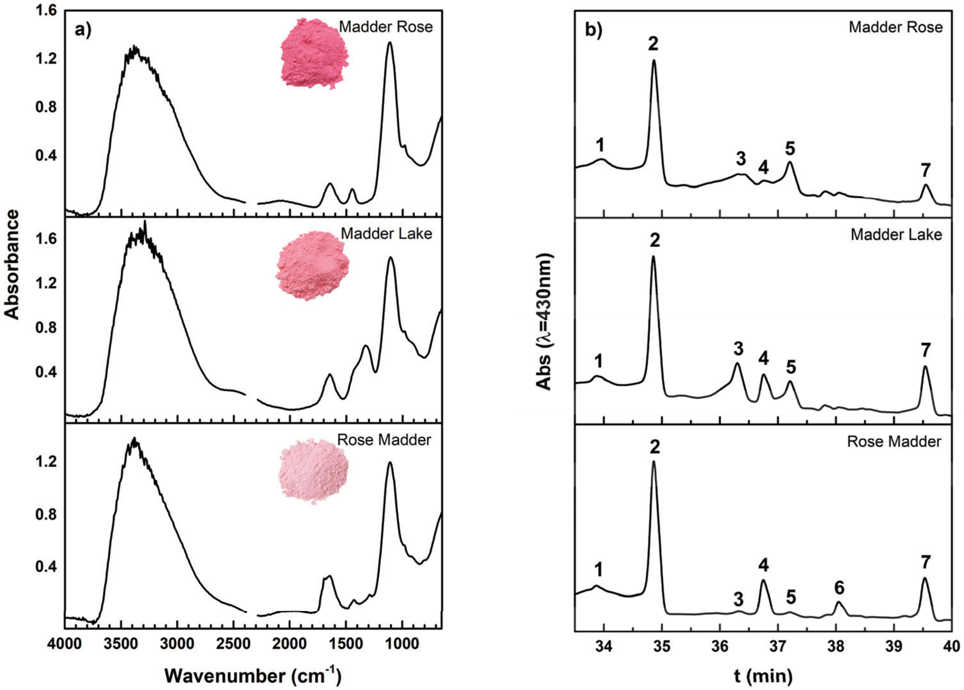

Figure 6. (**a**) Representative infrared spectra of the madder lake pigments produced and (**b**) chromatograms at 430 nm of MR1, ML1 and RM1 lake pigments; **1**—pseudopurpurin, **2**—alizarin, **3**—purpurin; compounds **4**–**7** were not identified.

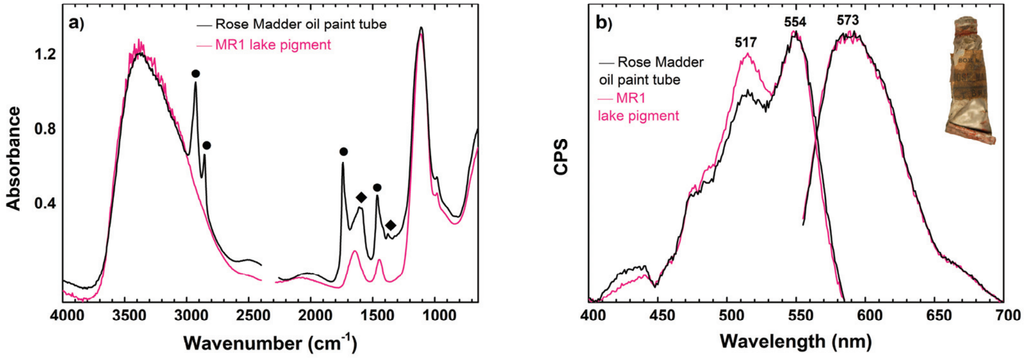

Figure 7. (**a**) Infrared spectra of a micro-sample from a Rose Madder W&N 19th-century oil paint tube and MR1 lake pigment; (●) bands assigned to the oil matrix and (◆) to an oxalate compound; (**b**) excitation and emission spectra acquired in painted samples of the Rose Madder 19th-century oil paint tube and MR1 lake pigment.

More importantly, by microspectrofluorimetry, a highly selective and sensitive in situ technique [15,19,36], it was also possible to find a very good match between the excitation and emission spectra of the historical W&N "Rose Madder" oil paint tube and MR1 lake pigment. As shown in Figure 7b, their spectra overlap very well, presenting excitation maxima at 517 nm and 554 nm and an emission maximum at 573 nm.

The powerful combination of these molecular techniques validates the Madder Rose lake pigment reconstruction as a historically accurate reference.

4. Conclusions

This work investigated the W&N 19th-century manufacture of madder red lake pigments for the first time. From 11 production records under the names Madder Rose, Madder Lake, Madder Carmine and Rose Madder, three main synthesis methods were found with three common steps: (i) washing of the madder roots from *Rubia tinctorum* L. with cold water, (ii) extraction in acid media and complexation with Al^{3+} using a solution of alum and (iii) precipitation using either ammonium carbonate or borate of sodium. All pigment reconstructions resulted in madder lake pigments with a rose hue, except for the Rose Madder formulation, which includes adding sulfuric acid. This strong acid significantly affects the process and the final product, and understanding its role in producing W&N's madder reds is crucial and will be assessed in the future.

The presence of Al^{3+}-purpurin and/or pseudopurpurin complexes was observed in the solution before precipitation, which resulted in the formation of an amorphous aluminate polymeric matrix identified by FTIR. Dye extraction of the madder lake pigments was revealed to be more complex than expected; however, pseudopurpurin, alizarin and purpurin were detected by HPLC-DAD.

Although preliminary, this work enabled the successful preparation of a historically accurate madder lake pigment that was analytically validated by the infrared and microspectrofluorimetry analyses of a Rose Madder W&N 19th-century oil paint tube.

This investigation intends to be the groundwork for comprehensively studying the W&N's 19th-century madder colours. A complete evaluation of W&N's 19th-century production records for madder colours will identify their primary manufacturing processes and pinpoint possible markers for W&N's 19th-century madder products. It will enable the creation of a robust analytical database made with historically accurate references that will be used to improve our analytical methodology to identify madder reds in heritage objects.

Author Contributions: Conceptualisation, V.O.; investigation, T.V., A.J.M., P.N. and V.O.; data acquisition, T.V., A.J.M., P.N. and V.O.; writing—original draft preparation, V.O. and T.V.; writing—review and editing, T.V., A.J.M., P.N., V.O. and M.V.; supervision, V.O. and A.J.M.; funding acquisition, V.O. and M.V. All authors have read and agreed to the published version of the manuscript.

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

Appendix A. Additional HPLC-DAD Analyses

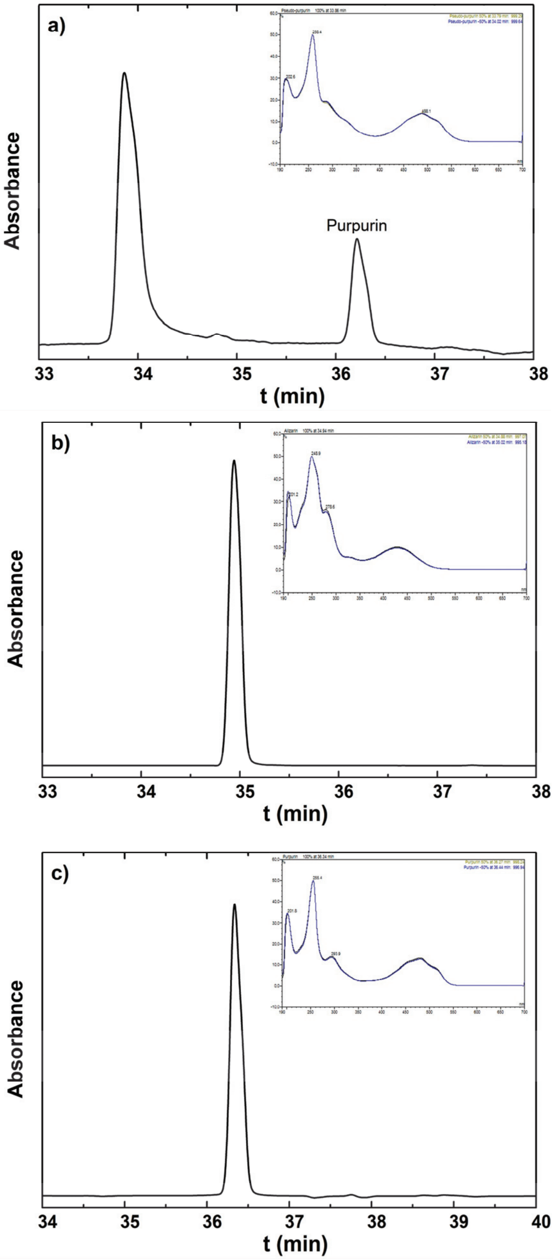

Figure A1. Chromatograms of (**a**) pseudopurpurin at t = 33.9 min with purpurin at t = 36.3 min (λ = 500 nm); (**b**) alizarin at t = 35 min (λ = 430 nm); and (**c**) purpurin at t = 36.3 min (λ = 500 nm). Insets of the corresponding UV-VIS spectra.

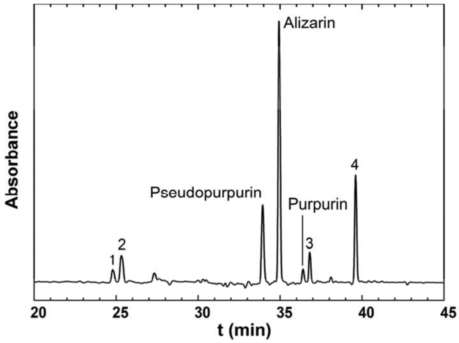

Figure A2. Chromatogram at 430 nm of water/methanol extract of the *R. tinctorum* roots used in this work; compounds **1**–**4** were not identified.

Appendix B. Additional Data on the W&N Production Records

Table A1. Formulation name, original production name and their unique recipe code (URC) for the eleven production records pertaining to the manufacture of madder red lake pigments in book P1.

Formulation Name ∣ Code	Original Production Name	URC *
Madder Rose ∣ MR	Madder Rose-colours Madder Carmine for Water	P1P025AL01 [¥] P1P257AL01
Madder Lake ∣ ML	Madder Lake §	P1P127AL05
Rose Madder ∣ RM	Rose Madder Madder Carmine Another formula [RM extra quality] Madder Carmine	P1P114AL13 P1P120AL11 P1P320BL01 P1P322AL01
-	Liquid Madder Lake	P1P030AL03
	Crimson Madder	P1P205AL12
	Madder with lime water	P1P299AL01

* The unique recipe code (URC) identifies the database record on the W&N Database. [¥] The URC P1P025AL10 also falls under the Madder Rose-colours production record. [§] This production record appears on the Rose Madder database record (URC P1P114AL13). In a database record (data from the RE database), the corresponding archive page can contain more than one production record (manufacturing data from the actual W&N archive).

Appendix C. Additional FTIR Analysis

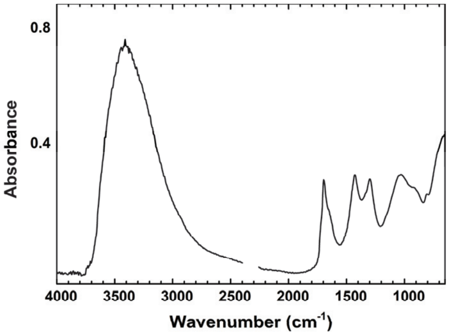

Figure A3. Infrared spectrum of RM2 pigment.

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Dye Identification in Mounting Textiles of Traditional Korean Paintings from the Late Joseon Dynasty

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Abstract: In the framework of the 'Amorepacific Project for the conservation of Korean pictorial art' (2018–2023) at the British Museum, three traditional Korean paintings have been investigated with the aim of supporting their conservation and obtaining information about the dyes used in the mounting textiles and other mounting elements. The paintings include a rare example of late 18th-century traditional Korean portraiture (accession number 1996,0329,0.1); a late 19th-century two-panel screen silk painting of *Pyeongsaeng-do-Scenes of life* (accession number 2016,3028.1); and a late 19th-century twelve-panel screen silk painting representing the *Five Confucian virtues* (accession number 1957,1214,0.1). The mounting textiles were investigated non-invasively by using digital microscopy and fibre optic reflectance spectroscopy (FORS), and the results guided a minimally invasive sampling campaign. Fourteen samples were analysed by using high-pressure liquid chromatography coupled with diode array and tandem mass spectrometry detectors (HPLC-DAD-MS/MS), leading to the identification of the natural dyes indigo, sappanwood (*Biancaea sappan*, formerly *Caesalpinia sappan*), amur cork tree (*Phellodendron amurense*) and safflower (*Carthamus tinctorius*) in the mounting elements of the 18th-century portrait. These results confirmed some of the non-invasive observations and were in agreement with the production date of the painting. Both natural and synthetic dyes were identified in the mounting textiles of the panel screens. Among the synthetic dyes, fuchsin (C.I. 42510), methyl violet 3B (C.I. 42536), methyl blue (C.I. 42780) and benzopurpurin 4B (C.I. 23500) were identified. These are early synthetic dyes first synthesised between the 1860s and the 1880s, suggesting that the silk textiles are likely to have been dyed in the last part of the 19th century.

Keywords: Korean art; textiles; dye analysis; HPLC-DAD-MS/MS; reflectance spectroscopy

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1. Introduction

Dye analysis is a powerful tool in textile research, as the identification of dyes not only informs on the manufacturing of a textile but can also point towards geographical provenance as well as refine the dating of textiles. This is particularly relevant for synthetic dyes, which were invented after 1856, as the date of their first synthesis is usually recorded [1]. Additionally, available information about the light sensitivity of dyes can be used to reconstruct the original appearance of textiles that have undertaken substantial fading or discolouration and to choose appropriate displaying strategies [2–4].

East Asian paintings are traditionally made on silk or paper and are mounted in different formats, such as hanging scrolls and folding screens [5–7]. Mounting encompasses a series of operations involving the application of several elements and materials to the back and sides of a painting, with the final outcome of framing it, strengthening it and protecting it, thus allowing for easier transportation, storage and display. The mounting elements also serve an aesthetic embellishing function and can even constitute additional spaces to carry symbolic meanings [8]. Among the mounting elements, borders are connected to the perimeter of the painting and are constituted of textile or paper, playing an important aesthetic and practical role, for example, in the case of scroll paintings that are rolled for ease of storage and transportation. Despite their important functions, textile borders and other mounting elements are often not considered an integral part of the artwork due to the fact that, in traditional practice, they are subject to replacement following their natural degradation [9]. As a result, they are often disregarded as an important research topic in art history. However, their study is fundamental for conservation, as the relative light sensitivities of the different dyes used to colour the textiles are a major factor in determining suitability for, and length of, any display. Furthermore, valuable information can be obtained about the traditional use of certain materials, the overall artistic intention, and sometimes the spiritual/religious significance behind the paintings [9]. Ultimately, researching the textile borders can help understand whether the textiles are original and contemporaneous with the painting.

Building on previous research on traditional Asian dyes [4,9–11], an investigation took place at the British Museum to study the mounting elements of three traditional Korean paintings. This research was undertaken in the framework of the 'Amorepacific Project for the conservation of Korean pictorial art' (2018–2023), sponsored by the Amorepacific Corporation to study and conserve historic and contemporary Korean pictorial art at the British Museum. The focus was on dye analysis with the main aim of informing the conservation process and obtain as much information as possible on the original dyes present on the mounting elements.

Recent developments in dye analysis have shown the potential of non-invasive methods to identify dyes, with reflectance and luminescence spectroscopic approaches being particularly promising [4,9,12–20]. Consequently, fibre optic reflectance spectroscopy (FORS) was used in this investigation to gather as much information as possible non-invasively. However, limitations in terms of identifying yellow dyes as well as mixtures of dyes are known drawbacks of this technique [4,21]. The conservation process of these paintings provided us with the opportunity to take small samples and apply high-pressure liquid chromatography coupled with diode array and tandem mass spectrometry detectors (HPLC-DAD-MS/MS). This is considered the state-of-the-art technique for identifying natural and synthetic dyes at a molecular level [22–29]. The technique requires minimal sampling (1–2 mm of a single thread) and provides insight into the molecular composition of dyes and dye mixtures, which is fundamental information for achieving straightforward identifications [11,30–32].

2. Materials and Methods

Accession number 1996,0329,0.1(P1)-Portrait scroll of Chae Je-gong

A rare example of late 18th-century traditional Korean portraiture, representing Chae Je-gong (1720–1799), Prime Minister of Korea under King Jeongjo (reign 1776–1800) of the Joseon dynasty (1392–1910), and made in 1789 by court artist Yi Myeong-gi (1756–before 1813) (Figure 1). Seen in a three-quarter view, the crossed-legged sitter sits on a cushion made of tiger skin, wearing a pink robe and a rhinoceros horn belt and a traditional Korean hat [33]. Chae Je-gong is known for having most of his portraits survived to this day. Nine portraits of him are known today. This British Museum portrait shows great similarity to the portrait in the Suwon Hwaseong Museum in Korea [34], which was painted in 1791.

The textile mounting is in silk. The recto shows a very light aqua colour, and the verso is a darker shade of blue. Several decorative elements are included, such as red knotted tassels (*yuso*), a roller knob, a hanging rod and a metal washer [35]. Following a non-invasive investigation whose results are presented in [9], three samples were taken from the light blue recto textile, the red/orange tassel and the red edge of the hanging rod. Figure S1 (Supplementary Material) shows the mounting elements under investigation.

Figure 1. Image of the recto and verso of hanging scroll 1996,0329,0.1 (P1), showing the portrait of Chae Je-gong (1720–1799 CE). Dimensions are 142.0 × 75.5 cm with mount and 96.5 × 59.5 cm without. Date is 1789 CE. © The Trustees of The British Museum.

Accession number 2016,3028.1(P2)-Two-panel screen painting of Pyeongsaeng-do (‘Scenes of life’).

A late 19th-century two-panel screen silk painting of *Pyeongsaeng-do-Scenes of life* (Figure 2). This genre of painting depicts an idealised biography of a scholar or official, usually starting from a scene of the first birthday and concluding with a scene of the 60th wedding anniversary and passing the civil examination. The right panel represents the 60th wedding anniversary, and the left panel commemorates the 60th anniversary of passing the civil service examination [36]. These two paintings constitute the last two panels of what would have originally been a ten-panel screen, as in the process of dismantling it, the numbers 9 and 10 were written in Chinese characters on each panel.

Figure 2. Image of the two-panel screen silk painting of *Pyeongsaeng-do-Scenes of life* 2016,3028.1 (P2). Dimensions per panel are 85.1 × 40.9 cm with mount and 62.2 × 36.7 cm without. Production date is late 19th century. © The Trustees of The British Museum.

The main mounting elements are composed of two horizontal blue silk textiles joined alongside the top and bottom of the painting. Brownish decorative bands that are bordered on either side by narrow pink and off-white strips surround the four edges of each panel. A purple damask silk textile covered the outside of the panels. These morphological characteristics constitute the typical mounting technique of Joseon screens. Four samples were taken from the blue, purple, pink and brown textile elements, which are shown in more detail in Figure S2 (Supplementary Material).

Accession number 1957,1214,0.1(P3)*-Twelve-panel screen painting of *Five Confucian virtues.

Seen below is a late 19th-century twelve-panel screen silk painting representing scenes of stories visualising the five Confucian virtues, which are about relationships between the king and his servants, father and sons, husbands and wives, the elders and the young and between friends (Figure 3) [37]. This painting is a rare example in terms of its size and highly decorative presentation.

Figure 3. Image of the twelve-panel screen silk painting representing scenes of stories visualising the *Five Confucian virtues* 1957,1214,0.1 (P3). Dimensions per panel are 127.9 × 31.5 cm without mount and overall, 171 × 434.7 cm with mount. Production date is late 19th century. © The Trustees of The British Museum.

The mounting elements are composed of the morphological features of the typical Joseon screen observed in P2. As well as this, the outer surface of each panel was covered with dark blue cotton fabric. In addition, as a more decorative element, pink and off-white narrow strips were inserted between the painting and the top and bottom blue silk mount.

Four samples were taken from the blue cotton, blue silk, pink and brown textile elements, shown in more detail in Figure S3 (Supplementary Material).

Reference Materials

Reference dye samples were analysed to confirm the identification of natural and synthetic dyes. For the natural dyes, the details of the reference samples are reported in [4,11]. For the synthetic dyes, methyl violet (C.I. 42535), methyl blue (C.I. 42780) and fuchsin (C.I. 42510) were available as both powders and dyed wool samples from the CHARISMA project (2009–2014) funded by the European Union FP 7 Research Infrastructures programme (CHARISMA Grant Agreement no. 228330). Additional samples of historic dyed fibres were available from copies of two historic books: "A Manual of Dyeing: For the Use of Practical Dyers, Manufacturers, Students, and All Interested in the Art of Dyeing (Specimen of dyed fabrics)" by Knecht, E., C. Rawson, and R. Loewenthal published in London in 1893 [38] and "The Coal Tar Colours of Farbwerke Vorm. Meister Lucius & Brüning, Hoechst on the Maine, Germany–A General Part" by Farbwerke Vorm. Meister Lucius & Brüning in 1896. In particular, benzopurpurin 4B (C.I. 23500) was available from the former one, whereas methyl violet 3B (C.I. 42536) was present in both books. The HPLC analysis of all samples present in these books will be the topic of upcoming publications.

Digital microscopy

High-magnification images were obtained using a Hirox Video 3D Digital Microscope HRX-01 mounted on a bi-dimensional frame and equipped with a TH-5 Motion Controller and a Hirox HR-2016E lens (magnification 20× *g*–160× *g*).

Optical microscopy

High-magnification images were taken for all samples under visible and ultraviolet (UV) light using a Leica DM 4000M UV microscope equipped with a halogen lamp.

Fibre optic reflectance spectroscopy

Fibre optic reflectance spectra were recorded for all the coloured areas of interest with an Avantes (Apeldoorn, The Netherlands) AvaSpec-ULS2048XL-USB2 spectrophotometer equipped with an AvaLight-HAL-S-IND tungsten halogen light source. The detector and light source were connected with a fibre optic bundle to an FCR-7UV200-2-1.5 × 100 probe. In this configuration, light was sent and retrieved by the bundle set at approximately 45° from the surface normal, thus excluding specular reflectance. The spectral range of the detector was 200–1160 nm; nevertheless, due to poor blank correction on both the extremes of the range, only the range between 400 and 900 nm was considered, as per the features of the monochromator (slit width 50 µm, grating of the UA type with 300 lines/mm) and of the detector (2048 pixels), the best spectra resolution was 2.4 nm calculated as the full width at half maximum (FWHM). The spectra were referenced against the WS-2 reference tile provided by Avantes. The diameter of the investigated area on the sample was approximately 1 mm, obtained by setting the distance between the probe and the sample at 1 mm. The instrumental parameters were as follows: 50 ms integration time and 20 scans for a total acquisition time of 1 s for each spectrum. The whole system was managed by the software AvaSoft 8 for Windows™.

High-pressure liquid chromatography coupled to diode array detector and electrospray ionisation followed by quadrupole and time of flight detection(HPLC-DAD-ESI-Q-ToF)

The dye extraction was performed using a method published in [10], which briefly consists of a double mild extraction procedure, using DMSO first, and secondly a mixture of methanol/acetone/water/0.5 M oxalic acid 30:30:40:1 (*v/v/v/v*). The size of the samples ranged from 2 to 5 mm of single threads of variable thickness, depending on the difficulty of accessing the already damaged areas.

Analyses were carried out using a 1260 Infinity HPLC (Agilent Technologies), coupled to an 1100 DAD detector (Hewlett-Packard) and to a Quadrupole-Time of Flight tandem mass spectrometer 6530 Infinity Q-ToF detector (Agilent Technologies) by a Jet Stream ESI interface (Agilent Technologies). Separation was achieved using a Zorbax Extend-C18 column (2.1 mm × 50 mm, 1.8 µm particle size) with a 0.4 mL/min flow rate and 40°C column temperature, and a gradient of water with 0.1% formic acid (eluent A) and acetonitrile with 0.1% formic acid (eluent B). The elution gradient was programmed as follows: initial conditions 95% A, followed by a linear gradient to 100% B in 10 min and held for 2 min. The re-equilibration time for each analysis was 10 min. A 10 µL injection volume was adopted for the MS experiments and 20 µL for the MS/MS experiments.

The DAD detector (cell volume 50 µL) scanned in the range 200–700 nm with 2 nm resolution. The ESI operating conditions were: drying gas (N_2, purity > 98%) temperature 350 °C and 10 L/min flow; capillary voltage 4.0 kV; nebulizer gas pressure 40 psig; sheath gas (N_2, purity > 98%) temperature 375 °C and flow 11 L/min. High-resolution MS and MS/MS spectra were acquired in both negative and positive modes in the range of 100–1700 *m/z*. The fragmentor was kept at 100 V, nozzle voltage 1000 V, skimmer 65 V and octapole RF 750 V. For the MS/MS experiments, different voltages (from 10 to 40 V) in the collision cell were tested for Collision Induced Dissociation (CID), in order to maximize the information obtained from the fragmentation of the single molecules. The collision gas was N_2 (purity 99.999%). The data were collected by targeted MS/MS acquisition with an MS scan rate of 1.0 spectra/sec and an MS/MS scan rate of 1.0 spectra/sec. Auto-calibration was performed daily using Agilent tuning mix HP0321 (Agilent Technologies) prepared in 90% water 10% acetonitrile.

MassHunter Workstation Software was used to carry out diode array detector and mass spectrometer control, data acquisition and data analysis. In particular, extract ion chromatograms were obtained using the software EIC function and selecting the mass range corresponding to the calculated mass ± 0.01 *m/z*. Chemical formula and molecular structures were assigned based on mass differences below 2 ppm.

3. Results

The results of this investigation are discussed for each painting and summarised in Table 1.

Table 1. Summary of the results obtained by HPLC-DAD-MS/MS analysis.

	Molecules	**Formula**	**$[M]^+/[M+H]^+$**	**$[M-2H]^{2-}$**	**$[M-H]^-$**	**Fragment Ions (+)**	**Fragment Ions (-)**	**Dye Sources**
			1996,0329,0.1-Portrait scroll of Chae Je-gong (P1)					
Light blue	Isatin	$C_8H_5NO_2$	148.0393		146.0248	130, 120, 102, 92, 77, 65	118	Indigo–unknown botanical origin
	Indigotin	$C_{16}H_{10}N_2O_2$	263.0815		261.067	235, 219, 206, 190, 132		
	Indirubin	$C_{16}H_{10}N_2O_2$	263.0815		261.067	235, 219, 206, 190, 132		
Dark red/orange from tassel	Brasilein	$C_{16}H_{12}O_5$	285.0757		283.0612	239, 175, 147, 123	265, 240, 196, 173	Sappanwod (*Biancaea sappan*)
	Urolithin C	$C_{13}H_8O_5$	245.0444		243.0299		226, 215, 198, 187, 171, 143	
	Hydroxyberberine	$C_{20}H_{17}NO_5{}^+$	352.1185			336, 320, 308, 290		Amur cork tree (*Phellodendron amurense*)
	Hydroxypalmatine	$C_{21}H_{21}NO_5{}^+$	368.1492			352, 338, 324, 310		
	Jatrorrhizine	$C_{20}H_{19}NO_4{}^+$	338.1387			323, 322, 308, 306, 294, 280, 279		
	Berberine	$C_{20}H_{17}NO_4{}^+$	336.123			321, 320, 306, 304, 292, 278		
	Palmatine	$C_{21}H_{21}NO_4{}^+$	352.1543			336, 322, 308, 294		
Bright red from hanging rod	Carthamin	$C_{43}H_{42}O_{22}$	911.224		909.2095		891, 847, 659, 501, 449, 407, 287	Safflower (*Carthamus tinctorius*)
	Carthamin degradation product I	$C_{21}H_{22}O_{11}$	451.1235		449.1089		299, 286, 261, 207, 153, 141, 119	
	Carthamin degradation product II	$C_{22}H_{22}O_{12}$	479.1184		477.1038		459, 339, 327, 314, 309, 287, 269, 179, 119	

Table 1. *Cont.*

	Molecules	Formula	$[M]^+/[M+H]^+$	$[M\text{-}2H]^{2-}$	$[M\text{-}H]^-$	Fragment Ions (+)	Fragment Ions (-)	Dye Sources
2016,3028.1-Two-panel screen painting of Pyeongsaeng-do ('Scenes of life') (P2)								
Purple	N-methyl-pararosaniline (rosaniline)	$C_{20}H_{20}N_3{}^+$	302.1656			286, 209, 195, 135, 119, 102, 62		Methyl violet 3B–C.I. 42536-1866
	N,N-dimethyl-pararosaniline	$C_{21}H_{22}N_3{}^+$	316.1808			300, 286, 223, 209, 106		
	N,N,N-trimethyl-pararosaniline	$C_{22}H_{24}N_3{}^+$	330.1965			314, 300, 223, 208, 120		
	N,N,N,N-tetramethyl-pararosaniline	$C_{23}H_{26}N_3{}^+$	344.2121			328, 313, 301 237, 223		
	N,N,N,N,N-pentamethyl-pararosaniline	$C_{24}H_{28}N_3{}^+$	358.2278			342, 326, 289, 237, 214, 133, 119		
	N,N,N,N,N,N-hexamethyl-pararosaniline	$C_{25}H_{30}N_3{}^+$	372.2434			356, 328, 251		
	N-benzyl-N-methyl-pararosaniline	$C_{27}H_{26}N_3{}^+$	392.2121					
	N-benzyl-N,N-dimethyl-pararosaniline	$C_{28}H_{28}N_3{}^+$	406.2278					
	N-benzyl-N,N,N-trimethyl-pararosaniline	$C_{29}H_{30}N_3{}^+$	420.2434			404, 328, 313, 300, 258, 223		
	N-benzyl-N,N,N,N-tetramethyl-pararosaniline	$C_{30}H_{32}N_3{}^+$	434.2591			418, 342, 314, 272		
	N-benzyl-N,N,N,N,N-pentamethyl-pararosaniline	$C_{31}H_{34}N_3{}^+$	448.2747			432, 356, 342, 328		
	N,N-dibenzyl-N,N-dimethyl-pararosaniline	$C_{35}H_{34}N_3{}^+$	496.2724			404, 376, 312, 284		
	N,N-dibenzyl-N,N,N-trimethyl-pararosaniline	$C_{36}H_{36}N_3{}^+$	510.2904			418, 390, 326		
	N,N-dibenzyl-N,N,N,N-tetramethyl-pararosaniline	$C_{37}H_{38}N_3{}^+$	524.3060			432, 404, 340, 312		

Table 1. *Cont.*

	Molecules	Formula	$[M]^+/[M+H]^+$	$[M-2H]^{2-}$	$[M-H]^-$	Fragment Ions (+)	Fragment Ions (-)	Dye Sources
Blue	Disulphonated N,N-diphenyl-N-methyl-pararosaniline	$C_{32}H_{27}N_3O_6S_2$	614.1414	305.5598	612.1269		532, 452, 367, 231, 80	Methyl blue-C.I. 42780-1862
	Disulphonated N,N-diiphenyl-N,N-dimethyl-pararosaniline	$C_{33}H_{29}N_3O_6S_2$	628.1571	312.5676	626.1425		546, 466, 375, 177, 80	
	Disulphonated N,N,N-triphenyl-pararosaniline	$C_{37}H_{29}N_3O_6S_2$	676.1571		674.1425	596, 583, 516, 503, 427, 412, 347, 332, 254, 239, 215	594, 530, 514, 156, 80	
	Disulphonated N,N,N-triphenyl-N-methyl-pararosaniline	$C_{38}H_{31}N_3O_6S_2$	690.1727		688.1582	610, 530, 426, 346, 254, 217	608, 544, 530, 453, 171, 156, 107, 80	
	Disulphonated N,N,N-triphenyl-N,N-dimethyl-pararosaniline	$C_{39}H_{33}N_3O_6S_2$	704.1875		702.1738	624, 597, 544, 517, 440, 360, 268	622, 542, 476, 171, 156, 80	
	Trisulphonated N,N,N-triphenyl-pararosaniline	$C_{37}H_{29}N_3O_9S_3$	756.1139	376.5460	754.0993	676, 596, 507, 412, 345, 254	674, 594, 514	
	Trisulphonated N,N,N-triphenyl-N-methyl-pararosaniline	$C_{38}H_{31}N_3O_9S_3$	770.1295	383.2253	768.1150	690, 610, 583, 521, 426, 262	688, 608, 528	
	Trisulphonated N,N,N-triphenyl-N,N-dimethyl-pararosaniline	$C_{39}H_{33}N_3O_9S_3$	784.1452	390.5617	782.1306	704, 597, 535, 377, 320	702, 622	
	Trisulphonated N,N,N-triphenyl-N,N,N-trimethyl-pararosaniline	$C_{40}H_{35}N_3O_9S_3$	798.1608	397.5695	796.1463			

Table 1. *Cont.*

	Molecules	Formula	$[M]^+/[M+H]^+$	$[M-2H]^{2-}$	$[M-H]^-$	Fragment Ions (+)	Fragment Ions (-)	Dye Sources
Pink	Pararosaniline	$C_{19}H_{18}N_3{}^+$	288.1495			271, 195, 168,137		Fuchsin-C.I. 42510-1856
	Methyl-pararosaniline	$C_{20}H_{20}N_3{}^+$	302.1656			286, 209, 195, 135, 119, 102, 62		
	Dimethyl-pararosaniline	$C_{21}H_{22}N_3{}^+$	316.1808			300, 286, 223, 209, 106		
	Trimethyl-pararosaniline	$C_{22}H_{24}N_3{}^+$	330.1965			314, 300, 223, 208, 120		
Brown	Brasilein, Urolithin C	See "Dark red/orange from tassel" sample from P1						Sappanwod (*Biancaea sappan*)
	Pararosaniline Methyl-pararosaniline Dimethyl-pararosaniline Trimethylpararosaniline	See "Pink" sample from P2						Fuchsin-C.I. 42510-1856
1957,1214,0.1-Twelve-panel screen painting of scenes of Five Confucian virtues (P3)								
Blue cotton	Isatin, Indigotin, Indirubin	See "Light blue" sample from P1						Indigo–unknown botanical origin
Blue silk	See "blue" sample from P2							Methyl blue
Brown	Ellagic acid	$C_{14}H_6O_8$	303.0135		300.999	284, 245, 228, 200, 173, 145, 117	285, 275, 257, 229, 201	Tannins–unknown botanical origin
	Pararosaniline Methyl-pararosaniline Dimethyl-pararosaniline Trimethylpararosaniline	See "Pink" sample from P2						Fuchsin-C.I. 42510-1856
Pink	Benzopurpurin 4B	$C_{34}H_{28}N_6O_6S_2$	681.1585	339.0683	679.1439	445.1322, 353.1609, 222.0241, 196.1157	663, 599, 571, 445, 427, 234	Benzopurpurin 4B–C.I. 23500-1884
	Benzopurpurin 4B + 1C	$C_{35}H_{28}N_6O_6S_2$	693.1585	345.0683	691.1439			
	Benzopurpurin 4B + 2C	$C_{36}H_{28}N_6O_6S_2$	705.1585	351.0683	703.1439		455, 391, 375, 247, 182, 167, 107	

3.1. P1-Portrait Scroll of Chae Je-Gong

The three samples taken from the textile border and mounting elements of P1 corresponded to the light blue border, the dark red/orange tassel and the bright red textile at the edge of the hanging rod (Figure S1—Supplementary Material). The observations under the microscope using UV light revealed that the red sample from the hanging rod exhibited a bright orange luminescence. A weaker luminescence was also exhibited by the orange sample from the tassel (Figure 4). As discussed in [4], several traditional Asian dyes have the property of emitting luminesce under UV light, including safflower, turmeric and amur cork tree. Interesting observations about safflower-dyed fibres investigated by UV light microscopy are also reported in [39,40].

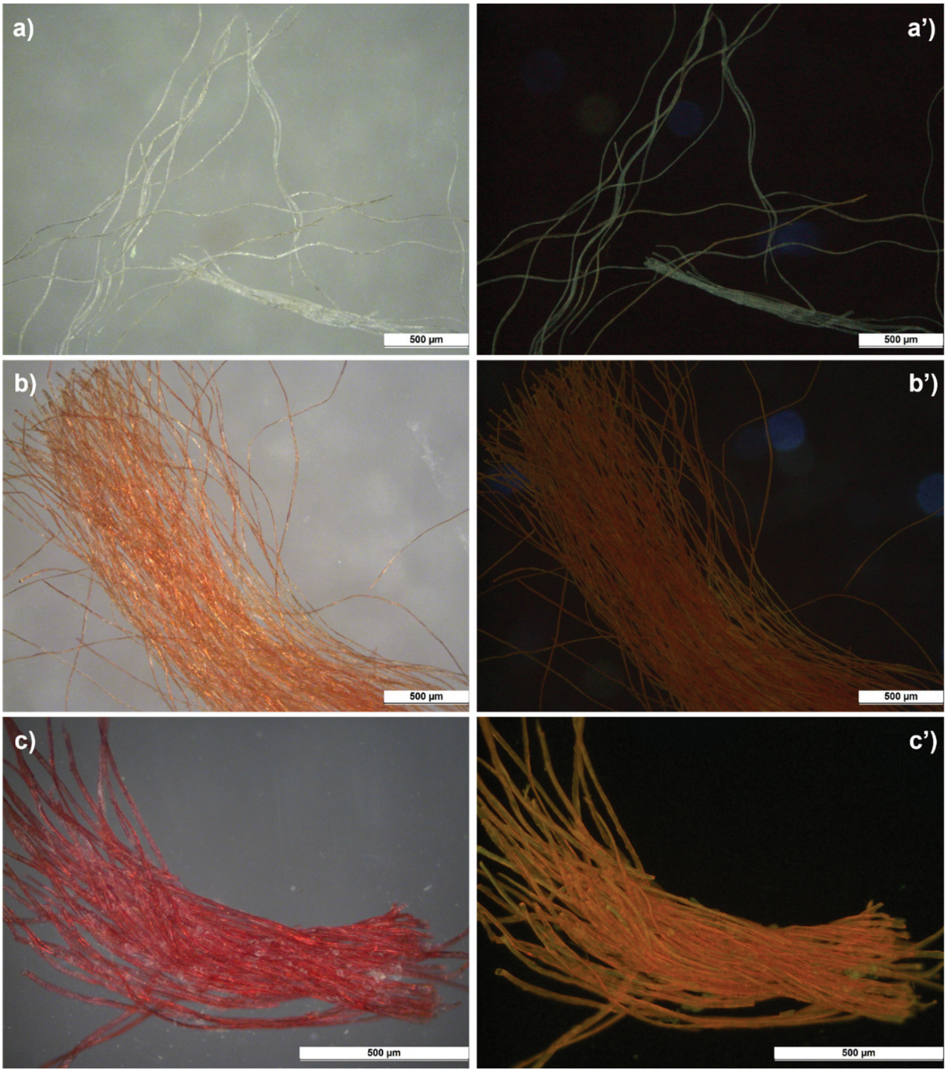

Figure 4. Microscopic images of the samples taken from P1 under visible (**a**–**c**) and UV (**a′**–**c′**) light. (**a**,**a′**) light blue sample from textile border; (**b**,**b′**) red/orange sample from tassel; (**c**,**c′**) bright red sample from hanging rod.

The HPLC analysis of the light blue sample revealed the presence of indigo, as indigotin was detected despite the extremely small amount of sample taken and the very light colour exhibited (Figure 5a). Traces of indirubin and isatin were also present, confirming the natural origin of the indigo [41], although the exact botanical source could not be ascertained. The non-invasive results obtained on the light and dark blue colours of the textile borders were very similar and already suggested the presence of indigo [9]. Hence, the dark blue colour on the back of the textile border is confirmed to be indigo as well.

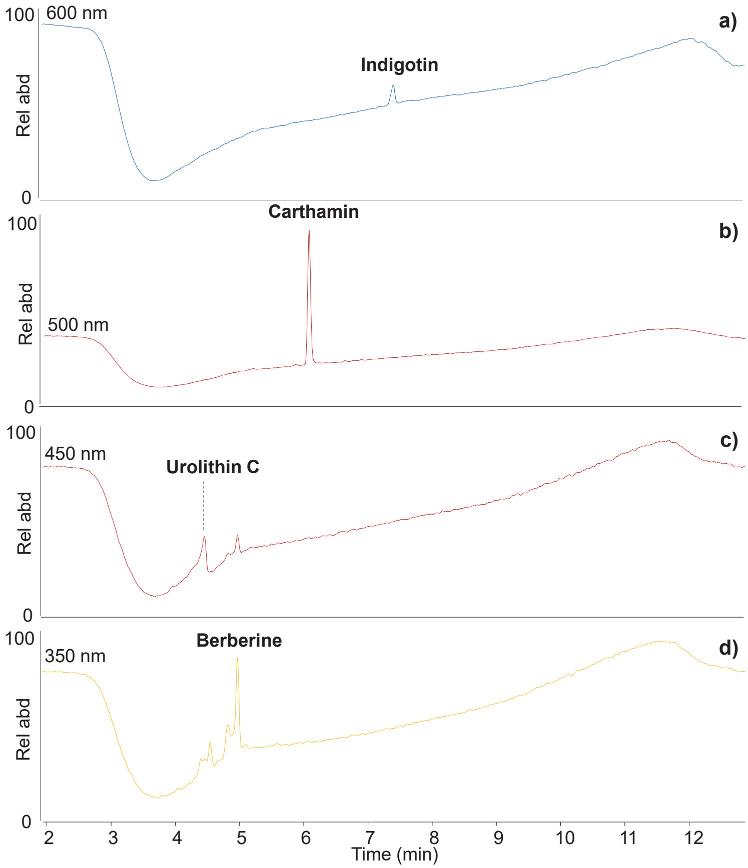

Figure 5. DAD chromatograms obtained by HPLC-DAD-MS/MS analysis of (**a**) light blue sample; (**b**) bright red sample from the hanging rod; (**c**,**d**) dark red/orange sample from tassel of P1.

The sample from the hanging rod contained carthamin (Figure 5b), which enabled the straightforward identification of safflower red. Carthamin is known to degrade easily [42–44]. However, the degradation products often detected in historic safflower samples [27,42] were present in very small relative amounts, and no trace of safflower yellow components was detected, which suggests the very good preservation of the dye and justifies the bright red colour observed on this textile. Additionally, in this case, the results confirmed the observation already obtained non-invasively [9] and are in agreement with the UV-induced luminescence observed.

The sample from the tassel contained sappanwood, identified by the presence of urolithin C (Figure 5c), a sappanwood marker component often used for diagnostic purposes [45,46]. The presence of urolithin C and other sappanwood degradation products highlights that the sappanwood is not in a good state of preservation and has partially discoloured. In addition, berberine, palmatine, jatrorrhizine, hydroxyberberine and other minor components were detected (Figure 5d), highlighting the presence of the yellow dye extracted from the amur cork tree [10,11,19]. This dye has strong UV-induced luminescence properties [4], and its identification adds to the observations obtained by FORS. Although the presence of a yellow dye was suspected together with a tentative identification of sappanwood, FORS could not give conclusive information on this dye mixture [9].

The identification of these traditional natural dyes is in agreement with the date of the painting (end of the 18th century). The combination of sappanwood and amur cork tree in the tassel is interesting, as Chinese dyeing recipes from the Ming and Qing dynasties report the use of sappanwood with several other yellow dyes, such as smoketree, pagoda bud and turmeric rather than amur cork tree to obtain orange shades [47]. Similarly, this particular combination is not reported in Korean dyeing recipes from the Joseon period [48].

3.2. P2-Two-Panel Screen Painting of Pyeongsaeng-do ('Scenes of Life')

Before and during the conservation treatment, digital microscopy was used to obtain a better idea of the areas of interest. In particular, the removal of the brown and pink mounting elements sitting on top of the purple damask revealed the extent of discolouration and dirtiness of the exposed area compared to the protected one, which still retained an extremely vibrant purple colour (Figure 6a,b). Similar observations were obtained from the blue textile border (Figure 6c,d). Furthermore, when the purple textile sitting on top of the blue one was removed, a colour transfer was evident (Figure 6c).

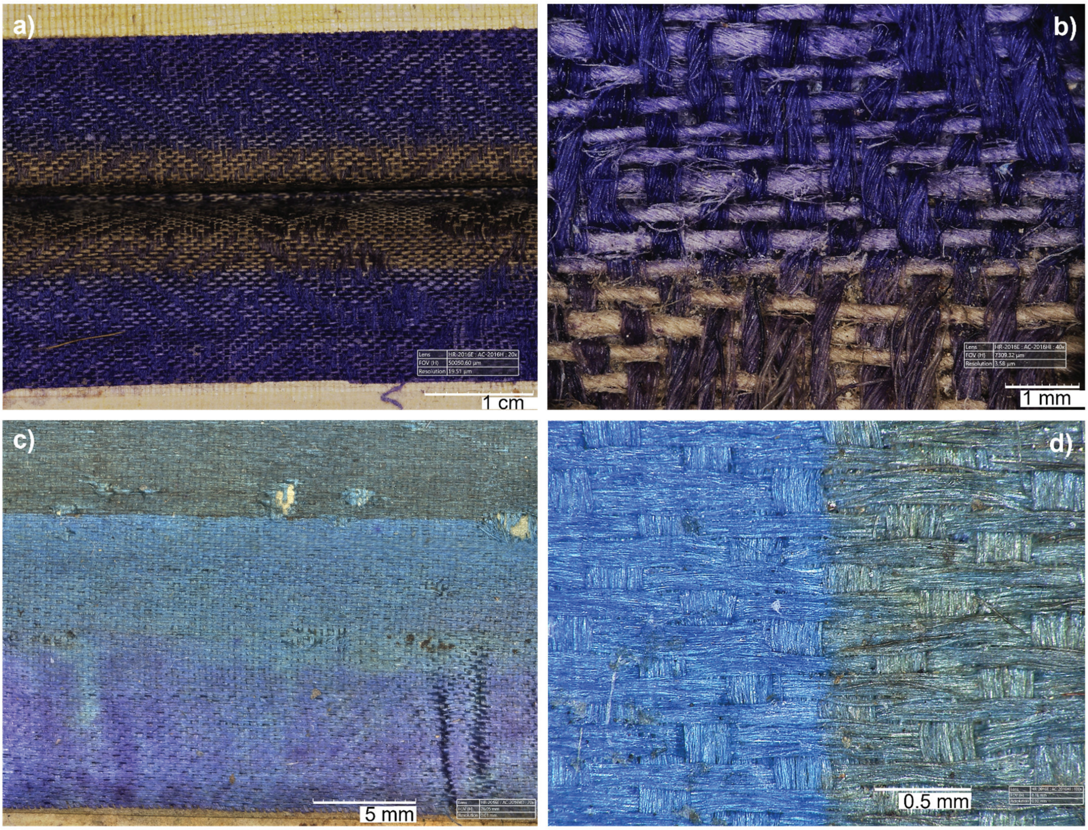

Figure 6. Images of the purple (**a**,**b**) and blue (**c**,**d**) textile borders of P2 obtained by digital microscopy, highlighting the discolouration of the exposed areas and the vibrant colours of the protected areas.

FORS spectra were acquired from the four textile borders corresponding to the purple, blue, pink and brown areas (Figure 7). The reflectance spectrum of the purple area showed a relatively broad absorption band between ca. 540 and 590 nm (Figure 7a), suggesting the presence of a synthetic purple dye [13,49]. The spectrum showed similarities with the results obtained from a reference sample of methyl violet (C.I. 42535), although the match was not perfect due to the absorption band of the reference sample being broader. Moreover, a high number of synthetic purple dyes with similar molecular structures and reflectance spectra [49] are available; hence the FORS results were not considered conclusive. In the case of the blue textile, the three different blue areas visible in Figure 6c were targeted and produced similar spectra with a relatively broad absorption band with a maximum between 605 and 615 nm (Figure 7b). A relatively good match was obtained with a reference sample of methyl blue (C.I. 42780), but also, in this case, the identification was not considered conclusive. The thin pink stripe produced a reflectance spectrum with an absorption maximum at ca. 570 nm (Figure 7c) and a characteristic shape that showed similarities with a reference sample of fuchsin (C.I. 42510). However, some differences were observed as well, which did not allow for a certain identification solely based on the FORS results. The darker colour of the brown textile resulted in a less intense reflectance spectrum. However, a maximum absorption at ca. 580 nm was obtained, suggesting the possible presence of fuchsin also in this textile, although a further investigation was needed, as the absorption maximum appeared significantly shifted.

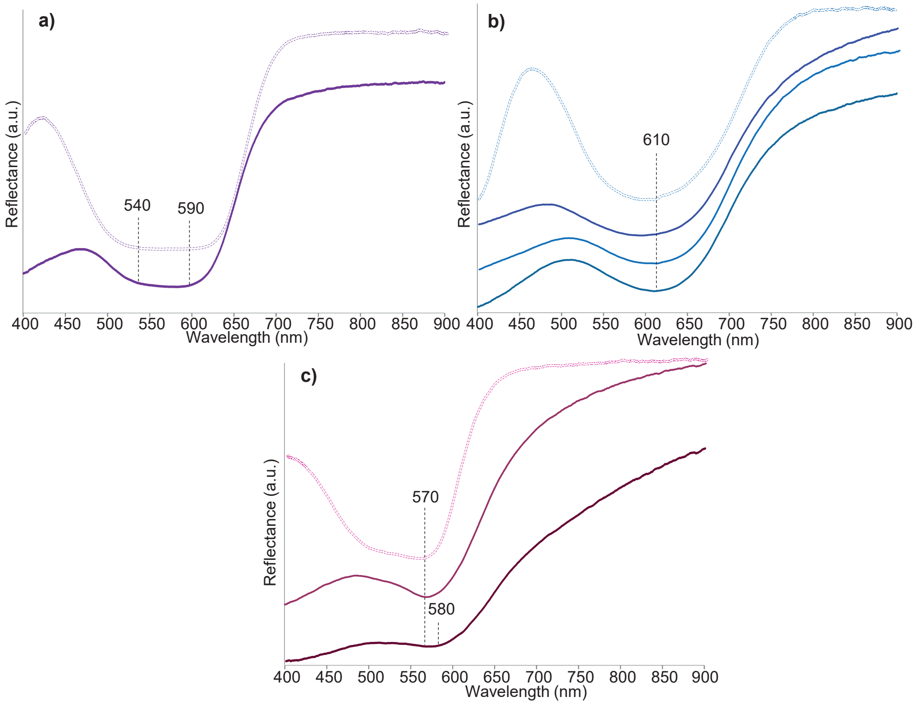

Figure 7. Reflectance spectra obtained by FORS analysis of P2 corresponding to (**a**) purple textile (full line) and reference sample of methyl violet (hollow line); (**b**) blue textile (full lines for the three areas visible in Figure 6c) and a reference sample of methyl blue (hollow line); (**c**) brown textile (full line, bottom), pink textile (full line, middle) and a reference sample of fuchsin (hollow line).

Four samples were therefore taken from the different textiles. The optical microscopy images are shown in Figure S4 (Supplementary Material).

The HPLC analysis of the purple sample produced a complex chromatographic profile, as shown in Figure 8. The molecules ranging from *m/z* 302.1656 to *m/z* 372.2434 were identified as the homologue series of N-methylated pararosanilines containing from one to six N-methyl groups. These are the main components of methyl violet (C.I. 42535) according to the literature [50] and are in agreement with the in-house analysis of the reference samples. However, two additional homologue series were detected. The former one included molecules with molecular ions $[M]^+$ = *m/z* 406.2278 (two isomers), 420.2434 (two isomers), 434.2591 and 448.2747. The latter one included molecules with $[M]^+$ = *m/z* 496.2724, 510.2904 and 524.3060. Tandem mass spectra (MS/MS) were acquired for these molecules in order to elucidate their molecular structures. The MS/MS spectra for the molecules with $[M]^+$ = *m/z* 448.2747 and 524.3060 are reported in Figure 9. The main fragmentation patterns revealed the neutral loss of C_7H_8 (92.0626 u) fragments corresponding to benzyl groups. The molecular structures were therefore assigned to N-benzyl and N-N-dibenzyl derivatives of N-methylated pararosanilines with different degrees of methylation. These compounds are reported as synthesis products associated with the production of methyl violet formulations [51,52]. In particular, methyl violet 6B is described as N-pentamethyl,N-benzylpararosaniline chloride produced by the action of benzyl chloride on ordinary methyl violet [51]. Furthermore, methyl violet 3B, 4B and 5B are described as mixtures of ordinary methyl violet and methyl violet 6B [51]. The reference samples of methyl violet 3B were available, and the results obtained from these samples indeed showed all the compounds detected in the purple sample from P2 (Figure S5a—Supplementary Material). These benzylated methyl violet formulations are given C.I. number 42536 and started to be produced after 1866 [52].

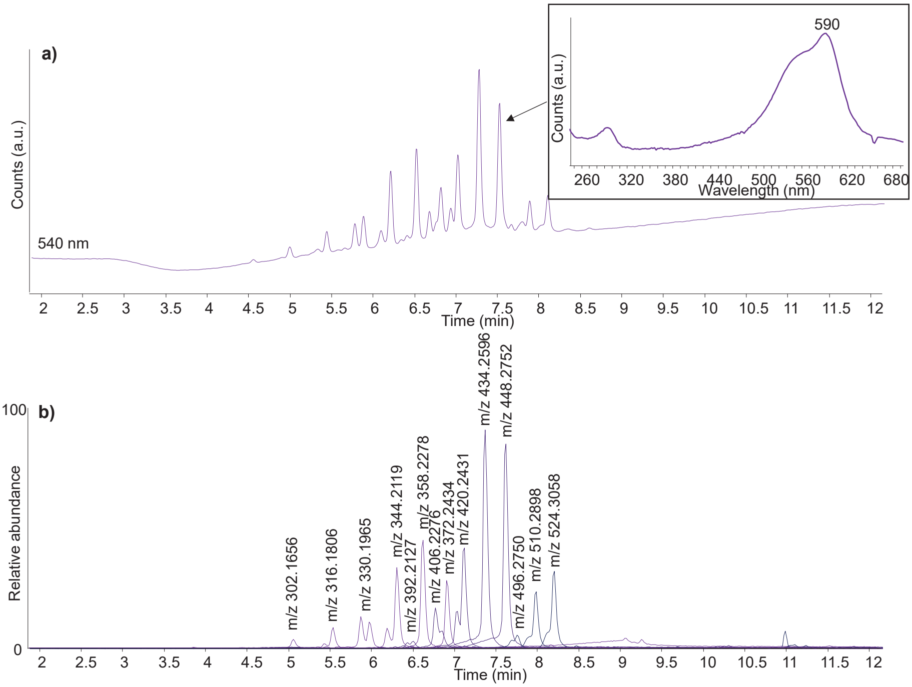

Figure 8. DAD (**a**) and positive ionisation extracted ion (**b**) chromatograms obtained by HPLC-DAD-MS/MS analysis of the purple sample from P2. The insert reports the UV-Vis spectrum of one of the molecular components. The experimental masses of the molecular ions $[M]^+$ are also reported.

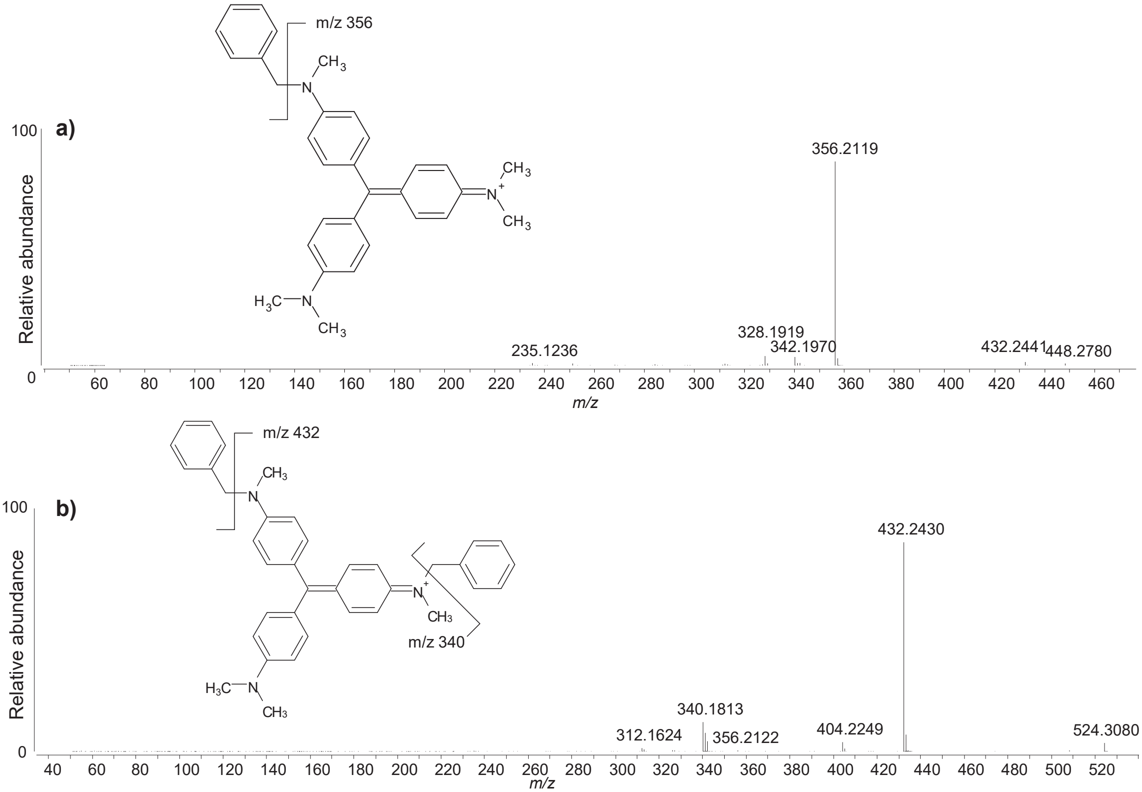

Figure 9. Tandem mass spectra (positive ionisation mode) of (**a**) N-benzyl-N,N,N,N,N-pentamethyl-pararosaniline (precursor ion *m/z* 448.2747; collision energy 50 keV) and (**b**) N,N-dibenzyl-N,N,N,N-tetramethyl-pararosaniline (precursor ion *m/z* 524.3060; collision energy 50 keV).

The HPLC analysis of the blue sample also produced a relatively complex chromatographic profile (Figure 10). In the negative ionisation mode, all molecules produced a strong doubly charged $[M\text{-}2H]^{2-}$ ion accompanied by a weaker single charged $[M\text{-}H]^{-}$ ion. The most abundant three molecules also produced weak ions in the positive ionisation mode. These three molecules are reported as the main components of methyl blue (C.I. 42780) [50] and correspond to the trisulphonated derivative of triphenylpararosaniline ($[M\text{-}2H]^{2-}$ = *m/z* 376.5460 and $[M\text{-}H]^{-}$ = *m/z* 754.0993), as well as its methylated ($[M\text{-}2H]^{2-}$ = *m/z* 383.2253 and $[M\text{-}H]^{-}$ = *m/z* 768.1150), dimethylated ($[M\text{-}2H]^{2-}$ = *m/z* 390.5617 and $[M\text{-}H]^{-}$ = *m/z* 782.1306) and trimethylated ($[M\text{-}2H]^{2-}$ = *m/z* 397.5695 and $[M\text{-}H]^{-}$ = *m/z* 796.1463) homologues. The isomers of the methylated compounds were also detected with lower abundance. The corresponding disulphonated derivatives (see Figure 10 and Table 1 for *m/z* values) eluted at slightly higher retention times. The compound with $[M\text{-}2H]^{2-}$ = *m/z* 312.5679 and $[M\text{-}H]^{-}$ = *m/z* 626.1426 was identified as the disulphonated derivative of diphenylpararosaniline. The identifications were supported by the tandem mass spectra (Table 1), and the molecular composition matched with reference samples of methyl blue (also referred to as soluble blue or Nicholson's blue) (Figure S5b—Supplementary Material). This class of dyes was synthesised in 1862 [52].

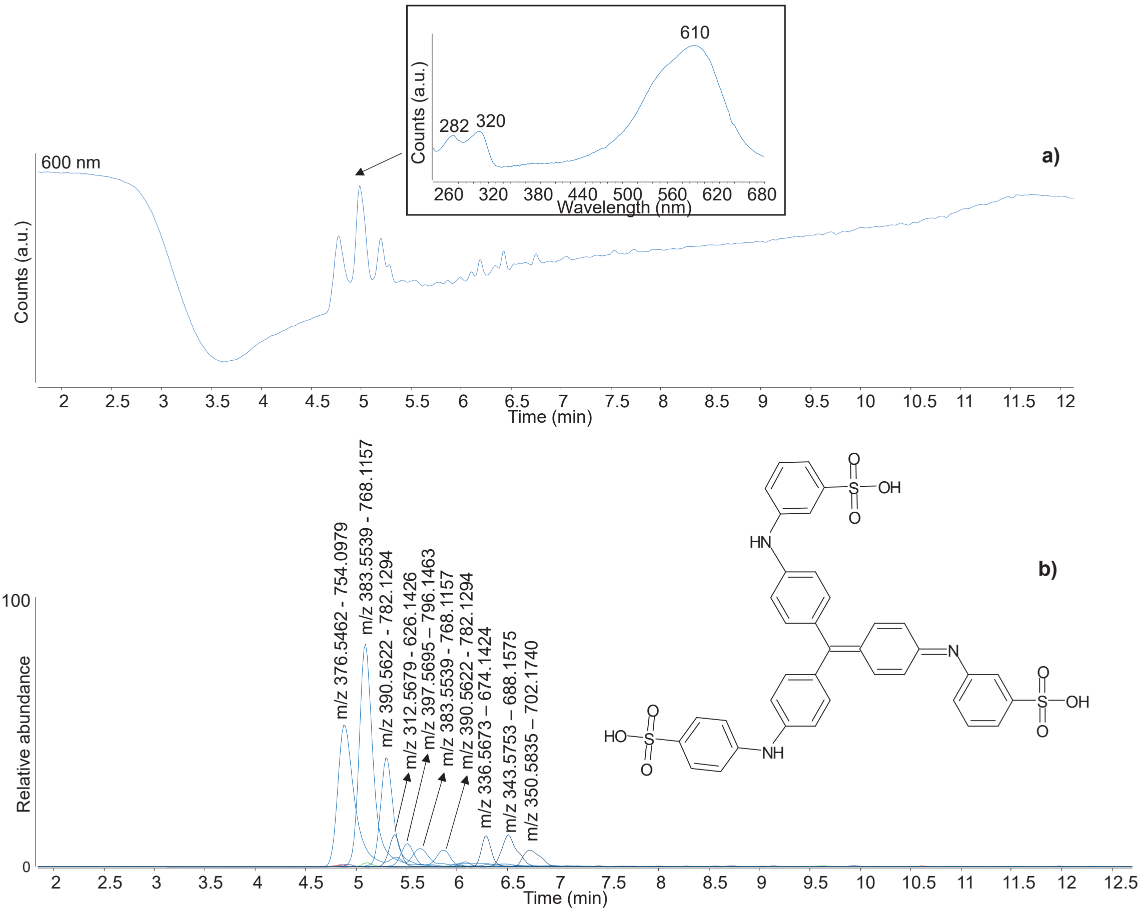

Figure 10. DAD (**a**) and negative ionisation extracted ion (**b**) chromatograms obtained by HPLC-DAD-MS/MS analysis of the blue sample from P2. The insert reports the UV-Vis spectrum of one of the molecular components. The experimental masses of the pseudomolecular ions are reported as pairs of doubly charged $[M-2H]^{2-}$ and single charged $[M-H]^{-}$ ions. The molecular structure of methyl blue ($[M-2H]^{2-}$ = *m/z* 376.5460 and $[M-H]^{-}$ = *m/z* 754.0993) is included.

Methyl violet compounds were also detected in the blue sample as part of the colour transfer from the purple damask textile.

The HPLC analysis of the pink sample showed the presence of four molecules, which corresponded to the main components of fuchsin (C.I. 42510), i.e., pararosaniline and its methylated, dimethylated and trimethylated derivatives (Figure 11) [25,50]. This dye is also referred to as magenta, and in the early synthetic process, the molecules were obtained by heating an oxidant with a coal tar distillate (or aniline oil) containing a mixture of aniline and toluidine at various ratios so that the resulting molecules were expected to be a mixture of pararosaniline and its methylated derivatives [51,53]. In 1889, the so-called new magenta started to be produced by condensing 4,4′-methylene-di-*o*-toluidine and *o*-toluidine with the aim of producing pure trimethylpararosaniline [51,53]. It is, therefore, evident that the fuchsine used in the pink sample is produced with the early process, which was adopted as early as 1858 [52]. The result was supported by the analysis of reference samples of magenta and new magenta, with magenta samples showing a distribution of the four molecular components similar to the pink sample, whereas new magenta samples showed a very different distribution with trimethylpararosaniline as the main component (Figure S5c,d—Supplementary Material).

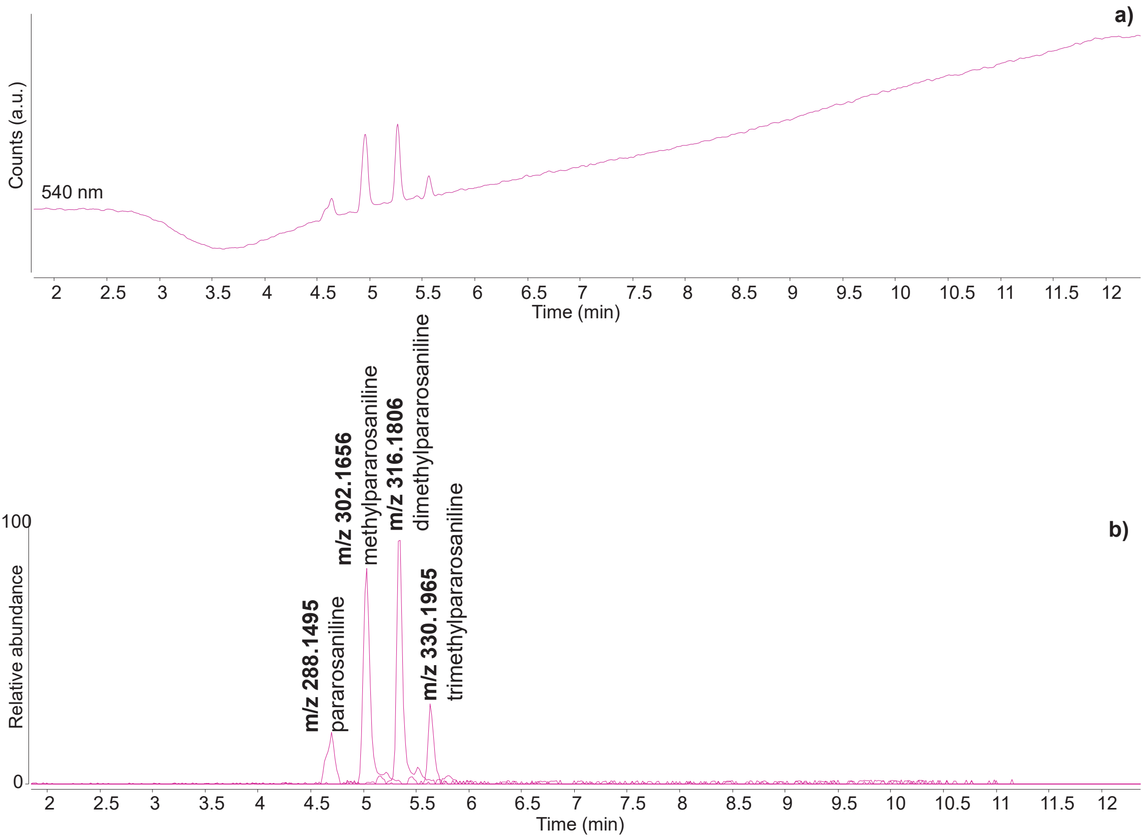

Figure 11. DAD (**a**) and positive ionisation extracted ion (**b**) chromatograms obtained by HPLC-DAD-MS/MS analysis of the pink sample from P2. The experimental masses of the molecular ions $[M]^+$ are reported.

The HPLC analysis of the brownish sample also revealed the presence of fuchsin synthesised with the early process method. Urolithin C was also detected, highlighting that this textile was dyed with a mixture of fuchsin and sappanwood (Figure S6—Supplementary Material). The discolouration of sappanwood to brownish shades is documented [11]; hence it is reasonable to suggest that this textile would have originally looked more reddish/pinkish than it appears today.

3.3. *P3-Twelve-Panel Screen Painting of Scenes of Five Confucian Virtues*

The FORS spectra were collected from the four areas of interest (blue cotton, blue silk, brown silk and pink silk). The blue cotton showed the characteristic inflection point of indigo at ca. 720 nm [54,55] (Figure 12a). The reflectance spectra from preserved and discoloured areas of the blue silk damask showed broad absorption bands centred at ca. 610 nm (Figure 12b), similar to what was observed for the blue textile of P2 (Figure 7b), thus suggesting the possible presence of methyl blue. The reflectance spectrum of the brown area was almost featureless, except for a small absorption band at around 580 nm (Figure 12c), which was difficult to interpret. The spectrum of the pink colouration only showed an inflection point at ca. 585 nm (Figure 12d), not specific enough to hypothesise the source of the colour.

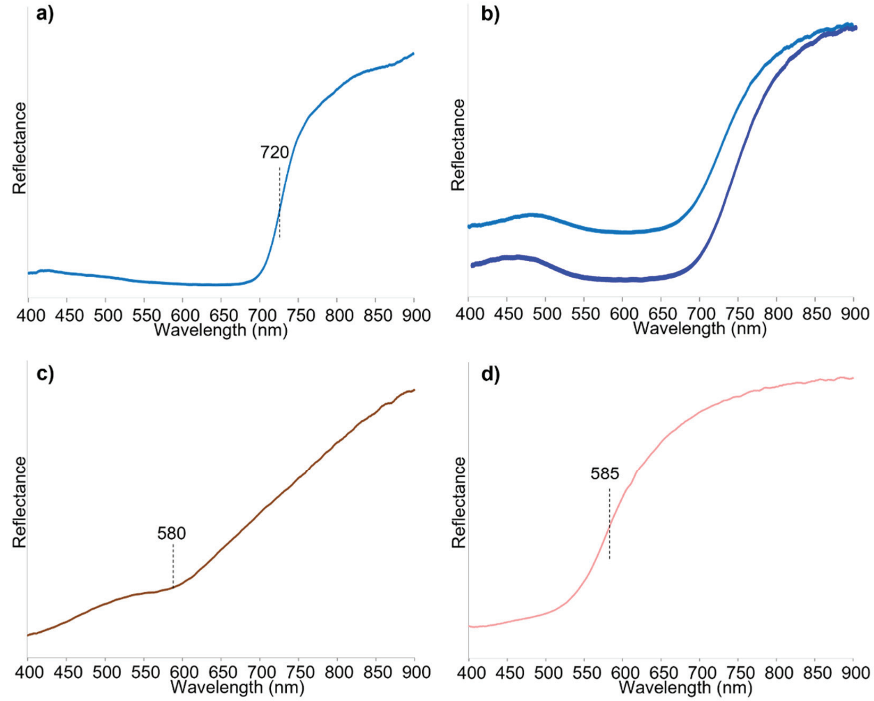

Figure 12. Reflectance spectra obtained by FORS analysis of P3 corresponding to (**a**) blue cotton; (**b**) blue silk; (**c**) brown silk textile; (**d**) pink silk textile.

As a consequence, four samples were taken from the four areas, and the microscopy images are shown in Figure S7 (Supplementary Material). The observations under the microscope revealed that the blue cotton textile was dyed as a fabric, as visible by the alternate colour pattern on the thread, indicating that the colour did not penetrate homogeneously due to the warp/weft structure. By contrast, a homogeneous dark blue colour was visible on the sample taken from the blue silk damask. The brown sample revealed a pinkish tone to it and a significant brittleness of the silk fibres. The pink sample appeared to be composed of fine silk fibres attached to a paper support, as all of the narrow strips were lined with thin paper. The pink colour appeared to emit a weak luminescence under UV light

The HPLC analysis confirmed the presence of indigo in the blue cotton sample. Indigotin and indirubin were identified (Figure S8—Supplementary Material).

Methyl blue was again identified in the blue silk damask, showing a very similar molecular distribution to the blue sample in P2 (Figure S9—Supplementary Material).

The sample taken from the brown silk damask was found to be dyed with a mixture of hydrolysable tannins–identified by the detection of ellagic acid and fuchsin synthesised via the early process (Figure S10—Supplementary Material). This dye combination is reported to obtain dark shades of magenta colour [52] and justifies the pink/purplish hue observed in the microscopy image as well as the brittleness of the fibres, as tannins are reported to enhance fibre degradation [39,40,56,57]. It is reasonable to have expected the red/pink hue to be originally more vibrant on this textile.

The HPLC analysis of the sample taken from the pink textile revealed the presence of three molecules, which were detected in the negative ionisation mode and produced doubly charged $[M\text{-}2H]^{2-}$ ions accompanied by weaker single charged $[M\text{-}H]^{-}$ ions (Figure 13). One of these molecules showed $[M\text{-}2H]^{2-}$ = *m/z* 339.0683 and $[M\text{-}H]^{-}$ = *m/z* 679.1439, which correspond to the chemical formula $C_{34}H_{28}N_6O_6S_2$. The other two molecules showed $[M\text{-}2H]^{2-}$ = *m/z* 345.0683 and $[M\text{-}H]^{-}$ = *m/z* 691.1439, and $[M\text{-}2H]^{2-}$ = *m/z* 351.0683 and $[M\text{-}H]^{-}$ = *m/z* 703.1439, corresponding to $C_{35}H_{28}N_6O_6S_2$ and $C_{36}H_{28}N_6O_6S_2$, respectively. The result produced a match with a reference sample of benzopurpurin 4B (C.I. 23500) available from the book "A Manual of Dyeing: For the Use of Practical Dyers, Manufacturers, Students, and All Interested in the Art of Dyeing (Specimen of dyed fabrics)" [38] (Figure S5e—Supplementary Material). The smaller molecule is the one corresponding to the actual formula of benzopurpurin 4B, whereas the other two molecules appear to have one and two additional carbon atoms, respectively. These compounds have been recently elucidated by Chen et al. [23] as deriving from a reaction with formaldehyde followed by cyclization on one or both sides of the molecule. Our MS/MS data are in perfect agreement with the ones reported in the literature [23]. Benzopurpurin 4B is a disazo dye that was first synthesised in 1884 [52].

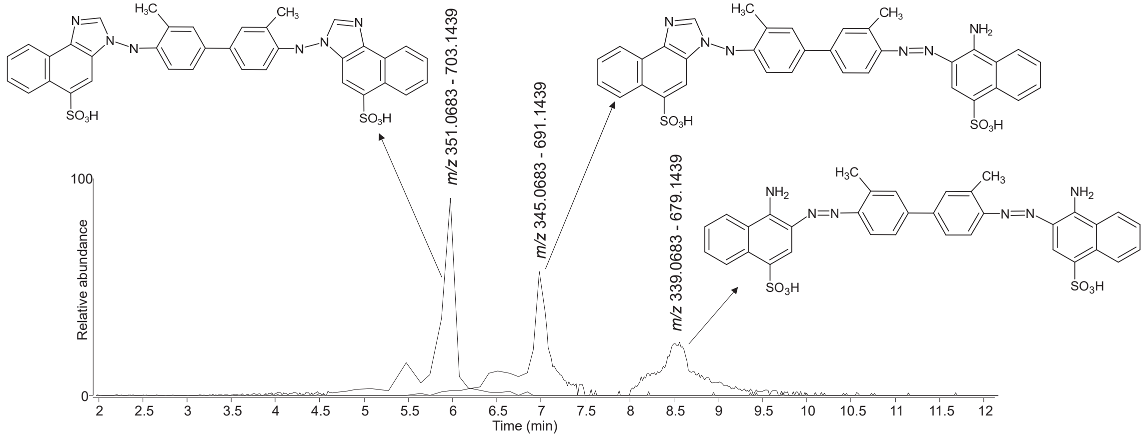

Figure 13. Negative ionisation extracted ion chromatograms obtained by HPLC-DAD-MS/MS analysis of the pink sample from P3. The molecular structure of benzopurpurin 4B and the two degradation products is included.

4. Conclusions

The scientific investigation conducted on the textile borders and other mounting elements of three traditional Korean paintings revealed the different dyes used. FORS proved to be useful in identifying some of the natural dyes, such as indigo, safflower red and sappanwood but confirmed its limitations in identifying yellow dyes. It was also useful to indicate the possible presence of synthetic dyes and to point towards the dye class, although a univocal identification was often not possible.

HPLC-DAD-MS/MS was therefore needed to provide a molecular identification of these dyes. Natural dyes were exclusively found on P1 (1996,0329,0.1). The use of indigo for various shades of blue, safflower for red, and a mixture of sappanwood and amur cork tree for orange were in agreement with traditional Korean dyeing practices in the 18th century.

Both natural and synthetic dyes were found in P2 (2016,3028.1) and P3 (1957,1214,0.1). Methyl violet 3B (C.I. 42536), methyl blue (C.I. 42780), fuchsin (C.I. 42510) and benzopurpurin 4B (C.I. 23500) are all early synthetic dyes, with benzopurpurin 4B being the latest one synthesised in 1884. Although it is difficult to establish exactly how long after their invention these dyes reached Korea and started being used, it is reasonable to assume that these textiles were dyed before the end of the 19th century. Of particular interest were the mixtures of natural and synthetic dyes, such as fuchsin and sappanwood/tannins. These mixtures are mentioned in early commercial formulations and dyeing recipes but could also suggest that the dyeing occurred at a time when synthetic dyes had just started to be introduced, hence dyers were still experimenting with these newly available products.

The light sensitivity of most of these dyes is known to be problematic, as was evident during the conservation process. This information contributed to the decision to retain or replacing the mounting elements of these paintings, which are now conserved and temporarily exhibited at the British Museum.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/heritage6010003/s1, Figure S1: Coloured areas of the mounting elements of hanging scroll 1996,0329,0.1 (P1) investigated. © The Trustees of The British Museum; Figure S2: Coloured areas of the textile borders of two-panel screen painting 2016,3028.1 (P2) investigated. © The Trustees of The British Museum; Figure S3: Coloured areas of the textile borders of twelve-panel screen painting 1957,1214,0.1 (P3) investigated. © The Trustees of The British Museum; Figure S4: Microscopic images of the samples taken from P2 under visible (a–c) and UV (a'–c') light. Image for the purple sample is not available; Figure S5: Positive ionisation (a) and negative ionisation (b) extracted ion chromatograms obtained by HPLC-DAD-MS/MS analysis of the brown sample from P2; Figure S6: Microscopic images of the samples taken from P3 under visible (a–d) and UV (a'–d') light. (a,a') blue cotton; (b,b') blue silk; (c,c') brown textile; (d,d') pink textile; Figure S7: DAD chromatogram obtained by HPLC-DAD-MS/MS analysis of the blue cotton sample from P3. The UV-Vis absorption spectrum of indigotin is reported in the insert; Figure S8: Negative ionisation extracted ion chromatograms obtained by HPLC-DAD-MS/MS analysis of the blue silk sample from P3; Figure S9: DAD chromatograms obtained by HPLC-DAD-MS/MS analysis of the brown sample from P3. Figure S10. DAD chromatograms obtained by HPLC-DAD-MS/MS analysis of the brown sample from P3.

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Article

Giving a New Status to a Dyes Collection: A Contribution to the *Chromotope* Project

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Abstract: Chromotope, the 19th Century Chromatic Turn, is a multidisciplinary ERC research programme that focuses on the “chromatic turn” of the 1860s in France and England, following the invention of the first synthetic dyes. This project, based on a partnership between Sorbonne University (PI: Charlotte Ribeyrol), Oxford University, and the Conservatoire national des arts et métiers (Cnam), investigates how this turn led to new ways of thinking about colour in art, literature, history, and science throughout the second half of the 19th century. One of the key aims of this research is to reappraise the role played by the Cnam in the dissemination of knowledge about synthetic dyes, from the creation in 1852 of the first chair in dyeing and printing until the Interwar period, when a collection of dyes including more than 2500 references, obtained from major European firms, was formed. A full inventory based on the description of each container has just been made together with a bibliographical research. Nevertheless, 2% of the containers are unlabeled and the reattribution of their composition is the main goal of our study. In order to set an appropriate analysis protocol to identify these orphan containers, a preliminary work was conducted on a random selection of identified dyes. For this purpose, electrospray ionization mass spectrometry and Fourier-transform infrared spectroscopy were used on 13 samples from different dye classes. The relevance of this protocol will be discussed for the identification of unknown compounds.

Keywords: synthetic dyes; industrial heritage; ESI-mass spectrometry; FTIR spectroscopy

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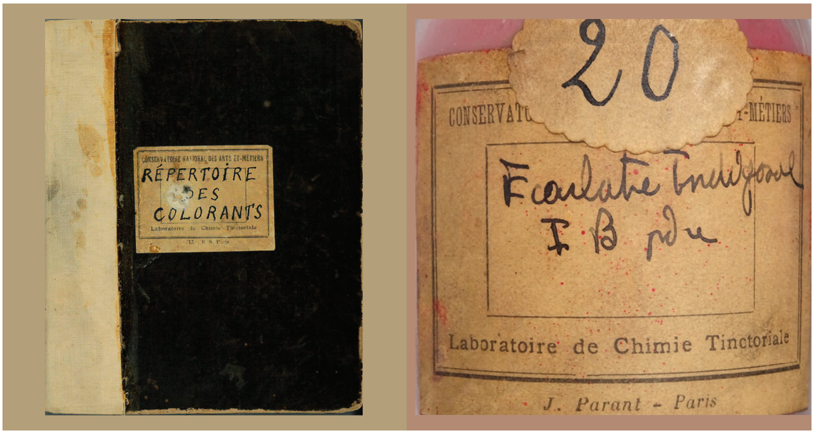
1. Introduction

The Conservatoire national des arts et métiers (Cnam) in Paris was founded in 1794 by Abbé Grégoire to support the new processes and technical innovations in the field of industry. Until today, it has been a major teaching center based on the practice and experience of skills acquired through application, and renowned for its defence of education for all. The musée des Arts et Métiers, which is part of the Cnam, has been involved in the preservation of technical and industrial heritage since its creation. Thus, the museum is particularly interested in objects or material testimonies that have enabled or represent major technological developments in various fields. Both institutions are participating in the ERC’s Chromotope, the 19th Century Chromatic Turn [1], held by Sorbonne University in Paris, which aims to better understand the cultural impact of the emergence of synthetic dyes in Europe in the second half of the 19th century. Indeed, the discovery of these new materials in Europe at the end of the 1850s transformed the way of thinking about colour. Synthetic dyes revolutionized the European textile dyeing and printing industry, radically modifying technical processes and diversifying the range of accessible colours. In this context, together, the musée des Arts et Métiers along with the molecular chemistry team of the GBCM laboratory from the Conservatoire have conducted a study on a synthetic dyes collection from the 20th century related to the teaching of dyeing and printing techniques at the Cnam, introduced in Figure 1.

Figure 1. Some dyes from the Cnam's collection. Copyright © 2022 Photo by Irene Bilbao Zubiri, musée des Arts et Métiers, Cnam.

Indeed, the Conservatoire took part in the history of this upheaval by creating in 1852, as a result of the Paris Chamber of Commerce funding, the first chair dedicated to the "Dyeing, Printing, and Finishing of Textiles". This chair, whose creation was almost synchronous with the discovery of the first synthetic dye in 1856 by Sir William Henry Perkin in England [2], aimed to meet the labour needs of Parisian textile printing companies. Jean-François Persoz (1805–1868), a Swiss practitioner and academic who trained with Louis Thénard at the Collège de France and wrote a famous Handbook [3], was appointed as the first professor. Four other professors succeeded him, but the content of the chair has evolved over time and has changed its name several times. The history of this chair and its evolution are well-known [4,5], and the period of interest here is that of André Wahl (1872–1944) [6], appointed in 1918 to the chair renamed chair of "Dyeing Chemistry". The chair kept this name until 1941, when it was renamed "Organic Chemistry for applications".

These dyes, collected as early as 1918 and until the 1970s, were probably used for educational purposes. However, there is no mention of their use in the rare documents relating to this chair, but its link is attested by the dye directory, a handwritten notebook that was retrieved at the same time as the collection, listing all the dyes and whose label on the front cover mentions the Cnam and the Dyeing Chemistry laboratory. Moreover, some objects of this collection have replacement labels, which also confirms their link with the chair. Both labels are presented in Figure 2. Moreover, in the dye directory, a number has been assigned to each container manufacture per manufacture, that allows us to identify each item. It brings also a dating element, as for the first dyes listed; Colour Index numbers are given, which refer to the first edition of the Colour Index of 1924 [7]. These data are consistent with the period of the chair of André Wahl.



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

Figure 2. (**a**) Front cover of the dye directory. (**b**) Replacement label from Durand et Huguenin's manufacture. Copyright © 2022 Photo by Irene Bilbao Zubiri, musée des Arts et Métiers, Cnam.

Moreover, as this collection of synthetic dyes was given to the museum at the time of the removal of the laboratory which sheltered it, at the beginning of the years 2000, this study aims to carry out the necessary research to register its heritage status [8], while contributing the maximum information. A particular approach has been taken for the containers that no longer have their labels. Our final aim is to give the orphan vials the status of heritage object and thus to determine which compounds they contain. For this purpose, we have chosen to analyse a small selection of labeled dyes in order to establish a suitable analytical protocol that will allow the identification of unknown dyes in the near future.

Many different techniques have been successfully used in the past to characterize natural and synthetic dyes in heritage objects, beyond the multi-technique approach that seems to be the most suitable protocol to characterize dyes [9–11]. On the one hand, analytical separation methods such as high-performance liquid chromatography (HPLC) combined with mass spectrometry [12–16] have been successfully performed and can provide a lot of information about the dyes' structure and their degradation products. In addition, non-invasive techniques are usually employed and their advantages and disadvantages have been highlighted in the literature [17]. Among these techniques, UV-Vis-NIR spectroscopy [18] and Raman spectroscopy [19–25] are mainly used. In the field of heritage conservation, often the dyes that are being examined have been used to dye textile fibres and so an extraction process is usually needed to get them off the fibre [26–29]; in addition, in the case of dyes with a high tinting strength, very little dye is actually present. Moreover, the frequent presence of dye mixtures further complicates the identification work and requires extensive reference work [30]. In addition, often the small amount of dye used to colour the fiber makes analysis difficult in the case of dyes with high dyeing strength [31,32]. In our study, these issues did not concern us because we had the advantage of working on powders, and assumed that the raw materials of the collection were free of mixtures insofar as these dyes were generally mixed later directly in the dye baths.

In our particular aim to identify the dyes in the unlabeled vials, we decided to combine two proven techniques: electrospray ionization mass spectrometry (ESI-MS) and Fourier-transform infrared spectroscopy (FTIR) [33–36]. ESI-MS as well as FTIR spectroscopy have been successfully used with other techniques by Longoni et al. [33] for the analysis of dyes very similar to those in the museum collection.

2. Materials and Methods

2.1. Inventory Work and Bibliographical Research on Dyes

The inventory work on the dye collection consisted of weighing, measuring, and giving detailed descriptions of each container. Photographs were also taken to assess a state of conservation at the time of the inventory. This work was carried out by first meeting the museum's inventory criteria and by relying on the pre-inventory work carried out in 2018 by the museum's inventory department. At that time, the containers were classified by manufacture and lists were drawn up of the containers present or absent in relation to the dye directory. The heritage we had at our disposal was therefore made up of containers from various factories, labelled or not, and some labels removed from the flasks. The classification work made it possible to locate them and to assign them an inventory number in the museum's database with one record per object.

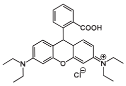
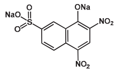
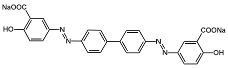
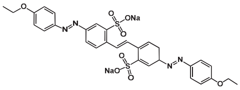
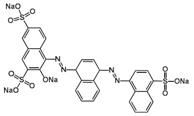
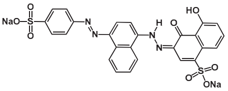
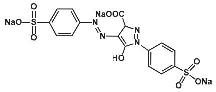
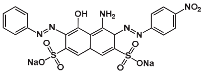
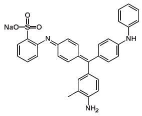
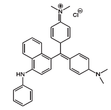
In parallel, we have carried out a bibliographical work [37–40] on the dyes present and well-named in the collection with the research of historical data on the one hand and chemical characteristics on the other hand to better define these dyes. Similarly, a great deal of work had to be done on containers that had very degraded and illegible labels or that had lost their labels, in order to attribute them to a manufacture and sometimes even to identify the dye from visual observations. These attributions are based on the typologies of the containers or flasks, sometimes on fragments of labels or on detached labels to re-attribute a flask.

2.2. The Collection and the Analysed Samples

About 2% of the collection involves gaps of attribution, as the concerned containers have lost their labels. Thus, we chose to perform chemical analyses on a selection of labeled vials containing dyes referenced in the literature [41]. These analyses performed on known products should be good indicators in terms of purity and chemical stability of the collection and should allow us to control the efficiency of the techniques chosen to analyse the different families of molecules and to evaluate the interest or the need of additional analyses. The first step in this work was to test the possibility of opening the containers as some of them cannot be opened because they kept their original corking, but also because these ancient stoppers present a certain resistance. It was a criterion included in the inventory work to know, before any sampling or analysis is considered and without further manipulation, the possibility of sampling each dye. For this purpose, 13 flasks were selected from 4 manufacturers. Before analysing the dyes, we were interested in the chemical properties of these compounds. Some parameters such as dye formula, molecular weight, dye class, and CAS number were collected. The dyes selected belong to different dye classes, taking into account that, for instance, azo dyes are much more represented in our collection (26% against 6% for anthraquinone dyes, for example). The compounds chosen were: Rhodamine B **1**, Naphthol yellow S extra **2**, Chrysamine G **3**, Chrysophenine G **4**, Naphthol black 6B **5**, Victoria black B **6**, Tartrazine **7**, Naphthylamine black 4B **8**, Alkali blue 4B **9**, and Victoria blue B **10**. Some of this data are summarized in Table 1 and supplemented in Section 3.

In addition, we have also compared samples with the same compound, produced by different companies: two vials for Rhodamine B **1** (one from Bayer and the other from Manufacture lyonnaise) and three vials for Alkali blue 4B **9** (two different from Bayer and one from Saint-Denis), in order to confirm and compare their composition, giving a total of 13 vials together. Indeed, the nomenclature of the dyes is an essential point which remains to be explored since, for certain products, several commercial names can correspond to the same molecule. It was decided to take samples only from unsealed vials (Figure 3). A very small quantity of powder was taken from the heart of the vial, excluding samples from areas exposed to light, as degradation could be observed in the case of photosensitive dyes. In the time available, the analysis strategy was to limit itself to one or two analytical techniques in order to obtain a quick response. For this purpose, ESI-MS and FTIR spectroscopy were chosen for this selection of dyes [42].

Table 1. Analysed samples, chemical information, and factories which have produced them.

Sample Number	Name	Class of the Dye	Molecular Weight	Molecule	Manufacture
1	Rhodamine B	xanthene	478.0		Bayer [1] M. lyonnaise [2]
2	Naphthol yellow S extra	nitro	358.2		Saint-Clair [3]
3	Chrysamine G	diazo	526.4		Bayer [1]
4	Chrysophenine G	diazo	680.7		Bayer [1]
5	Naphthol black 6B	diazo	860.7		M. lyonnaise [2]
6	Victoria black B	diazo	622.5		Bayer [1]
7	Tartrazine	monoazo	534.4		Saint-Clair [3]
8	Naphthylamine black 4B	diazo	616.5		Saint-Clair [3]
9	Alkali blue 4B	triarylmethine	555.6		Bayer [1] Saint-Denis [4]
10	Victoria Blue B	triarylmethine	506.1		Bayer [1]

[1] Farbenfabriken vormals Fried. Bayer & Co. [2] Manufacture lyonnaise de matières colorantes. [3] Compagnie française de produits chimiques et matières colorantes de Saint-Clair-du-Rhône. [4] Société des matières colorantes et produits chimiques de Saint-Denis.

Figure 3. Tartrazine from Compagnie française de produits chimiques et matières colorantes de Saint-Clair-du-Rhône. Copyright © 2022 Photo by Irene Bilbao Zubiri, musée des Arts et Métiers, Cnam.

2.2.1. ESI-Mass Spectrometry

A Shimadzu LCMS-2030 instrument was used, equipped with an automatic injector, electrospray ionization (ESI), and a quadrupole analyzer. The compounds were dissolved in methanol with a concentration of 0.1 mg/mL and no preliminary separation by liquid chromatography was carried out before direct injection into the mass spectrometer. Operation of the system and data analysis were performed using the LabSolutions software, and molecular detection was carried out in both the negative and positive ionization modes. The ESI experimental conditions were: interface voltage 4.5 kV, interface temperature 450 °C, desolvation line temperature 250 °C, nebulizing gas flow 0.5 mL/min, and heat block temperature 200 °C. MS data were acquired in the range 300–1000 m/z at scan speed 1500 u/s, and with Q-array RF voltage 60 V.

2.2.2. FTIR Spectroscopy

Infrared spectra were recorded over the 400–4000 cm^{-1} range with an Agilent Technologies Cary 630 FTIR/ATR/ZnSe spectrometer. All the samples were examined between 4000 and 650 cm^{-1}, at a resolution of 8 cm^{-1}, representing an average of 16 scans. The software used to acquire the spectra was MicroLab PC. The spectra were registered in transmission mode. The dyes, originally in a powder state, did not need additional sample preparation. These analyses were only carried out for compounds whose purity was attested by mass spectrometry.

3. Analytical Results

3.1. The Collection

First of all, the museum's collection includes about 2630 containers from 25 European manufacturers from France, Germany, Switzerland, and England. In the early 20th century, many manufacturers worked with subsidiaries in foreign countries [43], as shown in the graph with the German and Swiss subsidiaries in France (Figure 4). This is the case, for instance, with the German manufacturer Farbenfabriken vormals Fried. Bayer & Co, which opened in 1863 a subsidiary under the same name in the north of France, or with Meister Lucius & Brüning, which opened a subsidiary in France, the Compagnie parisienne des couleurs d'aniline in 1888. In fact, since the second half of the nineteenth century, Germany has had a monopoly on the dye market, which is confirmed in our collection, since German production, whether in Germany or in France, is the most represented [44,45].

Other collections of dyes for educational purposes of this type exist in Europe, such as the German collections of Dresden and Cologne studied in the framework of the Weltbunt project [46,47]. These collections provide a better understanding of the circulation of dyeing materials in the late 19th and early 20th centuries.

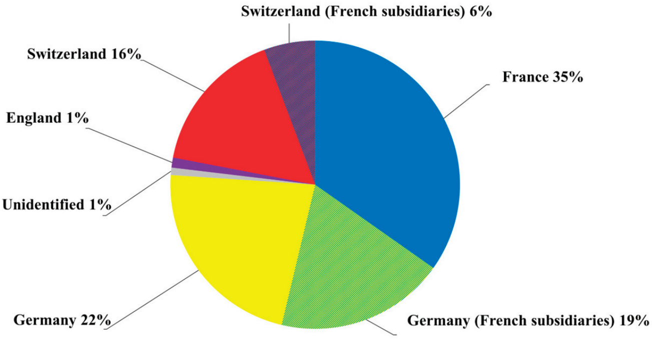


Figure 4. Distribution of the collection by country.

The vast majority is stored in glass containers, but the museum also owns 65 metal and 15 plastic containers. Among the glass bottles, there are different types of stoppers, mainly depending on the manufacturer, and almost 17% of the flasks keep the original glass stopper covered with paper, leather, or wax, and have never been opened (Figure 5). The dyes are mostly in powder form and this is particularly interesting in terms of analysis and sampling, in contrast to the analysis of textile samples which are more commonly studied [48,49]. The vials contain, on average, around 140 g of dye, and sampling does not denature the object.

Figure 5. Sealed flask from B.A.S.F.: Fuscaline orange GN powder. Copyright © 2022 Photo by Irene Bilbao Zubiri, musée des Arts et Métiers, Cnam.

Among the conservation issues encountered, we noticed on some bottles of this collection that the papers labels were degraded. Almost all the flasks from A.G.F.A. (Aktiengesellschaft für Anilinfabrikation), B.A.S.F. (Badische Anilin & Soda-Fabrik), and Société chimique des usines du Rhône have powdery labels on their entire surface (Figure 6). This very poor state of preservation was probably aggravated by the poor storage conditions. However, as all labels are damaged, the quality of the paper is certainly an aggravating factor. On the other hand, the labels of the Bayer factory are partly damaged because of an old pressure-sensitive adhesive tape, often on the name of the dye, that has become hard and highly discoloured. In this area, the yellowish-brown adhesive appears to have penetrated the paper, which is quite common on archives, books, and paper artworks [50]. It was beyond the scope of the current work to carry out analysis of the adhesive of the deteriorated pressure-sensitive tape. Unfortunately, half of Bayer’s labels are degraded, detached, or lost. We have been led to ask ourselves how to approach these objects of unknown composition in order to give them heritage status. We have therefore made hypotheses about their composition not only based on the fragments of labels still visible and the colours of the dyes, but also by referring to the dye directory. However, these hypotheses, which are often based on a limited number of elements, are not satisfactory for identifying them. Our objective is to identify the structures of the dyes contained in these flasks, by carrying out a series of chemical analyses, and to reassign their labels when they become available.

Figure 6. Pulverulent label from Société chimique des usines du Rhône: Phloxine TA extra. Copyright © 2022 Photo by Irene Bilbao Zubiri, musée des Arts et Métiers, Cnam.

3.2. The Analytical Data

3.2.1. Xanthene Dyes

One xanthene dye was analysed, Rhodamine B **1** [CAS 81-88-9, C.I. 45170], a red dye discovered in 1887 by M. Ceresole and marketed one year later by the Farbenfabriken vormals Fried. Bayer & Co. and by the Société pour l'Industrie Chimique in Basel. Its generic name is "basic violet 10". Here, two samples from two different factories, one German and one French, Bayer and Manufacture lyonnaise de matières colorantes, were analysed. The data presented here are from the analysis of the French manufacturer container. The results of the mass spectrometry and infrared spectroscopy analyses show that they are the same molecule, illustrating a good correspondence of the nomenclature between two dyes from two different European factories. Negative ionization ESI-MS analysis confirmed the presence of the expected dye with a base peak at *m/z* = 443 attributed to $[M\text{-}Cl]^+$ and a second peak at *m/z* = 444 attributed to [M+H-Cl] (Figure 7). Although a photo-degradation process of several rhodamines, including Rhodamine B **1**, has been reported in the literature [51], in the case of our vial, the product did not undergo degradation and remained pure.

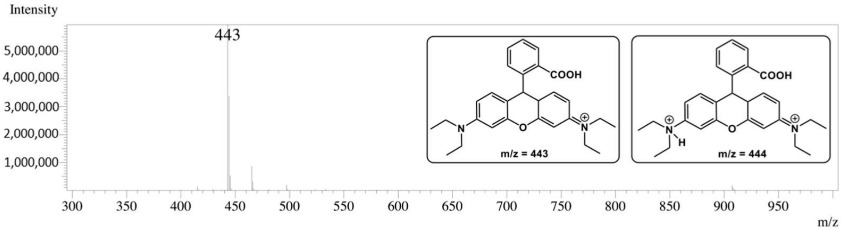


Figure 7. ESI-MS spectrum of Rhodamine B **1**.

The infrared spectrum of Rhodamine B **1** is reported in the literature [52]. It shows a broad band at 3267 cm^{-1}, characteristic of stretching vibrations of the O-H group, and the band at 1691 cm^{-1} has been attributed to the stretching vibration of the C=O bond, both related to the carboxylic acid (Figure 8). The conjugated C=C double bonds of the xanthene ring give three bands of varying intensities at 1469, 1587, and 1644 cm^{-1}, attributed to the stretching-type vibration. The bending of the C-H bond of the diethylamine group is visible at 1409 cm^{-1} and the band at 1341 cm^{-1} is here attributed to the stretching vibration of the Ar-N bond of the same group. Finally, the band at 1074 cm^{-1} is attributed to the stretching vibration of C-O-H and the very intense band at 1002 cm^{-1} to the stretching of the C-O bond.

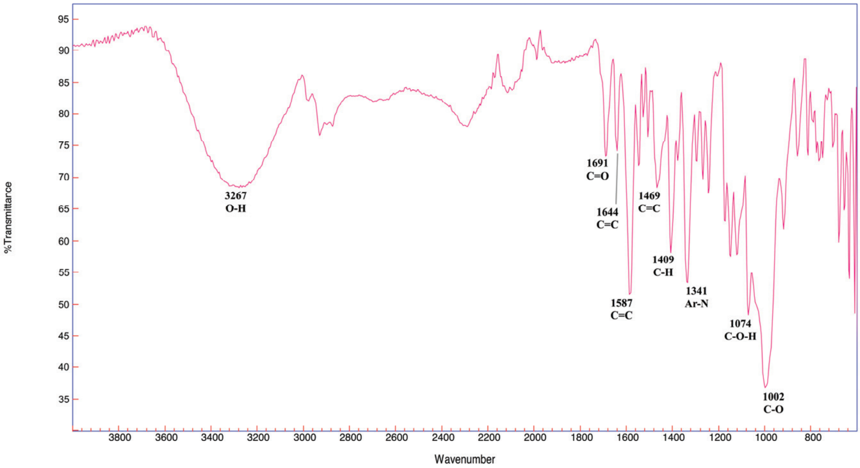


Figure 8. FTIR spectrum of Rhodamine B **1**.

3.2.2. Nitro Dyes

Naphthol yellow S extra **2** [CAS 846-70-8, C.I. 10316], a bright yellow dye belonging to the nitro dyes, was discovered in 1879 by Heinrich Caro from B.A.S.F., and was taken from a flask belonging to the Compagnie de produits chimiques et matières colorantes de Saint-Clair-du-Rhône. Its generic name is "acid yellow 1" and the extra mention refers to a product of great purity. The negative ionization spectrum for this compound gives a base peak at *m/z* = 313 attributed to [M+H-2Na]$^{-}$, resulting from the ionization of Naphthol yellow S **2** (Figure 9).

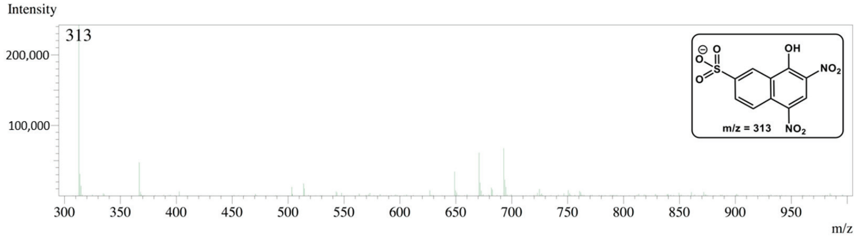


Figure 9. ESI-MS spectrum of Naphthol yellow S extra **2**.

Concerning the IR spectrum, as in the case of Rhodamine B **1**, the conjugated C=C bonds give three peaks of diverse intensity at 1458, 1583, and 1620 cm^{-1} (Figure 10). Concerning the two nitro groups, they should give a response for the N-O asymmetric stretch vibration in the range 1550–1475 cm^{-1} and the N-O symmetric stretch vibration around 1360–1290 cm^{-1}. In our spectrum, two bands at 1502 and 1323 cm^{-1} are attributed to the N-O asymmetric and symmetric stretching-type vibrations, respectively [53]. The band at 1323 cm^{-1} is here attributed to the S=O stretching-type vibrations of the sulfonate group and the strongest one at 1194 cm^{-1} can be assigned to the Ar-O stretching vibration on the naphthol ring.

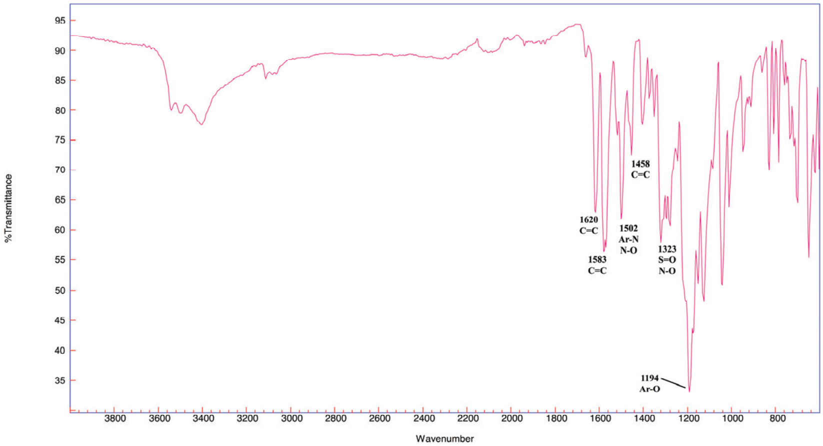


Figure 10. FTIR spectrum of Naphthol yellow S extra **2**.

3.2.3. Azo Dyes

Chrysamine G **3** [CAS 6472-91-9, C.I. 22250] is a diazo yellow dye that was discovered in 1884 by E. Franck. Its generic name is "direct yellow 1". An analysis by negative ionization mass spectrometry identified the peak at *m/z* = 503 attributed to the monosodium salt [M-Na]$^-$ and the base peak at *m/z* = 481 is assigned to [M+H-2Na]$^-$ (Figure 11). Moreover, the peak at *m/z* = 317 corresponds to an α-cutoff of the diazo bond.

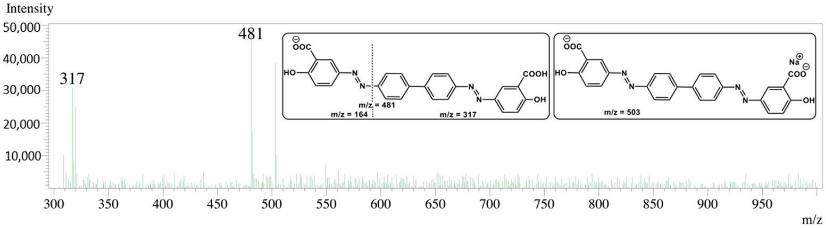


Figure 11. ESI-MS spectrum of Chrysamine G **3**.

The broad band at 3318 cm^{-1} is here attributed to the stretching vibration of the O-H band of both carboxylic acid and phenol (Figure 12). FTIR analyses on azo dyes are reported in the literature [54,55]. In our study, the band at 1583 cm^{-1} is assigned to the cumulative signal of the stretching vibration of the C=C and N=N bonds. Indeed, the 1400–1600 cm^{-1} region corresponds to the aromatic ring region, but between 1500–1600 cm^{-1}, we also have the signal of the azo bond, and usually the main band for this bond is around 1500 cm^{-1}. At 1457 cm^{-1}, the band is attributed to the C=C stretching vibration and the one at 1486 cm^{-1} to the azo bond. The very intense band at 828 cm^{-1} may correspond to a bending vibration on the Ar-H bond in trisubstituted aromatic rings.

Figure 12. FTIR spectrum of Chrysamine G **3**.

Victoria black B **6** [CAS 6226-94-4, C.I. 27510] was discovered in 1889 by M. Ulrich and C. Duisberg, and its generic name is "acid black 5". It was correctly identified in the negative ionization mode with a base peak at *m*/*z* = 599 which corresponds to the monosodium salt [M-Na]$^-$, but also with a secondary peak at *m*/*z* = 577 assigned to [M+H-2Na]$^-$ (Figure 13). The peak at *m*/*z* = 392 corresponds to an α-cutoff of the diazo bond. The three fragments assigned to this dye resulting from the ionization are very consistent with the composition expected. The mixing of compounds was a common practice in dyeing with natural or synthetic dyes, as has been pointed out in the literature [9,56,57]. It seems that mixing an orange dye with a black-based dye was a common practice to avoid purplish hues on black dyes. In [41], a textile sample theoretically dyed with Victoria black B contained orange I (*m*/*z* = 327). The peak we obtained at *m*/*z* = 327 could confirm this statement, even if it is very weak.

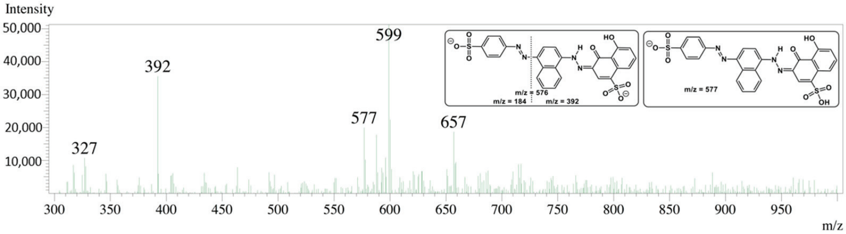


Figure 13. ESI-MS spectrum of Victoria black B **6**.

The infrared spectrum of Victoria black B **6** shows a broad band at 3381 cm^{-1} assigned to the stretching vibration of an O-H bond and the azo bond gives a response at 1497 cm^{-1} (Figure 14). Morever, the Ar-OH that is usually between 1000 and 1400 cm^{-1} is observed at 1000 cm^{-1}. This lower position is probably related to the sulfonate in para position as the substituent in the same benzenic ring. In addition, the sulfonate group should give a band between 1145–1200 cm^{-1}. Thus, in our sample the bands in the range 1145–1200 correspond to the stretching vibration in O-H and S=O. Moreover, the band at 1457 cm^{-1} is attributed to the stretching vibration of the C=C bond.

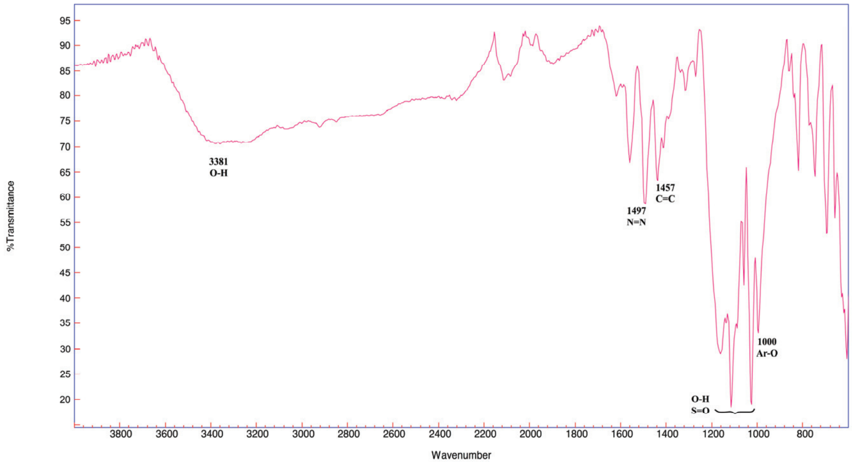


Figure 14. FTIR spectrum of Victoria black B **6**.

Naphthylamine black 4B **8** [CAS 1064-48-8, C.I. 20470] is a diazo dye whose family was discovered in 1888 by the German manufacture Leopold Cassella. Its generic name is "acid black 1". Negative ionization mode mass spectrometry analyses show a base peak at *m*/*z* = 690 and a secondary signal, very intense, at *m*/*z* = 610, which we have not attributed (Figure 15). A secondary peak at *m*/*z* = 571 is attributed to the ion [M+H-2Na]$^-$. Due to the numerous major bands we obtain, we assume a mixture of different dyes, perhaps with the same intention on black dyes mentioned above.

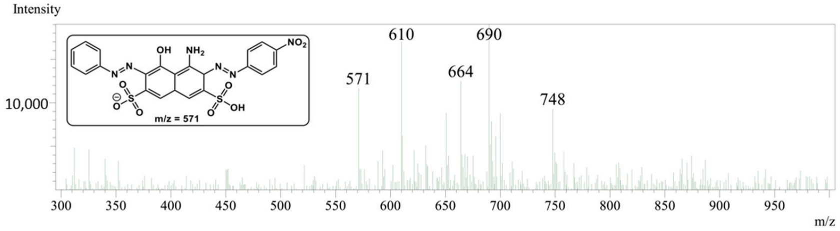


Figure 15. ESI-MS spectrum of Naphthylamine black 4B **8**.

Among the azo dyes that were analysed, three could not be identified by mass spectrometry. First, the yellow-orange monoazo dye Tartrazine **7** [CAS 1934-21-0, C.I. 19140], whose spectrum in both ionization modes shows too many peaks and none can be assigned to the expected dye. These statements suggest that this sample has probably degraded. This dye was not successfully identified on the fiber either, as reported by Baker in 2011 [26]. Secondly, Naphthol black 6B **5** [CAS 8004-66-8, C.I. 27240] was analysed and the mass spectrum shows numerous peaks throughout the spectrum range and the expected compound could not be identified, suggesting degradation as with the dye mentioned above. Thirdly, the analysis of the yellow dye Chrysophenine G **4** [CAS 2870-32-8, C.I. 24895] also provided attribution difficulties. In the negative ionization mode, we obtained a base peak at *m/z* = 303 that did not correspond to the dye expected or to an ion resulting from its fragmentation (Figure 16). Moreover, we observed a peak at *m/z* = 629, which does not correspond to this dye either. We conclude that we have found the presence of several unidentified compounds as the MS analysis gave a spectrum with three distinct peaks, which rather suggests a mixture of dyes than a degradation.

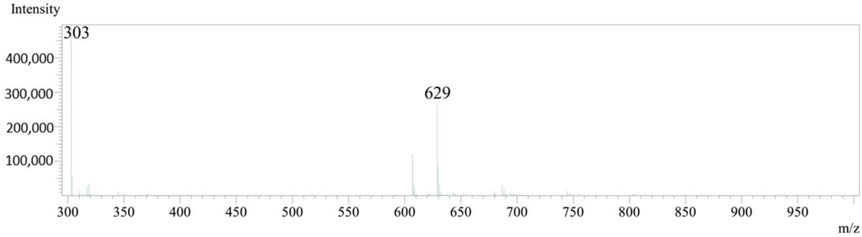


Figure 16. ESI-MS spectrum of Chrysophenine G **4**.

In these three cases, we can conclude that these products were not pure or have degraded. The protocol based on ESI-MS and FTIR spectroscopy analysis did not allow us to correctly identify these samples and other techniques should be used to confirm the presence of these compounds.

3.2.4. Triarylmethine Dyes

Alkali blue 4B **9** [CAS 62152-67-4, C.I. 42750] was discovered in 1862 by E.C. Nicholson and is identified in the Colour Index by the generic name "acid blue 110". Three samples of this dye, two different vials from Bayer and one from the Société des matières colorantes et produits chimiques de Saint-Denis, were analysed. Again, as in the case of Rhodamine B **1**, the ESI-MS and FTIR spectroscopy results give the same spectra, with minor differences in intensity in infrared spectroscopy. In the positive ionization spectrum, three peaks at *m/z* = 532, *m/z* = 531 and *m/z* = 530 can be observed. The peak at *m/z* = 532 is here attributed to $[M\text{-}Na]^-$ (Figure 17).

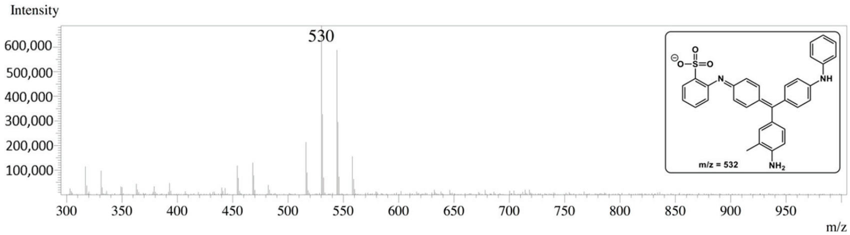


Figure 17. ESI-MS spectrum of Alkali blue 4B **9**.

In infrared spectroscopy, the band at 3347 cm^{-1} is attributed to the imine group and the Ar=N bond, as with the one at 1592 cm^{-1} (Figure 18). The band at 1495 cm^{-1} corresponds to the C=C bond stretching vibration in the aromatic ring but also to the azo bond, expected at approximately 1500 cm^{-1}. At 1312 cm^{-1}, we have a cumulative signal attributed to the Ar_2-N, Ar-NH_2, and S=O stretching vibration. The sulfonate group vibration is also present in the band at 1167 cm^{-1}. At 1120 cm^{-1}, the signal corresponds to the stretching vibration of the Ar-N bond and finally, at 1033 cm^{-1} we have a C-H bending vibration.

Victoria Blue B **10** [CAS 2580-56-5, C.I. 44045] is the second triarylmethine dye analysed. This blue dye was discovered in 1883 by Heinrich Caro and Adolf Kern. Its generic name is "basic blue 26". Mass spectrometry analysis allowed us to identify the peak at *m/z* = 471 to $[M\text{-}Cl]^+$, which proves the presence of the expected dye (Figure 19).

The FTIR spectrum of Victoria blue B **10** has been reported in the literature [58]. In our study, three distinct regions were identified between 1000 and 1600 cm^{-1} (Figure 20). Firstly, the band at 1582 cm^{-1} is here attributed to the bending vibration of the C=C of Ar=N^+ [59], or the stretching vibration of the aromatic C=C para-disubstituted ring (C-Ph-N). The one at 1490 cm^{-1} is related to the stretching vibration of C=C. The band at 1288 cm^{-1} is assigned to the stretching vibration of the C-N bond and the one at 1357 cm^{-1}

to the bending vibration of two bonds: CH_3 and N-H. Those at 1027 and 1162 cm^{-1} are here attributed to the Ar-H bond.

Figure 18. FTIR spectrum of Alkali blue 4B **9**.

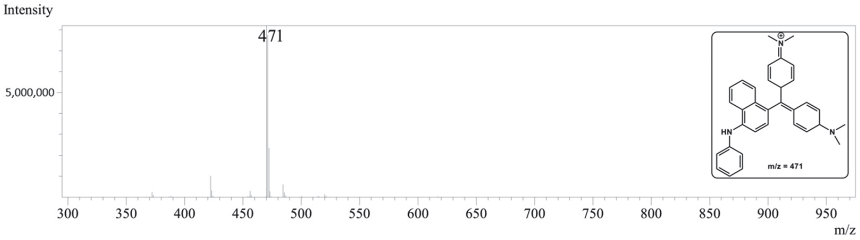


Figure 19. ESI-MS spectrum of Victoria Blue B **10**.

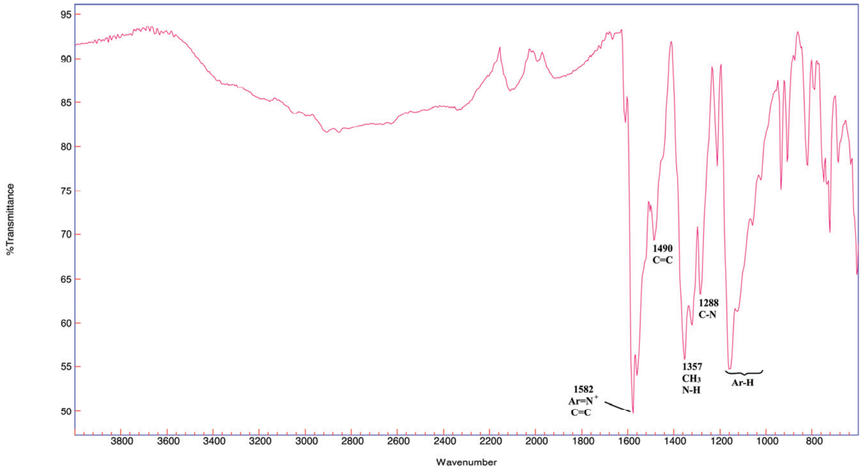


Figure 20. FTIR spectrum of Victoria Blue B **10**.

4. Conclusions

Analyses of the 13 samples corresponding to ten different dyes have helped to clarify some of the attribution issues. Nine samples corresponding to six different dyes were correctly identified by mass spectrometry and gave very consistent FTIR spectra. For the four remaining dyes, two cases were presented. Regarding the hypothesis of a mixture of a black dye with orange dyes, the analysis of Naphthylamine black 4B **8** could indicate that the mixing with dyes was done before the preparation of the dyebath, and before the marketing of the vials. To confirm this, it would be necessary to analyse a wider range of black samples. Moreover, mass spectrometry analyses of Chrysophenine G **4**, Naphthol black 6B **5,** and Tartrazine **7** did not allow us to identify these dyes. Moreover, the comparison of results for the same dye taken from vials of different manufactures was very conclusive, as the signals obtained attest to the same composition.

The analytical work carried out on a random selection of dyes has also allowed us to have a brief overview of the state of conservation of these compounds, which completes the visual observations made beforehand. Moreover, working on powdered dyes directly and without prior treatment of the samples represents a great advantage. Even if the dyes of the musée des Arts et Métiers collection are less pure than expected, these results are encouraging and the protocol could probably be applied to a particularly interesting part of the collection, the Bayer vials. Among the 288 dyes from this company, 47 containers have lost their labels. The next step will be to continue testing this group to identify the composition of these dyes, while referring to the dye directory and the currently missing dyes. ESI-MS and FTIR spectroscopy analysis seem appropriate for the identification of undegraded, unmixed compounds, as long as we know the molecular weights of the absent compounds. We plan to complete the characterization by other techniques such as UV-Vis spectroscopy when MS and FTIR spectroscopy do not provide sufficient identification arguments.

The collection of dyes will be accessible on the museum's database with limited scientific data, with each one signaled with a photograph and the commercial name of the product. This will allow a better knowledge of these chemicals and a broader perspective on the issues of the conservation of European chemical heritage.

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Data Availability Statement: The inventory work on the collection will be available on the musée des Arts et Métiers website at the following link https://www.arts-et-metiers.net/les-collections; (accessed on 14 February 2023).

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heritage

Article

Historical Textile Dye Analysis Using DESI-MS

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Abstract: Desorption electrospray ionization mass spectrometry (DESI-MS) is an ambient mass spectrometry technique that shows great potential for the analysis of fragile heritage objects in situ. This article focuses on the application of a recently built DESI source to characterize natural dyestuffs in historical textiles and a presentation of initial imaging experiments. Optimization of the instrumental settings, geometrical parameters, and solvent system on the DESI-MS analysis was conducted on rhodamine B samples. Some variables, including an increased flow rate, a narrower range of optimized geometrical variables and a solvent system without additives, were applicable to both early synthetic and natural dyes. Direct dye turmeric (*Curcuma longa* L.) could be reliably analyzed on both silk and wool, as could anthraquinone standards without mordanting. These preliminary results suggest that the dye application process (direct, mordant, vat) has a large impact on the ionization efficiency of DESI-MS. Imaging trials highlighted the suitability of DESI-MS for the analysis of patterned textiles that are difficult to sample, such as calico fabrics, or other currently inaccessible objects.

Keywords: mass spectrometry; non-invasive analysis; natural dyes; textile; mass spectrometry imaging

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1. Introduction

The analysis of dyes in heritage objects, in particular fragile objects such as textiles, requires a continuous development of new analytical approaches that reduce the physical impact of analysis on the objects whilst ensuring that maximum information is gained. The common techniques used in dye analysis are either invasive, e.g., liquid chromatography (HPLC, UHPLC) and mass spectrometry (MS) [1], requiring a sample to be physically removed from the object, or non-invasive, e.g., fiber optics reflectance spectroscopy (FORS) [2] or Raman spectroscopy [3], meaning that the analysis has no physical impact on the object. The analytical techniques used may also be destructive or non-destructive, resulting in the sample being consumed during analysis or not. Often a combination of both approaches is preferred, with non-invasive methods guiding object sampling [4–6].

Ambient MS techniques, such as desorption electrospray ionization (DESI) [7], matrix-assisted desorption electrospray ionization (MALDESI) [8], and direct analysis in real time (DART) [9], are non-invasive albeit micro-destructive techniques with a large potential to be used in dye analysis. Desorption electrospray ionization (DESI)-MS was developed in 2004 by the Cooks research group at Purdue University [7]. It is an electrospray ionization (ESI)-based technique that is popular for its versatility and speed. Ionization occurs outside of the MS inlet by an electrospray of charged liquid droplets being directed onto the sample. Secondary charged droplets containing dissolved analyte are formed and desorbed from the sample surface and led into the MS inlet by voltages [10,11].

Textile fibers have previously been studied using DESI-MS in forensic and environmental contexts [12,13], and a DESI source was recently developed for the study of ink in manuscripts [14]. However, the first successful application of DESI-MS for the study of historical dyes was only very recently reported by the authors of [15], focusing on the construction and optimization of a DESI source for early synthetic dye analysis. The work presented here is complementary to this study and highlights the initial investigations into the use of DESI-MS for the detection of natural dyestuffs and some preliminary imaging-type experiments facilitated by the XY stage set-up.

2. Materials and Methods

2.1. Materials

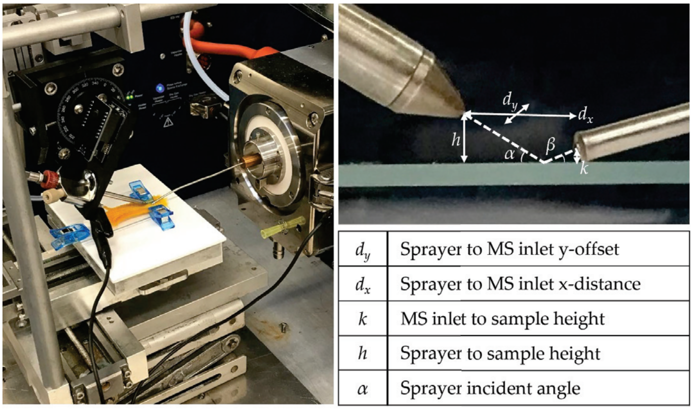
Alizarin, purpurin, carminic acid, and rhodamine B (CI 45170) were obtained from Sigma-Aldrich Inc., St. Louis, MO, USA. Fresh turmeric and turmeric powder were locally purchased. Samples of undyed, degummed, unmordanted silk (2-ply, 66 Tex, thread count 43 cm^{-2}) and undyed, washed, unmordanted wool cloth (3-ply, 158 Tex, thread count 36 cm^{-2}) were supplied by the Monitoring of Damage to Historic Tapestries project (MODHT) (FP5, EC contract number EVK4-CT-2001-00048) [16,17]. The H_2O, CH_3OH, and CH_3CN (LC-MS grade) were purchased from Fisher Scientific, Waltham, MA, USA. Fabric clips (Prym Love clips, 1.0 × 2.6 cm) and permanent markers (Lumocolor permanent pen 318, Staedtler, Nuernberg, Germany) were bought locally, while water-sensitive paper (Pentair Hypro) was purchased from Agratech NW Ltd., Rossendale, UK.

2.2. Dyeing Procedure

A mass of 100 mg ± 0.005 mg of each reference dyestuff was dissolved in 7.5 mL H_2O, and the dyebaths were heated to 75 °C before 100 mg ± 0.005 mg (ca. 1 cm^2) silk cloth was added. The dyebaths were kept at 75 °C for 15 min before the silk samples were removed and rinsed at least twice with cold deionized water and left to dry completely. The same dyebaths were used to dye the wool samples (150 mg ± 0.005 mg, ca. 1 cm^2) following the same procedure, except the wool samples were pre-wetted in deionized H_2O for 10 min before dyeing.

2.3. Instrumentation

A DESI source built in-house (Figure 1) attached to a Bruker 7T SolariX FT-ICR-MS using Compass HyStar 5.1 (Bruker Daltonik GmbH, Billerica, MA, USA) was used for all experiments. The commercial electrospray emitter (part number: 0601815, Bruker Daltonik) used for ESI-MS by the specified mass spectrometer was also utilized by the DESI source. The DESI source was constructed with an acrylic stage mounted on an XY stage controlled via an Arduino-compatible board (EleksMaker EleksMana V5.2) and LaserGRBL (v4.6.0). The sprayer holder was 3D printed in polylactic acid (Ultimaker 2, UltiMaker, Utrecht, Netherlands) and fitted onto a rotation mount (RP01 Manual Rotation Stage, THORLABS, Ely, UK) attached to three-direction positioners (Kite Manual Micromanipulator, WPI Inc., Sarasota, FL, USA). For spot monitoring, space for a camera (ESP32-CAM) was added above the sprayer tip. The sprayer set-up was mounted on stainless-steel rods attached to the stage and the whole assembly was affixed upon a lab jack for control of the sample-MS inlet height (*k*, Figure 1). The MS inlet was fitted with a 90 × 0.4 mm (length × i.d.) stainless-steel/brass extension, which was held in place around the MS capillary with a gold spring.



d_y	Sprayer to MS inlet y-offset
d_x	Sprayer to MS inlet x-distance
k	MS inlet to sample height
h	Sprayer to sample height
α	Sprayer incident angle

Figure 1. (**Left**): Photograph of constructed DESI source [15]. (**Right**): Detail of the sprayer and MS inlet of the constructed DESI source with key geometrical parameters. © University of Edinburgh/Edith Sandström.

2.4. DESI Analysis

Textile samples (ca. 1 cm^2) were placed on a glass slide and held in place with fabric clips (Prym Love clips, 1.0 × 2.6 cm). Larger textiles (ca. 10 × 10 cm) were clipped directly onto the plastic stage or, if large enough to not be affected by the nebulizing gas stream (ca. 25 × 25 cm), placed directly on the stage without clipping. DESI-MS spectra were acquired in the mass range of m/z 150–1000 and 20 mass spectra were summed unless otherwise stated. The solvent system used was 3:1 v/v CH_3CN:H_2O, and the MS inlet was cleaned with LC-MS grade CH_3CN and 3:1 v/v CH_3CN:H_2O between every analysis. All spectra were processed using Compass DataAnalysis (Bruker Daltonik GmbH, Billerica, MA, USA) and Origin 9.5 (OriginLab, Northampton, MA, USA). The imaging investigation graph was constructed in GraphPad Prism 9.5.1 (GraphPad Software, LLC, San Diego, CA, USA).

The following parameters were optimized and used for the early synthetic dye samples in positive mode: capillary voltage: 4.5 kV, end plate offset: −500 V, flow rate: 750 µL h^{-1}, nebulizing gas: nitrogen, nebulizing gas pressure: 3.9 bar, source temperature: 200 °C, and negative mode: capillary voltage: 4.2 kV, end plate offset: −800 V, flow rate: 750 µL h^{-1}, nebulizing gas: nitrogen, nebulizing gas pressure: 3.9 bar, source temperature: 200 °C, sprayer angle: 35°, ion accumulation: 1.5 s. The parameters used for the early synthetic dyes in positive mode were also used in the imaging investigation.

Negative mode was used for all natural dye samples for the practical ease of changing between the natural dye classes tested. The following parameters were used for the turmeric root and powder: capillary voltage: 3 kV, end plate offset: −800 V, flow rate: 300 µL h^{-1}, nebulizing gas: nitrogen, nebulizing gas pressure: 1.5 bar, source temperature: 200 °C, sprayer angle: 76°, accumulation: 1.8 s. Parameters used for silk and wool samples dyed with turmeric: capillary voltage: 4.5 kV, end plate offset: −1000 V, flow rate: 1200 µL h^{-1}, nebulizing gas: nitrogen, nebulizing gas pressure: 4.0 bar, source temperature: 200 °C, sprayer angle: 76°, ion accumulation: 2.0 s.

The parameters used for the silk and wool samples dyed with alizarin and purpurin were as follows: capillary voltage: 3.9 kV, end plate offset: −800 V, flow rate: 500 µL h^{-1}, nebulizing gas: nitrogen, nebulizing gas pressure: 3.5 bar, source temperature: 250 °C, sprayer angle: 74°, accumulation: 1.8 s. The following parameters were used for the silk and wool samples dyed with carminic acid: capillary voltage: 3.9 kV, end plate offset: −800 V, flow rate: 750 µL h^{-1}, nebulizing gas: nitrogen, nebulizing gas pressure: 4.0 bar, source temperature: 250 °C, sprayer angle: 83°, ion accumulation: 1.8 s.

3. Results

3.1. Optimization of DESI Source for Historical Dye Analysis

DESI-MS is dependent on multiple interconnected parameters; instrumental, geometrical, and chemical in nature. It is especially dependent on the geometrical parameters of the sprayer set-up (Figure 1) [10,11,18–20]. The optimized geometry often differs with the target molecule and substrate used, making it difficult to standardize optimum geometry for all applications.

The initial testing of the geometrical, chemical, and instrumental ranges were all conducted using the absolute ion abundance of the rhodamine B peak $[M\text{-}Cl]^+$ (m/z 443.23), which found that the solvent system and sprayer angle had the largest effect on the ion abundance. The optimization of these two parameters and application of DESI-MS analysis to early synthetic dyes across six dye families on both silk and wool, has been published elsewhere [15]. Here, the effect and limitations of other parameters that we found to differ significantly for the analysis of textile samples compared to the analysis of more common surfaces, such as glass, are discussed in more detail, and the application of DESI-MS is extended to natural dyes and imaging.

The optimum solvent flow rate for DESI-MS has been shown to be highly dependent on the surface being analyzed [21–23]. In contrast to DESI-MS analysis of biological and forensic samples, higher flow rates were required when analyzing cloth. The greatest signal-to-noise ratio of the rhodamine B $[M\text{-}Cl]^+$ and background peaks was achieved at 750 $\mu L\ h^{-1}$ [15], which is significantly higher than standard flow rates for biological and forensic samples (90–300 $\mu L\ h^{-1}$) [18,20,24]. The high flow rate required for textile samples has been reported previously [13], and it is likely needed due to the wicking properties of tightly woven cloths, reducing the formation of the thin liquid layer on the sample surface required for the proposed "droplet pick-up" mechanism for analyte transport [25]. Too low a flow rate resulted in the need for longer analytical times and gave a lower ion intensity, while higher flow rates (1500–1800 $\mu L\ h^{-1}$) resulted in the formation of water droplets on the cloth surface, particularly on wool (Figure 2).

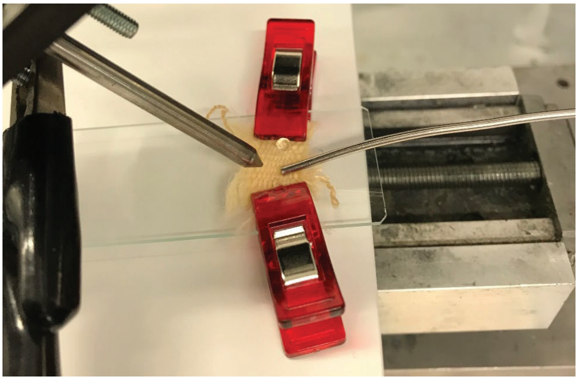


Figure 2. Undyed wool cloth being analyzed using too high a flow rate (1800 $\mu L\ h^{-1}$), resulting in droplet formation on the surface.

The sprayer–sample height (h, Figure 1) was found to be more limited when analyzing cloth compared to glass. Both cloth and glass showed higher ion abundances at lower heights. However, upon wetting, silk and wool become slightly conductive [26,27], which means that lowering the capillary too close to the sample resulted in burning of the cloth. This is an important difference to highlight, as any visual damage to the surfaces of objects needs to be avoided. The optimized height was h = 2 mm for most textile samples.

One of the major parameters investigated for the DESI-MS of textile samples was the sprayer angle, which has a direct influence on the spot area [11]. The effect of the sprayer angle on the spot geometry was further investigated using solvent-sensitive paper (Figure 3). A flow rate of 750 µL h^{-1}, a sprayer-to-sample height (h, Figure 1) of 5 mm, and an analytical time of 1 min was used for each spot. The resulting spot areas were measured in ImageJ (Rasband, W. S., National Institutes of Health, Bethesda, MD, USA).

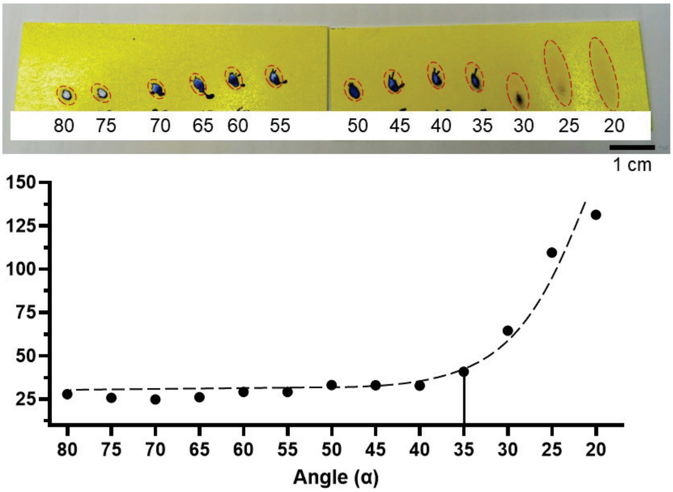


Figure 3. Solvent-sensitive paper (Pentair Hypro, Agratech NW Ltd., Rossendale, UK) showing the effect of different sprayer incident angles on the solvent (3:1 v/v $CH_3CN:H_2O$) spot shape and size. The solvent spot margins are marked by dotted lines. The measured area (mm^2) within the dotted lines is graphed below. The fitted curve is for data visualization only. An angle, α, of 35° is highlighted to show the critical point before the rapid increase in spot areas.

The spots which result from the use of higher angles show a more circular shape with a clear impact of the solvent in the center and fairly equal spot areas (Figure 3). As expected, the spot area increases, and the spot shape becomes more elongated, as the angle becomes shallower. Angles greater than 35° show similar spot areas across all solvent systems tested, while an exponential increase in spot area can be seen at angles 35°–20°.

The parameter values optimized on rhodamine B (listed geometrical parameters (Figure 1) and MS parameters (Appendix A, Table A1)) and tested on synthetic dye references, as well as historical early synthetic dye samples [15], were then applied to the analysis of natural dyes on textile samples and used with an imaging platform.

3.2. Natural Dyes

Turmeric (*Curcuma longa* L.) was chosen as a standard to determine the applicability of DESI-MS on natural dye chromophores based on it being a direct dye and readily available in both fresh and powder form. Initially, plant material was used to ensure that the DESI-MS set-up could ionize natural dye chromophores without interference from the cloth substrates. Fresh turmeric root purchased from a local grocery store was prepared in cryosections (50 µm), adhered to a glass slide, and analyzed using the DESI-MS set-up (Figure 4A). Additionally, turmeric powder was dissolved in H_2O, added to a glass slide, and left to evaporate overnight. The dried powder slides were then analyzed using DESI-MS (Figure 4B). Silk and wool cloth were also dyed with turmeric and analyzed by DESI-MS (Figure 4C,D).

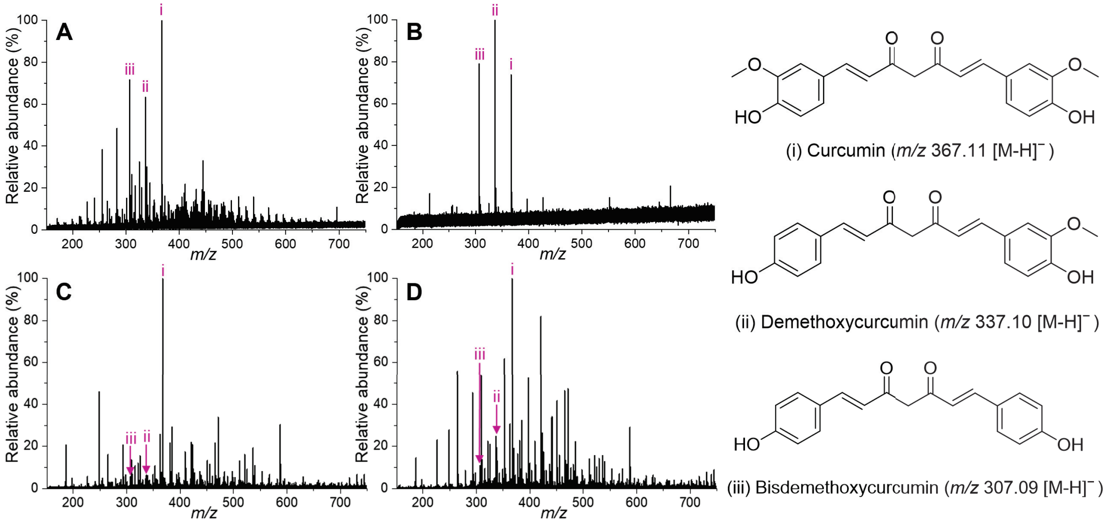


Figure 4. (**A**): Mass spectrum of 50 µm cryosections of fresh turmeric. (**B**): Mass spectrum of turmeric powder dissolved in H_2O and left to evaporate on a glass slide. (**C**): Mass spectrum of turmeric dyed on silk cloth. (**D**): Mass spectrum of turmeric dyed on wool cloth. The three main dye components of turmeric (i)–(iii) are labeled in pink, and their m/z and structure are shown on the right.

The three main dye components of turmeric—curcumin, demethoxycurcumin, and bisdemethoxycurcumin [28]—were all seen in the analysis of both the sectioned fresh and powder sample (Figure 4A,B). The mass spectrum obtained from the powder sample shows a less complex matrix than the fresh sample, likely due to processes during the drying step. Similar phenomena can be seen in the analysis of fresh and dried madder (*Rubia tinctorum* L.) [29], which is also a root used for dyeing. The noisier baseline in the turmeric powder spectrum (Figure 4B) compared to the fresh turmeric spectrum (Figure 4A) suggests that the chromophores are less concentrated in the powder sample. This change in concentration can be rationalized by the thinner sample layer on the glass slide, resulting in faster depletion of the analyte.

A signal from all three turmeric components could be seen on both the silk and wool cloth (Figure 4C,D), although these signals were less intense than they were for the fresh and powder turmeric samples (Figure 4A,B), and many background peaks could be seen. However, the signals were stable across the 20 mass spectra collected and showed a signal-to-noise ratio above 3:1, which is the common limit of detection used in the signal-to-noise method. The lower intensity peaks of turmeric compared to rhodamine B and the other early synthetic dyes tested show that the optimized set-up for early synthetic dyes [15] is not directly translatable to natural dyes and makes it likely that the lower ion abundance seen for the chromophores can be increased by optimizing the DESI parameters on a natural direct dye such as turmeric.

The silk and wool reference cloth dyed with mordant and vat dyes (weld (*Reseda luteola* L.), madder (*Rubia tinctorum* L.), cochineal (*Dactylopius coccus* Costa), and woad (*Isatis tinctoria* L.) for the MODHT project were investigated after the success of turmeric, but no expected m/z peaks could be seen. One possible explanation for the lack of a signal for natural chromophores on the dyed cloth could be the mode of dye application, as all the samples showing no signal were mordant or vat dyes. A likely explanation for the limitation in the analysis of vat dyes is the known poor solubility of these dyes in aqueous systems [30]. Circumvention of this issue would require the addition of solvents such as DMSO or DMF; however, the potentially damaging effects of these additional solvents on instrumentation, mass spectrum quality, and the objects themselves would need to be investigated.

This hypothesis was tested by dyeing unmordanted silk and wool cloth with standard references of anthraquinones (alizarin, purpurin, carminic acid) to see if any signal could be obtained from the silk and wool for common natural dye chromophores in the absence of mordant. The mass spectra obtained were promising as a high ion abundance of the [M-H]$^-$ peak was observed for each of the compounds tested (Figure 5). All natural dye components were analyzed with a higher angle (75°) than optimized for rhodamine B to obtain any signal, highlighting the need for natural dye optimization. However, the acquisition of signals for common chromophores such as the anthraquinones on silk and wool is a promising start for the application of DESI-MS for textiles dyed with natural dyes, but the limitations seen for mordanted and vat dye molecules require further investigation.

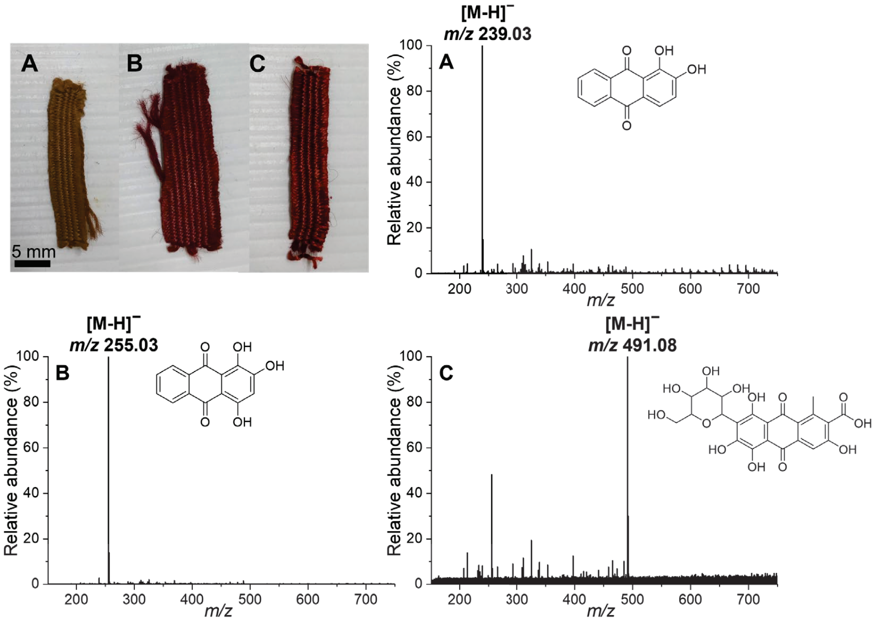


Figure 5. (**A**): Silk cloth dyed with alizarin, molecular ion labeled in mass spectrum A. (**B**): Silk cloth dyed with purpurin, molecular ion labeled in mass spectrum B. (**C**): Silk cloth dyed with carminic acid, molecular ion labeled in mass spectrum C.

3.3. Initial Imaging Experiments

One additional advantage of DESI is the possibility of mass spectrometry imaging (MSI) studies. Such an approach would be highly beneficial for the analysis of patterned textiles that are usually difficult to sample, such as printed calico and indienne fabrics. The DESI platform design included an electronically controlled stage for imaging purposes. Rhodamine B and a green ink (*m*/*z* 575.28) (permanent pen 318, Staedtler, Nuernberg, Germany) applied in stripes to a glass slide was used for the initial imaging investigations (Figure 6A).

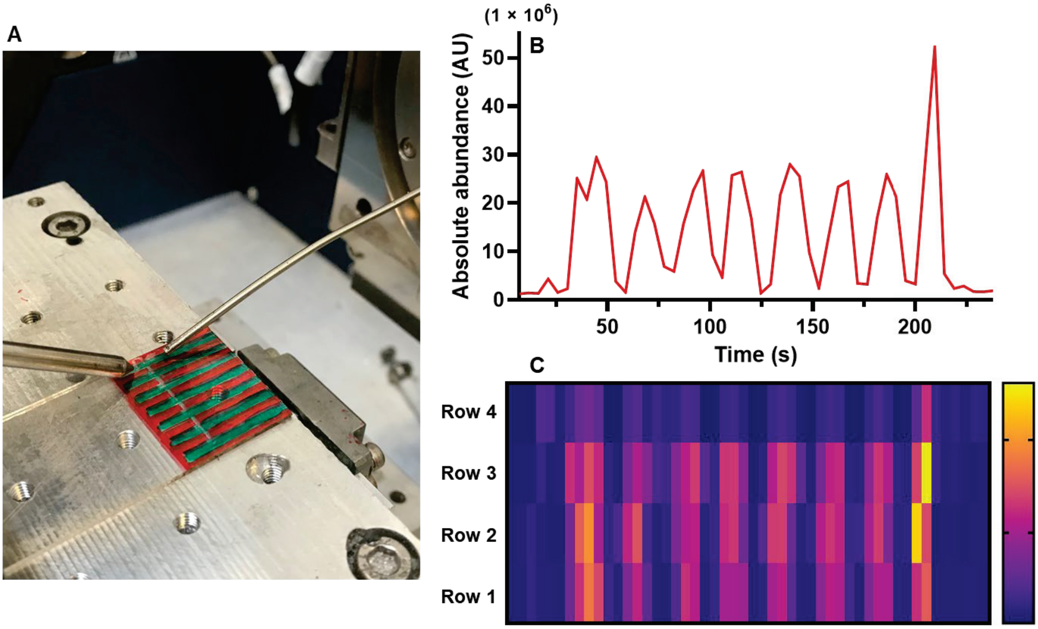


Figure 6. (**A**): Photograph of imaging set-up with rhodamine B and a green ink in lines on a glass slide. (**B**): Extracted ion chromatogram (*m*/*z* 443.23) recorded for row 3 showing the absolute ion abundance of rhodamine B recorded across the experimental time. (**C**): Heat map constructed from the extracted ion chromatogram (*m*/*z* 443.23) of rhodamine B showing the lines of the painted design on the glass slide. Graph constructed in GraphPad Prism 9.5.1 (GraphPad Software, LLC, San Diego, CA, USA).

The stage was programmed to go across the stripes of rhodamine B and the green ink (*m*/*z* 575.28) (permanent pen 318, Staedtler, Nuernberg, Germany) at a speed of 8 mm min^{-1}, with each row being recorded individually. The extracted ion chromatogram for the rhodamine B peak (*m*/*z* 443.23) for each row (Figure 6B) was then exported, tabulated, and plotted as a heat map (Figure 6C). The successful imaging of rhodamine B on a glass slide and the reliable acquisition of *m*/*z* data for early synthetic dyes using the DESI set-up [15] suggest that MSI investigations of textiles patterned with early synthetic dyes are possible.

Some MSI investigations on textiles, in both archaeological and forensic settings, have been conducted [12,31,32] using matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF-MS), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and infrared matrix-assisted laser desorption electrospray ionization (IR-MALDESI). The DESI-MS set-up developed shows a lower resolution but requires no sample preparation, in contrast to other MSI techniques. Thus, DESI-MSI could be of great use for the dye analysis field after the optimization of the spot to increase the spatial resolution and reduce the risk of cross-contamination.

The non-invasive imaging approach of DESI-MS offers an important method for the investigation of printed textiles, in which all of the colors present are often difficult to sample without threatening the structural integrity of the object. In the first instance, printed wool and silk fabrics, including pattern books and costumes, could be studied before moving to printed cotton textiles, such as calico and indienne fabrics [33]. Studies focused on cotton textiles would require further substrate-related optimization, including addressing considerations related to dye uptake and the strength of dye-fiber complexation. The imaging experiments conducted thus far will be followed up by further research into spatial resolution optimization. However, these initial trials have shown that DESI-MS analysis is a promising method for the analysis of historical textiles and of great potential benefit for the dye analysis field.

4. Discussion

The analysis of historical dyes poses unique challenges, including low dye concentration, complex dye mixtures, and ethical considerations. The optimized DESI-MS set-up included a solvent system with no additives to reduce the analytical damage to the sample. It also required a higher flow rate and shallower sprayer angle than typically used on glass surfaces.

The optimized solvent system showed splattering of the solvent on both glass surfaces and the water-sensitive paper, even at low angles, resulting from the aqueous content and high flow rate used (Figure 3). This splattering is less significant when analyzing cloth due to wicking properties of the fabric. Splattering and the less precise spots of lower angles are disadvantages in imaging and any type of precision work, as they increase the risk of cross-contamination. However, lower angles and larger areas result in less damage to the spot investigated (Figure 3), as the same volume of solvent is spread over a larger area. This means that shallower angles provide an advantage when analyzing fragile heritage objects. This can be seen in the softer impact on the water-sensitive paper when the sprayer angle is at 20–30°. Such larger, less precise spots are desirable in the analysis of historical objects where imaging analysis is not the aim. The inclusion of a movable stage makes future application to imaging using the DESI source possible, after the optimization of the spot size and further investigations on the balance between spot damage and spatial resolution are conducted.

The difficulty in analyzing natural dyes, particularly mordant and vat dyes, highlights the fact that the parameters optimized for rhodamine B are not directly translatable, and there is a need for a similar optimization of natural dye standards. The successful analysis of individual chromophores directly applied to cloth suggests that DESI-MS is a promising technique for natural dye analysis, but further studies are needed to determine why there is a lack of ionization for mordant and vat dyes. Such studies need to focus on the difference in solubility in the aqueous solvent systems of natural dyes compared to early synthetic dyes and circumvent the stronger bonds within dye-mordant-fiber complexes. These issues would require the exploration of other solvent systems, which needs to be balanced against the impact of such systems on the object, making sure the analyses can still be considered non-invasive.

Future work will involve quantitative damage assessment to confidently apply the technique to culturally important textiles. The use of this in situ approach for dye analysis will be particularly significant to study textiles that cannot be sampled, such as block printed calico, indienne textiles, and also textiles that have undergone conservation treatments where the reverse is inaccessible for sampling.

Additionally, analyses of more complex systems, as well as unknown analytes, are underway to expand the limits of DESI-MS application to the field of dye analysis. The undoubted potential of in situ mass spectrometric analysis has been demonstrated, and future studies will hopefully expand its applications and give access to valuable information on hitherto inaccessible objects.

5. Conclusions

A DESI-MS source has been built in-house to allow for the non-invasive analysis of historical dyes. The set-up used the ESI sprayer attached to a Bruker 7T SolariX FT-ICR-MS instrument and included x-, y- and z-positioners, an angle mount for manual control of the geometrical parameters, and an electronically controlled stage. DESI-MS has been used successfully to analyze early synthetic dye references and historical samples using a higher flow rate and shallower sprayer angle compared to forensic and biological samples. The technique shows great potential for natural dye and imaging studies after further optimization.

Author Contributions: C.L.M., A.N.H., L.G.T., E.S. conceptualized the study. C.L.M., A.N.H., E.S., C.V. designed the experiments. E.S., C.V. carried out the experiments. E.S., C.V., C.L.M., A.N.H. analyzed the data. E.S. wrote the manuscript. A.N.H., L.G.T., C.L.M., C.V. read and edited the manuscript. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are openly available at https://datashare.ed.ac.uk/handle/10283/4853.

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

Appendix A

Table A1. MS parameters tested for their effect on the absolute ion abundance of Rhodamine B $[M\text{-}Cl]^+$ peak (m/z 443.23), the range tested, and the optimized ranges.

MS Parameter	Range Tested	Range for Greatest Absolute Ion Abundance (m/z 433.23) (n = 3)
Sweep excitation energy	12–15%	15%
Skimmer voltage	5–30 V	15–25 V
Source temperature	200–300 °C	250–300 °C
Sprayer capillary voltage	1–5 kV	4–4.5 kV
Dry gas flow	1.0–5.0 bar	3.5–4.0 bar
Accumulation	0.2–3.0 s	1.5–2.5 s
Time-of-flight (ToF)	0.2–0.8 ms	0.5–0.7 ms
Flow rate	200–2000 μL h^{-1}	700–800 μL h^{-1}

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Article

Ancient Chromophores and Auxiliaries: Phrygian Colorants from Tumulus MM at Gordion, Turkey, ca 740 BCE

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Abstract: This paper discusses colorants found in Tumulus MM, the tomb of King Midas or his father, at Gordion, the capital of the Phrygian kingdom. Chromophores, colorants, and auxiliaries are preserved largely independent of the textiles they once colored. The Tumulus MM textiles are now fragmentary due to the degradation processes that occurred inside the tomb chamber. For DHA 26 (Vienna, Austria, 2007), we discussed a group of golden-yellow fragments from Tumulus MM that appeared to be tabby cloth but were skeletal lattices of goethite, $\alpha FeOOH$ (yellow ochre), as identified by FTIR, with SEM/EDS, XRD with molybdenum Kα radiation, NIR, and Raman spectroscopy. The "dyeing" has been replicated using a patented method; originally it may have involved a controlled redox reaction, based on our preliminary experiments. Amidst the goethite lattices, some skeletal fragments were green, with near-black lines within the yarn spiral, identified as indigo by FTIR at the time. Other masses with colorations of red, orange/brown, and purple with deep red veins did not yield identifiable inorganic coloration profiles with SEM/EDS. A purple fragment (2003-Tx-6 Front) was assayed by ICP-MS for mordants and for bromine, but neither could be found. Recently, direct analysis in real time mass spectrometry (DART-MS) enabled us to successfully detect organic colorants. For one fragment, indoxyl, isatin, indigo, and *leuco*-indigo were identified. One striated red-to-brown mass (2003-Tx-3) contained alizarin, purpurin, xanthopurpurin, lucidin, and other madder substituents; it also contained indigo/isatin but neither indoxyl nor *leuco*-indigo. Other beige-brown masses like 2003-Tx-5 sometimes contained alizarin, xanthopurpurin, rubiadin, and lucidin but rarely purpurin or indigo-related compounds. The purple (2003-Tx-6) shared the madder analogues with browner hues. The versatility appears related to that found in Anatolian pile carpets and flat weaves. Our new analyses confirm that the Phrygian textile colorists were indeed superb, versatile dyers.

Keywords: Iron Age; goethite; madder; indigo; Gordion; King Midas; Anatolia; weaving; dyes; City Mound; Phrygia

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1. Introduction

New research has identified the colorants in the royal textiles from Tumulus MM, the tomb of a great Phrygian king—King Midas or his father—who ruled at Gordion, Turkey, in the 8th century BC. The kingdom of Phrygia, then at the height of its power, extended over much of central Anatolia, with the capital at Gordion, located approximately 80 km (50 miles) southwest of modern Ankara (Figure 1) [1] (p. 136). Tumulus MM, called "MM" for "Midas Mound", is the largest burial mound at the site, now preserved to a height of 53 m. The tomb was excavated by the University of Pennsylvania Museum in 1957, under the direction of archaeologist Rodney S. Young [2]; research on the contents of the burial has continued up to the present day.

Figure 1. The Phrygian kingdom in the 8th century BC.

The tomb chamber was constructed of finished pine planks erected on a floor of cedar beams. Surrounding the chamber was an enclosure of juniper logs and rubble packing, and over this was piled the huge mound of earth. The rich burial had contained an impressive collection of bronze vessels, bronze-and-leather belts, bronze fibulae (brooches), pottery jars containing food residues, and 15 pieces of fine wooden furniture, along with numerous textiles associated with the furniture and bronzes [3] (pp. 79–190) [4]. At the north of the chamber lay the remains of the king, lying on a mass of degraded textiles that covered the wood of his open log coffin, which had broken apart and collapsed onto the tomb floor (Figure 2).

Figure 2. View of the remains of the king buried in Tumulus MM, Gordion, lying on the degraded textiles covering his log coffin, as excavated in 1957. Photo courtesy of the Gordion Project, Penn Museum.

The organic finds were remarkably well preserved due to the constant relative humidity that had prevailed inside the tomb chamber, although some deterioration had occurred. The excavators had drilled a series of holes into the surface of the mound in order to locate the chamber. The water used in the drilling, along with a gradual alkaline seepage into the tomb, had compromised the integrity of the wooden furniture and dissolved the fibers of the textiles buried with the king [5]. While some textile fragments were intact, most were recovered as amalgamated, dense, powdery solids. Nonetheless, the colors survived, ranging from a deep yellow to orange, reds, purples, and green. These rare Phrygian textile remains have been analyzed in terms of their materials, weave structures, and colorants [6]. The new research outlined in this paper highlights the dyes, their sources, and the processes used to achieve the results.

Southwest of the cemetery is the City Mound (Citadel Mound), situated above the Sakarya River (Figure 3) [7]. The Phrygians who settled at Gordion are thought to have originated in Thrace, making their way eastward to the central Anatolian plain. A porous gypsum plateau lay to the west of Gordion, while further east were sedimentary lowlands and uplands of basalt and marl [8] (p. 690). Contemporary with or somewhat earlier than Tumulus MM, the Early Phrygian settlement on the City Mound had burned in a fire and was subsequently rebuilt with minor alterations [9] (pp. 8, 10). Archaeologists have been particularly interested in the burnt layer, called the Destruction Level, as it was covered over largely intact, leaving a good record of Phrygian activities at the site ca 800 BC (Figure 4).

Figure 3. Aerial view of Gordion in the early days of excavation, with the City Mound (Citadel Mound) at the lower left and Tumulus MM at the upper right. Photo courtesy of the Gordion Project, Penn Museum.

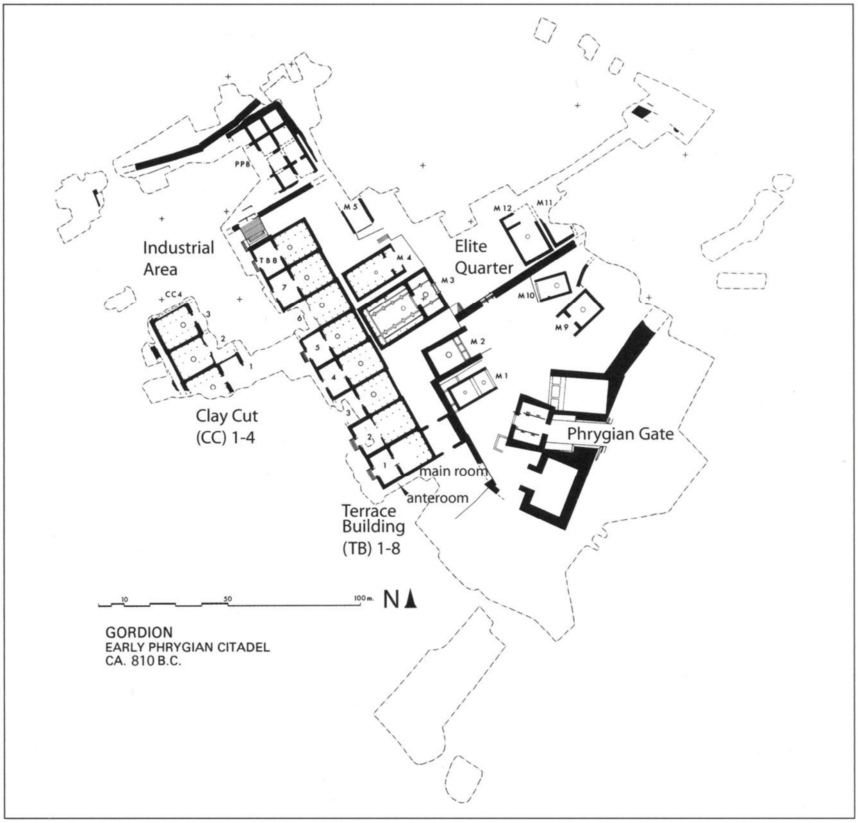

Figure 4. Plan of the City Mound at Gordion during the Early Phrygian period [9] (p. 8).

The burnt level of the City Mound has provided context for the Tumulus MM textiles, both in terms of surviving fragments of cloth and also loom weights and other tools indicating large-scale textile production [10]. Excavations in the central part of the mound revealed numerous buildings of megaron type with anterooms and spacious back rooms containing weaving equipment: needles, knives, combs, more than 1000 spindle whorls, and around 3000 loom weights, most in the range of 400–600 g (Figure 5) [11] (pp. 112–153) [12] (p. 65). In the largest of these buildings, Megaron 3, fragments of charred textiles were recovered, with their patterns visible but lacking their original colors (Figure 6) [13,14] (pp. 15–16). These charred fragments feature tapestry, soumak, and gauze weaves, as well as tablet work, in various gray shades as though the color of the ash might indicate different mordants [15].

Taken together, the textiles from Tumulus MM and the remains from the City Mound provide evidence for wide-scale textile manufacture and use at Gordion, which yielded fabric in a variety of weaves, some with geometric patterning, and in subtle and vivid hues achieved by ingenious dye chemistry. While it has not been shown that the Tumulus MM textiles were woven in workshops on the City Mound, the materials and colorants of these textiles are consistent with the resources present at Gordion. Although the Tumulus MM fabrics do not exhibit elaborate weaves or patterning, such as those from Megaron 3, they were clearly costly items—valuable enough to be deposited as grave goods in the largest tomb at Gordion. Their characteristics indicate an interest and expertise in colorants and dye technology, an advanced knowledge of chemistry and geology, and a good understanding of the natural products—plants and minerals—available in the vicinity. Beyond their inherent cultural value, the dyed textiles from the tomb suggest what the Megaron 3 textiles might have looked like before losing their color to the fire. This paper will focus on the dyes of the Tumulus MM textiles, their chemistry, and their use as colorants for these royal Phrygian cloths.

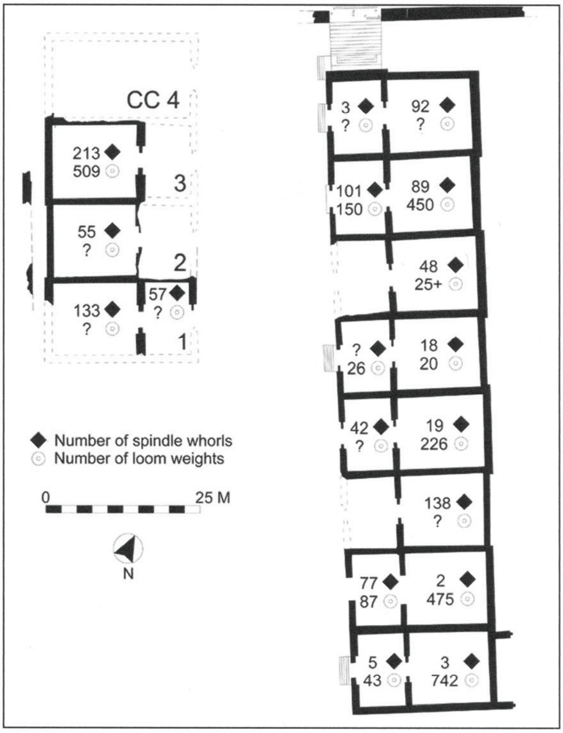

Figure 5. Workrooms in the Terrace Building complex on the Gordion City Mound, with the numbers of loom weights and spindle whorls reported for each room [12] (p. 65). Plan courtesy of Brendan Burke.

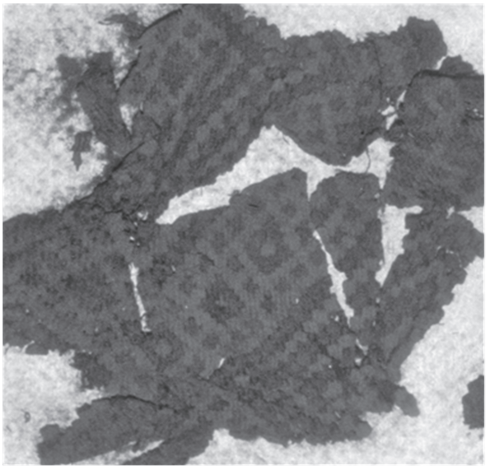

Figure 6. A charred textile fragment from Megaron 3 on the City Mound, stored at the University of Pennsylvania Museum (Bellinger Box 12) [13]. Photo courtesy of Mary Ballard.

2. Materials and Methods

Eleven textile samples from Tumulus MM were lent to the Museum Conservation Institute, Smithsonian Institution, in 2003 for analytical research; these were labeled 2003-Tx-1 through 2003-Tx-11, with 2003 indicating the date that the samples were catalogued for the purpose of study. Initial efforts on fiber, weave, and dye analysis were summarized elsewhere in 2007 [16] and published at length in 2010 [6]. The present paper combines old and new methods and results to provide a full range of archaeological and scientific data regarding the dyes. A synopsis of the defining characteristics of the textile samples, where such features could be obtained, is given in Table 1; a fuller description and extensive imaging are available in the 2010 publication [6].

Table 1. Summary of textile features associated with samples 2003-Tx-1 through 2003-Tx-11 [6].

Compendium of Textile Features Found in Tumulus MM					
Sample	**Color**	**Images (Figures)**	**Fiber**	**Yarn and Count**	**Constuction or Weave**
2003-Tx-1	gold	14, 19	bast	2 Z, S-plied 18 × 21 cm	balanced plain weave
2003-Tx-2 Front	(orange) red	13	—	—	—
2003-Tx-2 Back	gold	15	bast	2 Z, S-plied 18 × 21/cm	balanced plain weave
2003-Tx-3 Front	white-cream	22	—	—	—
2003-Tx-3 Front	brightest red	21, 22	unknown	unknown	unknown
2003-Tx-3 Front	mixed reddish			unknown	
2003-Tx-4 F&B	reddish	23, 24	unknown	unknown	unknown, twining
2003-Tx-5 F&B	type B fibrous	—	unknown	Z twist	twining
2003-Tx-5 F&B	type A	—	—	—	—
2003-Tx-6 Front	reddish/purple layer	25, 26	—	—	—
2003-Tx 6 Front	varied	25, right	unknown	S-twisted	cord
2003-Tx-6 Back	dark red	—	unknown	unknown	twining
2007-Tx-7 Front	gold	17	bast	2 Z, S-plied	plain weave
2007-tx-7 F&B	brown fibrous mass	17, 29	—	—	—
2003-Tx-7 Back	dark fiber A	29	unknown	floss/S	twining
2003-Tx-7 Back	dark fiber B	29	—	—	—
2003-Tx-8 Front	whitish pale tan	27	—	—	—
2003-Tx-8 Front	single fiber/yarn	27	unknown	floss/S	twining
2003-Tx-8 Back	gold	18	bast	2 Z, S-plied 28 × 23/cm	plain weave
2003-Tx-8 Back	dark, fibrous	18	unknown	unknown	unknown
2003-Tx-9 Front	whitish tan	—	—	—	—
2003-Tx-9 Front	gold	—	unknown	—	—
2003-Tx-9 Back	gold	28	bast	2 Z, S-plied ca 35 × 35/cm	plain weave
2003-Tx-9 Back	dark	28	unknown	floss/S	twining
2003-Tx-10	dark	30, 31	flax	2Z, S-plied, 35 × 35 cm	balanced plain weave
2003-Tx-11	dark blue strands	16, 20	bast	2Z, S-plied	balanced plain weave
2003-Tx-11	bicomponent gold strands	16, 20	bast	2Z, S-plied	balanced plain weave

The research detailed in this section is divided into two conventional categories: inorganic and organic. The inorganic studies were carried out during the period 2003–2008 with some recent reconsiderations in 2021–2022 [6,17]. The organic work, except for 2003-Tx-11, was carried out in 2019–2022. The largest volume of color is associated with the coffin textiles (Figures 2 and 7), with additional fragments found in the northeast corner and at the east wall of the chamber. The textile fragments from Tumulus MM were obtained on loan for analysis from the Museum of Anatolian Civilizations, Ankara, Turkey, under the auspices of the Gordion Furniture Project. Their find spots within the chamber are shown on the tomb plan (Figure 8).

Figure 7. Storage drawer of material from Tumulus MM adjacent to the head of the corpse, similar to 2003-Tx-4 Front and Back. Photo courtesy of the Gordion Furniture Project.

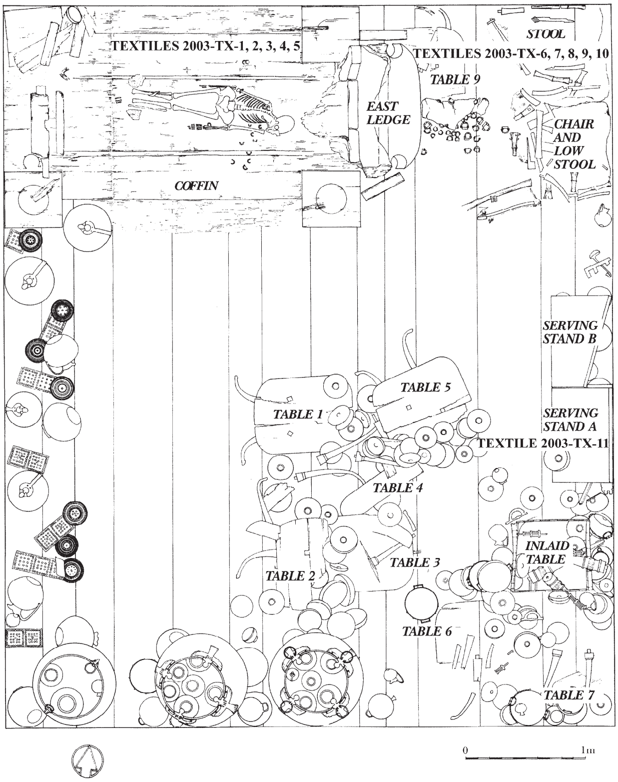

Figure 8. Plan of the Tumulus MM chamber showing the locations of the wooden furniture and textiles. Plan courtesy of the Gordion Project, Penn Museum, and the Gordion Furniture Project.

2.1. Inorganic

The inorganic analyses were carried out using a JEOL JXA-840A Scanning Electron Microscope (SEM) with a Thermo NORAN TN-5502 energy dispersive analytical attachment (EDS) and its compatible NORAN Vantage spectrum processing software. The system was also fitted with a low atomic number detector (Pioneer Premium detector with a Norvar window). Self-sampling powder from the periphery of the sample was transferred to a carbon-coated carbon stub and stored in a desiccant chamber until used. A sketch of the stub was made; sketches and stubs remain archived and available. This equipment was used for the inorganic analysis of all samples except 2003-Tx-10 [6,17].

An Aventa visible through near infrared and shortwave infrared portable spectrometer (VIS-NIR-SWIR) also characterized the inorganic material present in fragment 2003-Tx-2. A Thermo Nicolet Almega XR Dispersive Raman Spectrometer provided further spectra of 2003-Tx-1 [16,18].

A Perkin Elmer Elan 6000 Inductively Coupled Plasma Mass Spectrometer (ICP-MS) connected to a Scott-type Tyron® double pass spray-chamber fitted with a standard crossflow nebulizer as sample-introduction device was used on samples from 2003-Tx-6. A review of this method to search for mordants or inorganic substituents such as bromine has been described elsewhere [19].

The Rigaku D/MAX-RAPID X-Ray Diffraction spectrometer was initially used to confirm the presence of goethite on 2003-Tx-1, but its reliance on K_β copper radiation was thought to be inadequate. Additional X-Ray Diffraction spectrometer data were obtained from the Smithsonian National Museum of Natural History using a Rigaku DMax/Rapid; the X-rays are Mo $K\alpha$ with wavelength of 0.71 angstroms. The data were processed in Rigaku AreaMax software and analyzed with Jade software and matched to references in the PDF database [16].

2.2. Organic

A direct analysis in real time for mass spectrometry (DART-MS) [20] probe operated by an SVP controller was mounted in front of a differentially pumped Vapur interface (IonSense, Saugus, MA, USA) on a high-resolution Orbitrap Elite mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). A 40 mm stainless steel transfer tube was used in place of the typical ceramic transfer tube on the Vapur interface. Solid fragments 0.5–3 mm wide that had fallen off larger pieces of compressed and degraded textiles were collected from material containers and, prior to analysis, stored in paper or aluminum foil to prevent any further contamination by contact with residues from modern materials. The miniscule fragments were too brittle and irregularly shaped to be mounted in forceps without crushing, and fragments were manipulated for analysis by forceps in hand to pass in the 7 mm gap between the DART probe and transfer tube (Figure 9). DART analysis was performed at 350 °C helium. MS data were acquired in the profile mode at 120 k resolving power with a maximum ion trap fill time of 100 ms [21].

High-performance liquid chromatography (HPLC) was carried out on samples from 2003-Tx-2 Front in order to determine whether there was any protein fiber (i.e., wool felt) in the orange-red mass. Analysis was performed using a St. John Model 2000 Amino Acid Analyzer with Alcott 708AL Autosampler. Post-column derivatization with ortho-phthalaldehyde (OPA) and 2-mercaptoethanol (MCE) were used as detecting reagents [22].

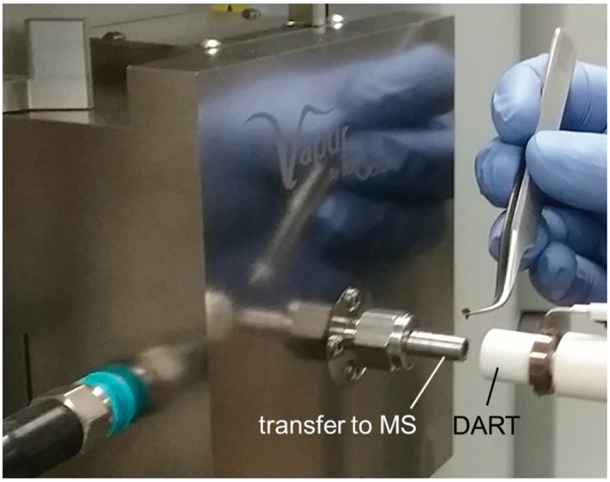

Figure 9. Textile fragment about to be manipulated for DART-MS analysis.

3. Results

Where the results by instrumental analysis deal with a single fragment, the results are described. Where the instrumental results provide data for more than a single fragment, the analyses have been combined into tables based on the inorganic or organic spectra. The Tumulus MM textiles are listed according to their find spots (from the coffin, the northeast corner, and the east wall) and their color: Table 2 for indigo, and Tables 3 and 4 for Madder.

Table 2. Results for indigo from DART-mass spectrometry for samples 2003-Tx-1 through 2003-Tx-11 from Tumulus MM [21].

		Indigo Group Compounds, Neutral Chemical Formula, and Intact Ion *m*/*z*						
Sample	**Color**	**Indigo**	**Indican**	**Isatan A**	**Isatan B**	**Indoxyl**	***Leuco*-Indigo**	**Isatin**
		$C_{16}H_{10}N_2O_2$	$C_{14}H_{17}NO_6$	$C_{17}H_{17}NO_9$	$C_{14}H_{15}NO_6$	C_8H_8NO	$C_{16}H_{12}N_2O_2$	$C_8H_5NO_2$
		263.082	**296.113**	**380.098**	**294.096**	**134.06**	**265.096**	**148.039**
2003-Tx-1 F	gold							
2003-Tx-2 F	(orange) red	√						
2003-Tx-3 F	white							
2003-Tx-3 F	brightest red	√				√		√
2003-Tx-3 F	mixed reddish							
2003-Tx-4	reddish	√						
2003-Tx-5 F	type A							
2003-Tx-5 F	powder							
2003-Tx-6 F	reddish/purple	√				√		√
2003-Tx-6 B	reddish/purple							
2003-Tx-7 F	tan							
2003-Tx-7 B	brown fibrous mass							
2003-Tx-7 B	dark fiber A							
2003-Tx-7 B	dark fiber B							
2003-Tx-8 F	white, tan							
2003-Tx-8 F	fiber/yarn							
2003-Tx-8 B	dark, fibrous					√		√
2003-Tx-9 F	whitish tan							
2003-Tx-9 B	dark	√				√		√
2003-Tx-10	dark							
2003-Tx-11	blue strand	√				√	√	√
2003-Tx-11	bicomponent	√						√

Table 3. Results for madder from DART-mass spectrometry for samples 2003-Tx-1 through 2003-Tx-11 from Tumulus MM [21].

		Madder Group Organic Compounds, Neutral Chemical Formula, and Intact Ion *m*/*z*							
Sample	**Color**	**Alizarin or Xanthopurpurin**	**Purpurin**	**Munjistin**	**Lucidin**	**1-Methoxy-2-methylanthraquinone**	**Alizarin 1 (or 2)-methyl Ether, or Rubiadin**	**Xanthopurpurin Dimethyl Ether**	**2-Hydroxyanthraquinone**
		$C_{14}H_8O_4$	$C_{14}H_8O_5$	$C_{15}H_8O_6$	$C_{15}H_{10}O_5$	$C_{16}H_{12}O_3$	$C_{15}H_{10}O_4$	$C_{16}H_{12}O_4$	$C_{14}H_8O_3$
		241.049	257.045	285.040	271.061	253.087	255.066	269.081	225.055
2003-Tx-1	gold								
2003-Tx-2 F	(orange) red	√	√		√	√	√	√	√
2003-Tx-3 F	white								
2003-Tx-3 F	brightest red	√	√		√	√	√	√	
2003-Tx-3 F	mixed reddish								
2003-Tx-4	reddish	√	√		√	√	√		
2003-Tx-5 F	type A	√			√		√	√	
2003-Tx-5 F	powder	√							
2003-Tx-6 F	reddish/purple	√	√		√	√	√	√	√
2003-Tx-6 B	reddish/purple								
2003-Tx-7 B	tan								
2003-Tx-7 B	brown fibrous mass								
2003-Tx-7 B	dark fiber A	√				√	√	√	
2003-Tx-7 B	dark fiber B								
2003-Tx-8 F	white, tan								
2003-Tx-8 F	fiber/yarn								
2003-Tx-8 B	dark, fibrous					√	√	√	
2003-Tx-9 F	whitish tan								
2003-Tx-9 B	dark					√	√	√	
2003-Tx-10	dark	√			√	√	√	√	
2003-Tx-11	blue strands					√	√	√	
2003-Tx-11	bicomponent								

Table 4. Additional results for madder from DART-mass spectrometry for samples 2003-Tx-1 through 2003-Tx-11 from Tumulus MM [21].

		Madder Group Organic Compounds, Neutral Chemical Formula, and Intact Ion *m*/*z*							
Sample	**Color**	**2-Methoxyanthraquinone, or 1-Hydroxy-2-methylanthraquinone**	**Pseudopurpurin**	**Damnacanthal**	**Rubianin**	**Christofin**	**Physcion**	**Physcionanthranol A/B**	**Copareolatin Dimethylether**
		$C_{15}H_{10}O_3$	$C_{15}H_8O_7$	$C_{14}H_{10}O_5$	$C_{20}H_{18}O_9$	$C_{17}H_{14}O_5$	$C_{16}H_{12}O_3$	$C_{16}H_{14}O_4$	$C_{17}H_{14}O_6$
		239.071	301.035	283.061	403.103	299.092	285.076	271.097	315.087
2003-Tx-1	gold								
2003-Tx-2 F	(orange) red	√		√		√	√	√	√
2003-Tx-3 F	white								
2003-Tx-3 F	brightest red	√		√		√	√		
2003-Tx-3 F	mixed reddish								
2003-Tx-4	reddish	√		√					
2003-Tx-5 F	type A	√							
2003-Tx-5 F	type B powder								
2003-Tx-6 F	reddish/purple	√				√	√	√	√
2003-Tx-6 B	reddish/purple								
2003-Tx-7 B	tan layer								
2003-Tx-7 B	brown fibrous mass								
2003-Tx-7 B	dark fiber A	√				√	√	√	√
2003-Tx-7 B	dark fiber B								
2003-Tx-8 F	whitish pale tan								
2003-Tx-8 F	single fiber/yarn								
2003-Tx-8 B	dark, fibrous	√							
2003-Tx-9 F	whitish tan								
2003-Tx-9 B	dark	√							
2003-Tx-10	dark	√				√	√		
2003-Tx-11	blue strands					√			
2003-Tx-11	bicomponent								

3.1. Inorganic

3.1.1. ICP–MS

No bromine was found on 2003-Tx-6F, among six samples taken in the deep purple areas. Note that the ablation system was modified to identify labile halides such as bromine, and was found to be a somewhat awkward but feasible method to identify mordants in antique textiles, based on comparison with a collection with known, identified samples [19,23,24].

3.1.2. SEM/EDS

The results in Table 5 show the elements as a percentage of weight/volume as reported by the instrumentation. The results of this instrument are qualitative; precise quantities cannot be determined. An exception was made to the reporting of these results because the differences in values of some of the results are extreme, as with samples 2003-Tx-1 and 2003-Tx-11 [6,16,17,25,26].

Table 5. Results from Energy Dispersive Spectroscopy for samples 2003-Tx-1 through 2003-Tx-11 from Tumulus MM [6,15,17].

Amalgamated SEM/EDS Charts of Tumulus MM Samples 2003-Tx-1 through 2003-Tx-11													
Sample	**Color, Magnification, Sample Runs (if not 4)**	**Weight Percentage of Elements by Position in the Periodic Table**											
		Na	**Mg**	**Al**	**Si**	**P**	**S**	**K**	**Ca**	**Ti**	**Fe**	**Ni**	**Cu**
2003-Tx-1 F	gold 100X	0.48	—	0.52	1.12	0.60	0.18	—	—	—	97.05	—	—
2003-Tx-2 F	red 1000X	—	2.92	17.45	30.32	2.87	10.88	7.59	6.63	—	18.97	—	—
200x-Tx-3 F	white	—	1.12	5.92	13.11	1.75	25.21	1.43	36.89	—	6.12	—	8.36
200x-Tx-3 F	brightest red	—	2.92	10.02	15.76	4.98	7.08	2.24	18.16	—	7.25	—	31.39
200x-Tx-3 F	mixed reddish	—	3.44	10.04	12.83	4.69	8.98	1.97	20.07	—	5.61	4.49	29.21
2003-Tx-4	reddish 500X	—	3.41	13.59	33.98	4.68	9.40	5.61	17.01	—	11.48	—	4.21
2003-Tx-5 B	type A surface	0.95	2.35	8.23	22.27	1.69	23.10	2.50	30.72	—	6.88	—	—
2003-Tx-5 F	type B fibrous	1.20	4.33	11.87	36.07	2.24	12.86	3.90	17.15	—	9.90	—	—
2003-Tx-6 F	type A upper	—	2.59	9.81	25.05	1.29	6.30	3.89	11.89	—	10.03	—	28.41
2003-Tx-6 B	reddish/purple	—	2.86	8.75	13.76	4.08	15.61	1.95	23.40	—	4.75	—	24.83
2003-Tx-7 B	tan layer 500X	—	0.92	2.04	5.59	0.59	30.84	0.65	46.36	—	3.65	—	9.35
2003-Tx-7 B	brown fibrous mass	—	1.06	5.44	9.44	1.50	1.51	0.70	1.73	—	78.65	—	—
2003-Tx-7 B	dark fiber A	—	2.43	15.18	42.71	1.72	3.83	7.53	2.57	1.36	19.74	—	—
2003-Tx-7 B	dark fiber B	—	0.55	25.09	12.53	4.85	24.34	16.20	5.28	0.51	9.94	—	—
2003-Tx-8	white, tan 100X (3)	—	2.14	4.48	15.32	0.98	23.08	1.97	34.96	—	4.40	—	12.42
2008-Tx-8 B	dark fiber 90X (2)	—	2.77	5.16	1.88	2.07	12.22	1.26	25.22	—	3.11	—	36.23
2003-Tx-8	strand 100X (3)	—	3.09	5.21	13.20	2.23	5.70	1.55	28.77	—	3.61	—	35.75
2003-Tx 8	dark, fibrous 100X (3)	—	3.27	5.38	13.42	2.18	6.00	1.56	31.11	—	2.95	—	34.61
2003-Tx-9 F	white tan 45X (3)	—	3.23	7.38	23.11	1.52	15.22	2.52	19.95	0.41	5.85	—	20.80
2003-Tx-9	dark 45X (1)	—	4.11	8.57	25.58	1.57	5.58	3.56	10.60	0.85	8.22	0.83	30.52
2003-Tx-9	dark fiber 45X (2)	—	1.41	3.40	9.03	—	29.57	1.20	39.02	—	3.30	—	12.37
2003-Tx-11	dark strands (6)	—	0.40	0.80	2.28	0.81	0.85	0.51	1.60	—	90.06	—	2.56
2003-Tx-11	bicomponent (3)	—	1.57	1.42	3.36	5.54	1.35	0.89	7.30	—	63.29	—	14.76

3.1.3. VIS-NIR-SWIR Spectroscopy

The results of the spectra compared the goethite minerals in its database to fragment 2003-Tx-1. Critical points match in the visible and near infrared at 761 nm and 920 nm, respectively (Figure 10). Generally, natural iron pigments contain clays, and the mixtures will vary [18,27].

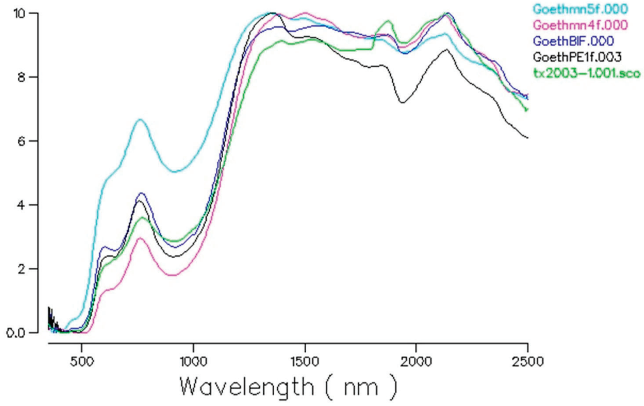

Figure 10. Fragments of 2003-Tx-1 are compared with five samples of known goethite from the Aventa geological reference library. Measurements plot pseudo reflectance versus wavelength [18].

3.1.4. XRD

In the case of 2003-Tx-1, the initial XRD was considered indeterminate; the use of X-rays from a molybdenum source was recommended. The comparison to a synthetic, pure standard is both more accurate and more precise (Figure 11) [16,28].

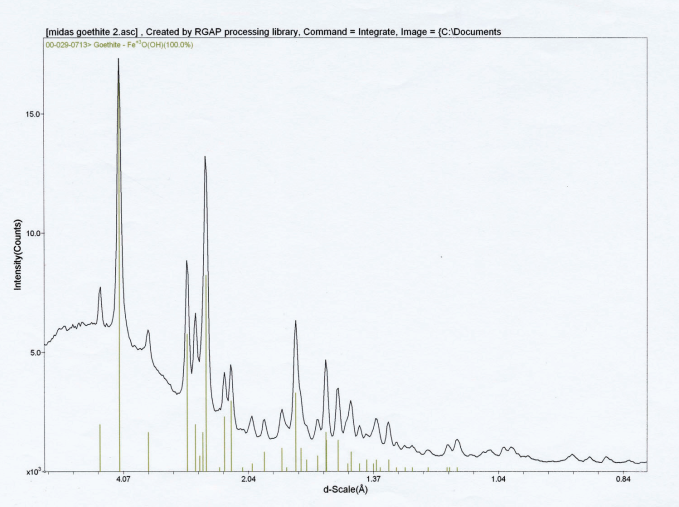

Figure 11. Spectrum taken with Rigaku DMax/Rapid with a Mo Kα wavelength of 0.71 angstroms X-Ray Diffraction Spectrometry. Measurements plot a scale x10^3 between 5 and 15 versus a d-scale in Angstroms (Å) [6,22].

3.2. Organic

3.2.1. DART-MS

Spectra from each Tx sample were examined for ions related to indigo ($C_{16}H_{10}N_2O_2$), madder ($C_{14}H_8O_4$), and Tyrian purple ($C_{16}H_8O_2N_2Br_2$), as well as other materials (Tables 2–4). No madder samples were found to contain munjistin (C.I. 75370, $C_{15}H_8O_6$, *m/z* 285.0399) or pseudopurpurin (C.I. 75420, $C_{15}H_8O_7$, *m/z* 301.035); their *m/z* were absent from all samples. Isomers, because they have identical formulae and *m/z*, are not separated by this method. No forms of bromoindigo were encountered [21].

The timing of the DART analysis was noted to compensate for unstable manual positioning, leaving collection periods before and after analysis to compare signal to background. The qualitative presence of a dye compound was confirmed by sustained appearance in mass spectra during the analysis window. Although in some samples the protonated molecule signal for dyes was quite large, even above all others observed in the spectrum (Figure 12a), in others the abundance was so low that it could be discerned only by the high resolution of the mass measurement (Figure 12b). Given the history of the samples, the origin of the other organic compounds observed in spectra is speculative.

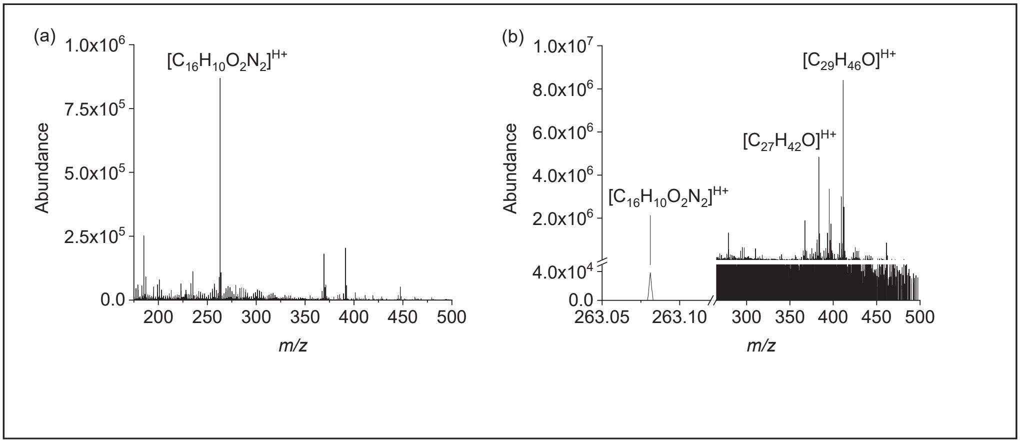

Figure 12. DART mass spectra of fragments (**a**) 2003-Tx-9 and (**b**) 2003-Tx-6 highlighting indigo [22].

3.2.2. FTIR

When the initial search for fibrous materials in 2003-Tx-1 failed using polarized light microscopy (PLM), a back-up method using FTIR was attempted as a last resort. An unexpected result occurred using the spectral library attached to a Thermo Nicolet 6700 Fourier Transform Infrared Spectrometer with Centaurus microscope and Golden Gate micro Attenuated Total Reflectance (ATR) accessory: inorganic goethite. More predictably, FTIR-ATM was also able to discern indigo in 2003-Tx-11 [6,16].

3.2.3. HPLC

No protein was found on the front side of 2003-Tx-2 in the orange-red mass (Figure 13) [22].

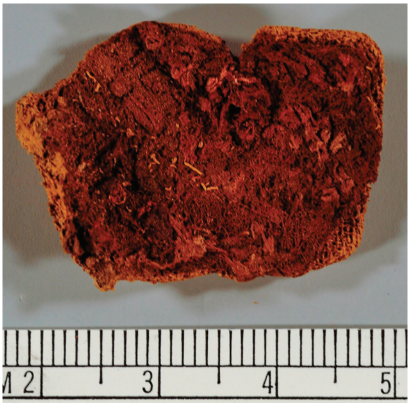

Figure 13. 2003-Tx-2 Front.

4. Discussion

4.1. Iron, Goethite

The amalgamation of materials into a single spectrum limits the reliability of the spectrum when the material is composed of multiple components, as with a dyed textile. For organic analysis, a dyed textile with 3% organic dye relative to the 97% weight of fabric would reflect the composition of the fabric and not the dye. Similarly, inorganic analysis without separating the components limits the usefulness of the analysis. Goethite is typically found as a clay, a mixture of components [29,30]. In the case of 2003-Tx-1, its best mineral match is a banded iron formation from the Karoo of South Africa, the "Tiger Eye" Mine, with a golden-brown color. In the best of circumstances, such a goethite mineral is summarized as follows:

> *FeO(OH), with common substituents Al, Mn, Ni; polymorphous with lepidocrocite. The most common iron oxide mineral in the regolith. Structure: double chains of Fe-O octahedra linked laterally. Yellow-brown, forming as compact aggregates of sub-micron-sized crystals or as dispersed micro-crystals; common as cutans on ferruginous nodules.* [18]

With over two millennia of leachate and microbiological decay, the presence of a highly pure goethite component reflecting a prior life as a textile colorant is extraordinary. Beyond the fragments 2003-Tx-1, 2003-Tx-2 Back, and 2003-Tx-11 (Figures 14–16), similar goethite-colored weaving can be seen as part of laminated textile packages from the tomb (Figures 17 and 18). While the yarns of the goethite-colored weavings studied here are hollow and entirely devoid of fiber, it is clear that these fragments do represent a dyed textile product, once fully colored and malleable.

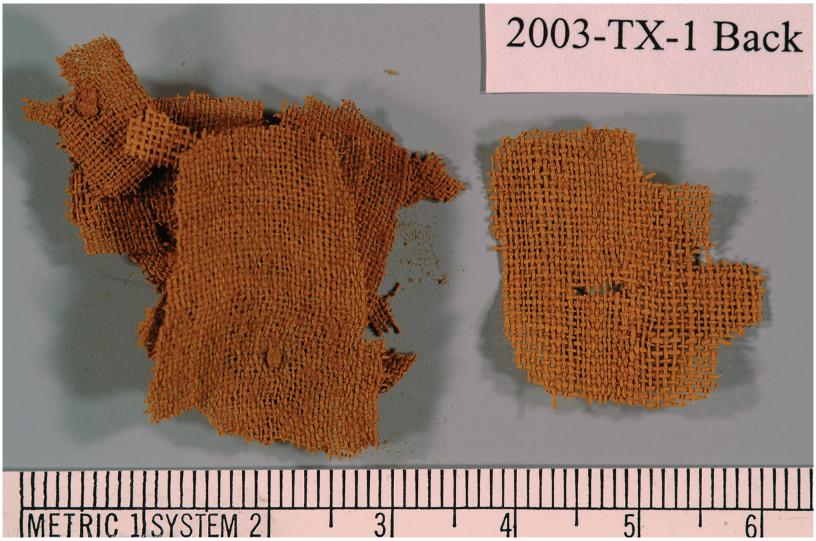

Figure 14. 2003-Tx-1 Back.

Figure 15. 2003-Tx-2 Back.

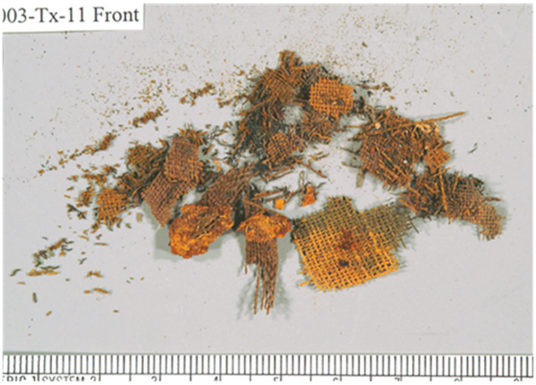

Figure 16. 2003-Tx-11 Front (fragment group).

Figure 17. 2003-Tx-7 Front.

Figure 18. 2003-Tx-8 Back.

In recent decades, a reasonably stable version of goethite-coated polyester was developed under laboratory conditions while exploring the potential for making fabrics conductive. The inventor kindly recreated his treatment on modern linen on our behalf (Figure 19) [16,31–34]. This suggests that under the right circumstances, it is possible to produce a laboratory version—or to manufacture fabric of this sort. The modern facsimile is flexible and has a soft handle; it is a purer yellow, more a limonite, as might be expected with modern purified chemical agents.

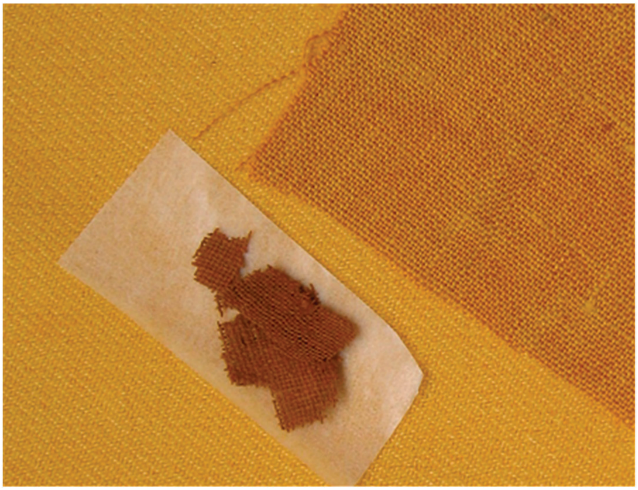

Figure 19. Three forms identified as goethite with VIS-NIR-SWIR spectroscopy. In the background, a piece of modern polyester coated with goethite; on glassine paper, some fragments of 2003-Tx-1; at upper right, modern linen coated with goethite.

Yet, the feasibility of goethite-treated cloth for use as a garment or furnishing fabric is somewhat questionable. The modern samples and the ancient ones are “ring dyed”: it is the surface layer that has been coated. As a surface layer, the coating would be subject to abrasion and wear. Depending on the depth of surface and size, goethite coating might be somewhat irritating to the skin, and scratchy and hard (5–5.5) on the fibrils, comparable to a fine sandpaper on the Mohr’s scale.

Fragment 2003-Tx-11 (Figure 16) provides interesting insight into an unusual means of coloration that was developed by the Phrygians. Goethite is present, with some of it dissolved and some tinged green or blue-green. When examined under a low-powered microscope, the golden strands were found to have been dabbed with indigo before the yarns were plied (Figure 20). That is, it appears that the oxidized indigo solution was lifted by brush hairs and dotted onto a yarn where it might coalesce as droplets or dabs. Here, the goethite seems a lighter shade, a thinner coating or film of the mineral. Was this complex fabric placed in Tumulus MM as an experimental success and an example of ingenuity? Whatever the significance of this colorful cloth, its striped yarn is intriguing now.

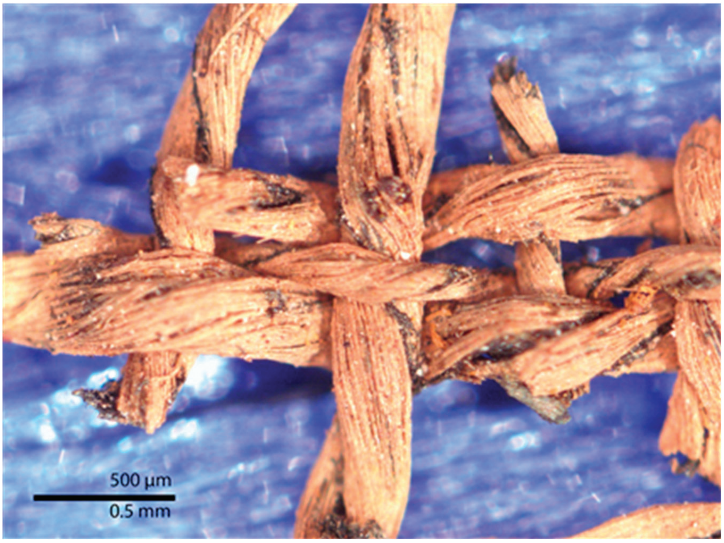

Figure 20. Detail of 2003-Tx-11 showing indigo between single strands of goethite-infused fibers (lying on a modern medical antistatic fabric).

4.2. Indigo

The fragment 2003-Tx-11 with its lighter goethite layer and semi-dyed, *leuco*-indigo state suggests that goethite had a second, perhaps more common use: to make a green color that would fade so slowly that the fading would match the rate of fabric wear, unlike the fading rates of fugitive yellow plant dyes. For indigo itself, it might have been processed from woad that could have been cultivated in Anatolia or from indigo that could not [35] (pp. 335–408). There is no plant record of woad seeds or vegetation at Gordion [36]. The ingenuity and frugality used to produce a more uniform dyeing is seen in the presence of its being dabbed on one of the two singles subsequently plied together. Here, indigo was partnered with goethite, already in place on the adjacent strand (see Figure 20). Various reduction methods were utilized for dyeing indigo; these might well have been adjusted to accommodate goethite [37–39].

While fragment 2003-Tx-11 is the only textile sample from Tumulus MM with *leuco*-indigo ($C_{16}H_{12}N_2O_2$), several others have stable forms: indigo (indigotin) the oxidized dye, as well as two unreacted oxidized forms isatin and indoxyl (Table 2). This presence of multiple forms of indigo on the samples from 2003-Tx-3 (Figures 21 and 22), 2003-Tx-4 (Figures 23 and 24), 2003-Tx-6 (Figures 25 and 26), 2003-Tx-8 (Figures 18 and 27), and the back of 2003-Tx-9 (Figure 28) may have contributed to the shades of maroon, purple, or brown. The combined presence of chemistry and color suggests the possibility that two bath dyeings might have been used: a vat for indigo and a mordant dyeing for madder. Fragment 2003-Tx-11 promotes the concept of creative planning and dyeing with indigo; the distinctive contrast between the front and back of fragment 2003-Tx-2 (Figures 13 and 15) does not. The others lie somewhere in between.

Figure 21. 2003-Tx-3 Front.

Figure 22. 2003-Tx-3 Back with spherical clover-burr (a plant seed burr).

Figure 23. 2003-Tx-4 Front.

Figure 24. 2003-Tx-4 Back.

Figure 25. 2003-Tx-6 Front.

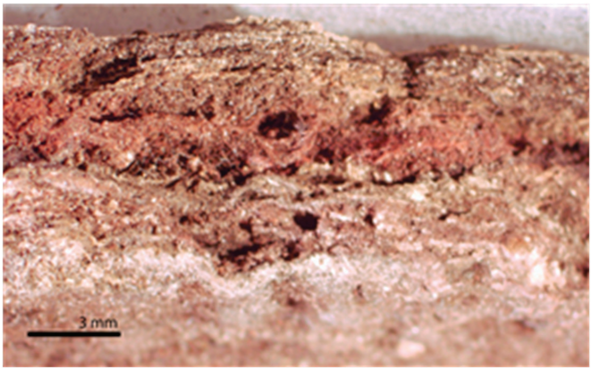

Figure 26. Side view of the upper right edge of 2003-Tx-6 exposing diverse colored layers.

Figure 27. 2003-Tx-8 Front.

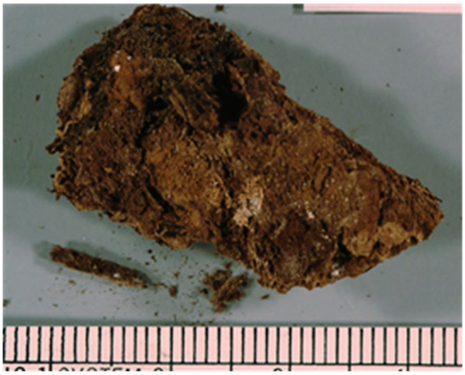

Figure 28. 2003-Tx-9 Back.

4.3. Madder

For the textile fragments in Tumulus MM dyed with madder-related dyeings, the treatment is more likely to be wholesale immersions, but the various constituents of madder may or may not be present (Tables 3 and 4). Only 2003-Tx-2 Front (Figure 13), the red matte fragment, and 2003-Tx-6 (Figures 25 and 26), the reddish-purple fragment, contained almost the full list of the chemical components of madder found among the Tumulus MM textiles. These include alizarin, purpurin, lucidin, 1-methoxy-2-methylanthraquinone, rubiadin, xanthopurpurin dimethyl ether, 2-hydroxyanthraquinone, and 2-methoxyanthraquinone (Table 3); 2003-Tx-6 lacks damnacanthal (Table 4). All the Tumulus MM madder-containing fragments lack munjistin, pseudopurpurin, and rubianin, all typical of *Rubia tinctorum*.

With the exception of 2003-Tx-2 the madder fragments fall into two distinct hue ranges: the purple and reddish-purple fragments of 2003-Tx-3 (Figures 21 and 22) and 2003-Tx-6 (Figures 25 and 26) and the softer, darker brown-beiges of 2003-Tx-8 and 2003-Tx-9 Back (Figures 27 and 28). The latter may have been processed with a different end-use in mind, or they may have received their final coloration by different techniques, such as repeated dyeings, i.e., repeated dyebaths.

Fragments 2003-Tx-8 Front and Back (Figures 18 and 27) and 2003-Tx-9 (Figure 28) did not contain alizarin, purpurin, or lucidin but were also brown. Avoiding these components, the dye produced a brown shade, perhaps with the aid of inorganic components, such as aluminum, iron, and copper (Table 5)). In fact, they are a near match for the dark fibers of

2003-Tx-7 Back, which did have alizarin and a number of other chromophores they lacked (Figure 29, Tables 3 and 4)).

Figure 29. 2003-Tx-7 Back.

Perhaps the most unusual fragment of the madder group is the seemingly unfinished fragment 2003-Tx-10. This consists of several apparently identical layers of fine plain weave fabric now laminated together. They have been molded over time as though around the stretcher of a stool or some other shape (Figures 30 and 31). 2003-Tx-10 was overlooked for SEM/EDS, possibly because it appears as though its dyeing had not been completed. Nonetheless, madder dye components were identified—alizarin, lucidin, 1-methoxy-2-methylanathraquinone, rubiadin, xanthopurpurin dimethyl ether (Table 3) and others (Table 4). In some places, the dark madder appears to have been dabbed or smeared on with a viscous material. In other places it has merged with the fiber and darkened it as a dye. Despite its fine, delicate weave count, 2003-Tx-10 alone among the textiles from Tumulus MM is well enough preserved well to identify the type of fiber (flax), as confirmed by conventional polarized light microscopy (Table 1).

Figure 30. Fragment 2003-Tx-10 Back.

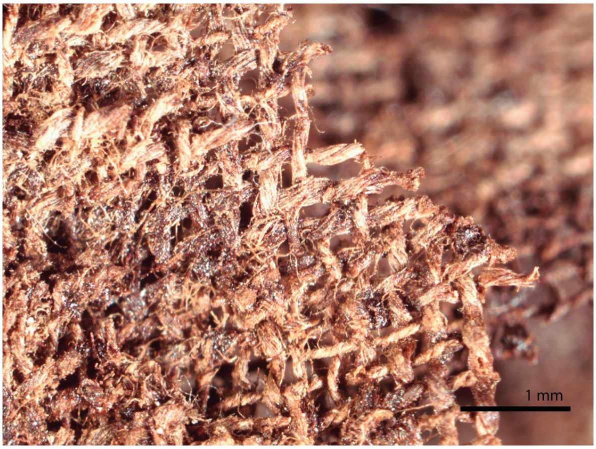

Figure 31. Detail of a single layer of 2003-Tx-10 on the back.

2003-Tx-10 has the lucidin previously found in samples Tx-1 through Tx-6 (Tables 3 and 4)) but lacks the purpurin found in the reddish-purple samples. The lack of purpurin, and sometimes alizarin, may indicate the use of other red chromophoric plants as components of the dye liquors. Helmut Schweppe lists Abyssinia (modern Ethiopia) as a source for *Oldenlandia umbellata* L. or chay root, which contains alizarin and lucidin but no purpurin and no xanthopurpurin [40]. At the time of the construction of Tumulus MM, the Kushite empire on the Upper Nile or the D'mt (Da'amat) kingdom in east Africa might have provided a source closer than India for Phrygian trade. Schweppe also suggests that some components present in the plant might not be taken up by fiber in the dyeing [40] (p. 195); other botanists, dyers, and dye chemists have reported similar issues with *Rubia peregina* (Wild Madder), *Rubia tinctorum* (Madder), and *Galium* sp., all of which are native to Anatolia [35] (pp. 107–166), [41]. Indeed, the textile fragments from Tumulus MM that contained madder lack a full, clear, parallel with any particular classic madder. Future analyses employing MS/MS may resolve this question.

4.4. Mordants

The specific identification of high iron content was confirmed for two fragments as the result of a mineral "dyeing". Early in this study, ICP-MS analysis for bromine was utilized to look for metal mordant ratios, using modern reference standards of mordanted wools, mordanted dyed wools, and previously analyzed historic samples. Nothing comparable to the established ratios was found for 2003-Tx-6, due to loss, diagenesis, contamination, or all of these factors [19,24]. Alum has elsewhere been identified as "Phrygian stone" and described by Charles Singer as an indication of the earliest chemical industry [35] (pp. 20–49), [42]. This interesting topic is outside the scope of the present paper and the self-sampling procedure used in these analyses. The processes used cannot satisfactorily separate functional mordants from soil, seepage, and dirt after 2700 years. Instead of hypothesizing about which metal moiety or moieties may have been active, permission for destructive testing might be sought in the future, in order to provide specific samples that could be cross-sectioned, imbedded, and polished for SEM/EDS with XRF capacity for quantitative analysis. After thorough discussion and permissions for such destructive testing, samples from the City Mound textiles and the Tumulus MM fragments might be successfully assayed and surveyed in this manner.

4.5. Gums and Resins Such as Myrrh

Present on 2003-Tx-10 and 2003-Tx-11 is some type of viscous gum or resin, as yet unidentified, which held the dyestuffs of madder and indigo, respectively, in place. Both gums and resins produce a wide swath of compound peaks in spectra, to the extent that they are ionizable by DART. To characterize such complex samples with DART-MS or pyrolysis gas chromatography-electron impact ionization-MS, results would have to be compared to a reference database of salient gums and resins from that historical context.

5. Conclusions

For those familiar with the Greco–Roman legends of Midas and his "golden touch", the golden-hued goethite-treated textiles from Tumulus MM suggest a tantalizing link to the fabulously wealthy Phrygian king. For the purples of 2003-Tx-3 and 2003-Tx-6, dye scholars and technologists such as Harald Böhmer make a convincing case for iron-mordanted fiber or fabric in single bath madder dyeing being acidified. But these two examples from Tumulus MM both contain forms of stable indigo, and one (2003-Tx-6) has a lower range of iron (Table 5) [43]. Among the various samples analyzed for the present study, there remain confusing patterns of components, hue, and depth of shade. These cannot easily be explained by such things as the selection of old madder roots vs. younger plants, by the re-use of unexhausted or contaminated dye baths, by intentional additional auxiliaries, or by the use of mixed or contaminated mordants [43]. A somewhat haphazard dye process could produce a uniform effect, if the fibers were dyed prior to spinning to even out coloration—creating a heather-like effect.

Somewhat more specificity might be needed to weave small repeating patterns as seen in the fragments from the City Mound (Figure 6). Indeed, skeins could be sorted as lots, and a raised pile, as formed for toweling or carpets, would blend close shades quite well. This might suffice for a single village product. Yet, for commercial scale, a reproducible product and color would be required. Fundamentally, an advanced knowledge of the properties of the dye plants, preparatory methods prior to dyeing, and the effect of auxiliaries and assists are essential. This lends substantial credence toward an extension of Singer's theory to include dyes and dyeing as part of the first chemical industry, where accuracy and precision are necessary. Paradoxically, it also supports the importance of substitution, because the same level of knowledge is required to achieve the same color, to maintain a consistent product over time, when supplies and sources change from year to year [44].

Given the colorants identified in Tumulus MM and the textile equipment excavated in the Terrace Building complex on the City Mound, one can posit a highly developed textile industry at Gordion that was chemically advanced, technically sophisticated, and industrial in scope. One still cannot say how the textiles from Tumulus MM and the operation on the City Mound were related. Whatever the purpose of the charred textiles found on the mound—utilitarian or prestige, luxury gifts or tribute, furnishings or clothing—future study of these fragments may yet establish a correlation. We hope that this paper will serve as incentive for such research, and will underline the importance of colorants, dyeing techniques, and mordants in the ancient Near East, as dyes and colored textiles must have played a major role in economic and social organization, as attested for the kingdom of Phrygia.

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

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Colorants Detected by HPLC-PDA in Textiles from 13th Century Lieto Ristinpelto, Finland

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Abstract: Organic colorants of textiles found in the female burial of Lieto Ristinpelto, SW Finland, were analyzed by HPLC-PDA. The textiles' visible colors varied from different brownish shades to blueish, greenish, and reddish hues. The aim of the chromatographic analysis was to deepen the current understandings of the dyes used in Finland at the transition between the 12th and 13th centuries AD, i.e., at the beginning of the local Medieval period, and to contribute important new information about dyes and clothing from this less-known period of textile history of Finland. The textile finds consisted of a bronze spiral ornamented shawl, an apron tied at the waist, two tablet-woven bands, and a diagonally plaited band with plaited tassels. A unique find was a textile possibly made using the sprang technique. Other textile finds were an orange wool tabby and twill fragments. Analysis of thirty samples from fourteen different textiles indicated that woad colorants were present in most samples, accompanied with lichen compounds, and dyer's madder was in two visually orange fragments. The visually reddish samples contained luteolin, but no red colorants.

Keywords: organic colorants; woad; dyer's madder; luteolin; unknown orange compounds; HPLC-PDA; wool textiles; Medieval period

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1. Introduction

This study focuses on the dye investigation of wool textiles found in the Lieto Ristinpelto 86 female burial, situated in SW Finland (Figure 1). Thirty samples from 14 different textiles (Figure 2; Table 1) were analyzed for organic dyes at the textile laboratory of the Royal Institute of for Cultural Heritage in Belgium. As chromatographic techniques require only very small samples, this method has been applied widely in archaeological textile research to detect organic colorants [1–3]. Moreover, this method was considered the most suitable for the unique textiles of Lieto Ristinpelto, as it allows direct comparison with the analyzed dye composition made from several Finnish traditional dye plants in the reference collection [4,5]. From an archaeological perspective, this is the second time that dye analyses have been carried out on Finnish textiles from this period, and thus, the current study of Lieto Ristinpelto 86 burial's textiles, together with the dyes found in textiles from Ravattula Ristimäki site (4 km from Ristinpelto), brings an important new contribution to the knowledge of dyes used and available in early Medieval Finland.

Figure 1. Location of Lieto Ristinpelto and Ravattula Ristimäki sites near the city of Turku in southwest Finland.

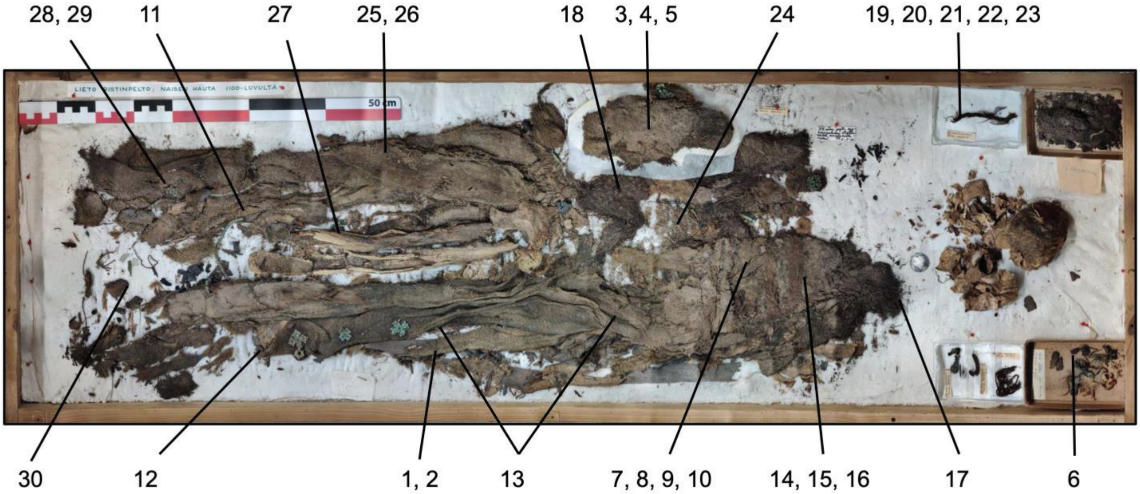


Figure 2. Lieto Ristinpelto grave 86 textiles and the sampling spots for fiber and dye analysis.

Table 1. HPLC results of the wool textile fragments from Lieto Ristinpelto grave 86, with the detected molecules and reference to the possible dye source(s).

No.	Item	Yarn	Detected Molecules	Dye Source(s)
1	Twill dress	Warp	pca, phb, pmb	NDD
2		Weft	Traces of isatin Compounds 1 and 2 pca, phb, pmb	Trace of woad or indigo Compounds 1 and 2

Table 1. *Cont.*

No.	Item	Yarn	Detected Molecules	Dye Source(s)
3	Tablet-woven band with square pattern	Red warp	Trace of luteolin pca, phb, pmb, phc	Trace of luteolin yellow
4		Light warp	pca, phb, pmb	NDD
5		Blue warp	Indigotin, isatin, indirubin Compounds 1 and 2 pca, pmb	Woad or indigo Compounds 1 and 2
6	Diagonally plaited headband of temple ornaments	Warp	-	NDD
7	Diagonally plaited band with plaited tassels	Red warp	Trace of luteolin pca, phb, pmb, phc	Trace of luteolin yellow
8		Blue warp	Indigotin, isatin, indirubin pca, phb	Woad or indigo
9		Light warp	pca, phb, pmb	NDD
10		Blue tassel yarn	pca, phb, pmb	NDD
11	Orange wool tabby	Warp	Alizarin, purpurin (72/28, 255 nm) pca, phb	Dyer′s madder
12	Tubular tablet-woven band bordering the bronze spiral decorated shawl	Weft	phb	NDD
13		Warp	Indigotin, isatin, indirubin Compounds 1, 2 and 3 pca, pmb	Woad or indigo Compounds 1, 2 and 3
14	Tablet-woven band from the chest	Red warp	pca, phb	NDD
15		Light warp	pca, phb, pmb	NDD
16		Dark red warp	Luteolin, apigenin pca, phb, pmb, phc	Luteolin yellow
17	Sprang-like textile	Dark yarn	pca, phb, pmb	NDD
18		Light yarn	Trace of isatin, indirubin Compounds 1 and 2 pca, phb	Trace of woad or indigo Compounds 1 and 2
19	Tubular band bordering the sprang-like textile	Red warp	pca, phb, pmb, phc	NDD
20		Dark red warp	Trace of a luteolin pca, phb, pmb, phc, fea	Trace of luteolin yellow
21		Light warp	pca, phb, pmb	NDD
22		Green warp	Indigotin, isatin, indirubin Compound 2 pca, phb, pmb	Woad or indigo Compound 2
23		Yellow weft	Trace of indigotin, isatin Compound 2 pca, phb, pmb	Trace of woad or indigo Compound 2

Table 1. *Cont.*

No.	Item	Yarn	Detected Molecules	Dye Source(s)
24	Threading yarn for bronze spirals bordering the apron	Dark threading yarn	pca, phb	NDD
25	Apron tied at waist	Warp	Traces of isatin, indirubin Compounds 1 and 2 pca, phb, pmb	Trace of woad or indigo + Compounds 1 and 2
26		Weft	Traces of isatin, indirubin Compound 2 pca, phb, pmb	Trace of woad or indigo Compound 2
27	Constructing yarn for a bronze spiral rosette	Threading yarn	Indigotin, isatin, indirubin pca, pmb	Woad or indigo Compound 1 and 2
28	Shawl with bronze spiral rosettes	Warp	Isatin, indirubin Compounds 1 and 2 pca, phb, pmb, phc, fea	Trace of woad or indigo Compounds 1 and 2
29		Weft	Compounds 1 and 2 pca, phb, pmb	Compounds 1 and 2
30	Orange twill	Warp	Alizarin, purpurin (89/11, 255 nm) pca, phb, pmb	Dyer's madder

Previously, dyes of rich textile materials from the Finnish Late Iron Age sites Turku Kirkkomäki, Masku Humikkala, Eura Luistari, and Perniö Yliskylä were analyzed by the means of optical microscopy [6–9] and wet chemistry [10–13]. These analyses detected visually reddish and blue yarns, and indigotin. Absorption spectroscopy and thin layer chromatography (TLC) were applied in Late Iron Age and Medieval textiles from Turku Kirkkomäki, the Turku Åbo Akademi site, and Mikkeli Tuukkala [14–17], with a positive a match for madder or bedstraws, tannin, and indigotin. Recently, HPLC and UHPLC analyses have been applied on archaeological textiles from several inhumation sites from Finland, resulting in the detection of indigoids, anthraquinones of madder or bedstraws, lichen orchil, and several unknown colorants [18–22]. In HPLC analyses of Medieval 14th–15th century textiles from Turku and Masku, the detected dyes were madder anthraquinones, tannin, indigoids, and weld compounds [23–26]. HPLC analyses of Early Modern period textiles from northern Finland have detected madder, indigoids, and unknown red colorants [19,27].

2. Archaeological Background

The textile preservation in the Lieto Ristinpelto grave 86 is exceptionally rich for Finnish materials. Generally, in the local acidic soil, only small pieces of textiles can survive when in direct contact with copper alloy objects. In this grave, the maximum length of some textile fragments is 70 cm; they have survived mainly due to the textiles' bronze spiral decorations. These textiles contain many features found in Finnish Late Iron Age clothing, such as bronze spiral decorated textiles, but also include Medieval influences such as madder dyed fabrics [28–32].

The Lieto Ristinpelto site was archaeologically excavated between 1949 and 1950, when the rich textile and fur materials of the grave 86 were put into storage in the archives of the Finnish Heritage Agency; only the tablet-woven and diagonally plaited bands were analyzed and published [33], while rest of the material remained unexamined until recently.

The only jewelry in the burial was a round silver pendant that imitates a silver coin. Based on the 14C dates from fur [AD 1224–1289 (95.4% probability); 751 ± 30 BP], wool textiles [95.4% probability AD 1044–1086 (26.9%), AD 1093–1105 (3.6%), AD 1118–1219 (64.8%); 896 ± 29 BP], and human bone samples [95.4% probability AD 1034–1178 (92.4%), AD 1192–1202 (2.9%); 926 ± 29 BP] interred in the burial, it dates from the transition between the 12th and 13th centuries AD [34].

Dress finds from 13th century Finland are rare. Accordingly, this study brings remarkable new information about clothing from this less-known period of textile history of Finland. Based on the 150 examined graves in the Lieto Ristinpelto inhumation cemetery, it was used from the 12th to 13th centuries. This period represents a transition between the inhumation practices and rich grave goods of the local Late Iron Age (ca. 800–1150 AD), and the sparse grave goods and churchyard burials of the Medieval period (ca. 1150–1550 AD), with Catholic parishes formed in south-western Finland during the 13th century [35] (pp. 342–344). At Lieto Ristinpelto some individuals were buried in full costume with jewelry, furs, knives, and other supplies, while most burials contained little or no grave goods [36]—a phenomenon acknowledging both the old, local beliefs and the new Christian burial customs. Additionally, the site has the remains of a small building (7 × 7 m), which has been interpreted as serving an ecclesiastical purpose [36,37].

3. Materials and Methods

3.1. Archaeological Materials

A recent survey revealed several textiles in burial 86 (catalogue number KM 8656:15 H15). The textiles were examined and documented in Finland on the premises of the Finnish Heritage Agency using a OnePlus7T mobile phone, and a Leica S6D stereomicroscope with a Leica EC6 camera and Las EZ 3.4.0 software. One-millimeter-long yarn cuts were placed on glass slides, mounted with Entellan New rapid™ and covered with coverslips. These fiber samples were examined in the Nanomicroscopy Center of Aalto University using a Leica 2500 transmitted light microscope (TLM), imaged with a Leica MC190HD camera, and measured with LAS V4.13.0 software to acquire more information about the wool fibers and their natural pigmentation.

All yarns were of wool (Figure 3) according to their morphology and scale patterns [38] (pp. 261–273), except two that were identified as bast fibers. Their identification was based on a three-stage protocol [39], including longitudinal and cross-sectional observation as well as determination of microfibrillar orientation by the modified Herzog test [40] and SFS-EN ISO 20706-1:2019 standard [41]. Threading yarn of the apron's bronze decorations was flax (Figure 4a–d). The tabby veil (or sheet), of which there were only scanty remains, showed a microfibrillar Z orientation, indicating hemp [42].

The dress was 2/2 twill, woven with Sz-plied yarns in the warp and z-spun yarns in the weft (Figure 5a). The shawl's weave and yarns were consistent with the dress and the fabric having a tubular selvedge; the textile was decorated with bronze spiral rosettes, and bordered with a tubular tablet-woven band (Figure 5b). It is likely that when worn, the shawl was held at the shoulders, but in the burial, it was used to cover the deceased. Similar weave and yarn properties were used for the bronze spiral decorated apron, which also had diagonal-plaited bands in its upper corners to tie the apron at waist (Figure 6a). These bands had plaited tassels (Figure 6b), which is a finishing technique found in Finnish Iron Age bands [43].

Two colorful tablet-woven bands rested on the chest area; they were woven using Sz-plied warp yarns and the double-face weaving technique previously only identified in Finland in a single 12th century burial [43,44]. The better-preserved band had a pattern forming squares (Figure 7a), while the pattern was not as apparent in the second band (Figure 7b). Fragments of a diagonally plaited band with hanging temple ornaments and small bronze spiral rosette were found near the skull.

Figure 3. Wool fibers of the shawl's warp band with some visible scales and blue dye.

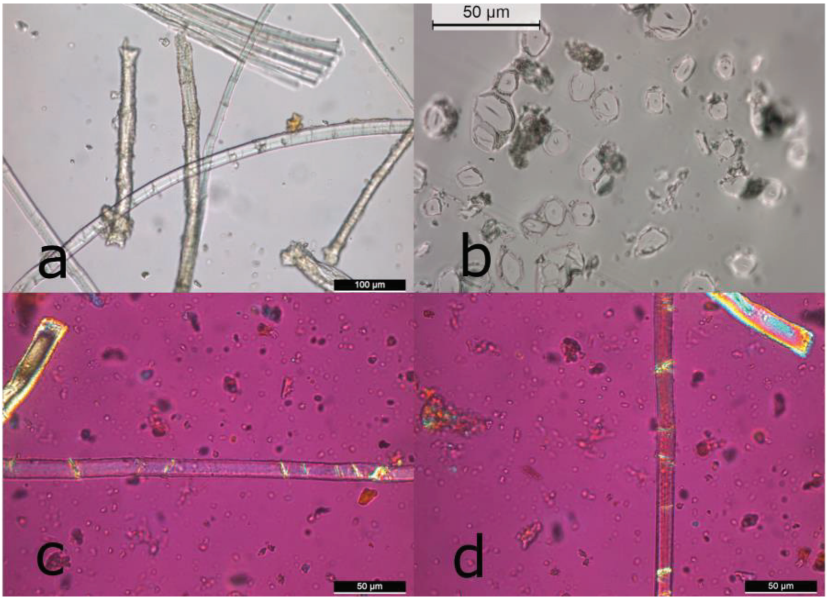


Figure 4. Flax (*Linum usitatissimum* L.). (**a**) Longitudinal view, (**b**) cross-sections showing fiber's polygonal shape, (**c**,**d**) color changes in the Herzog's test revealing microfibrillar S orientation.

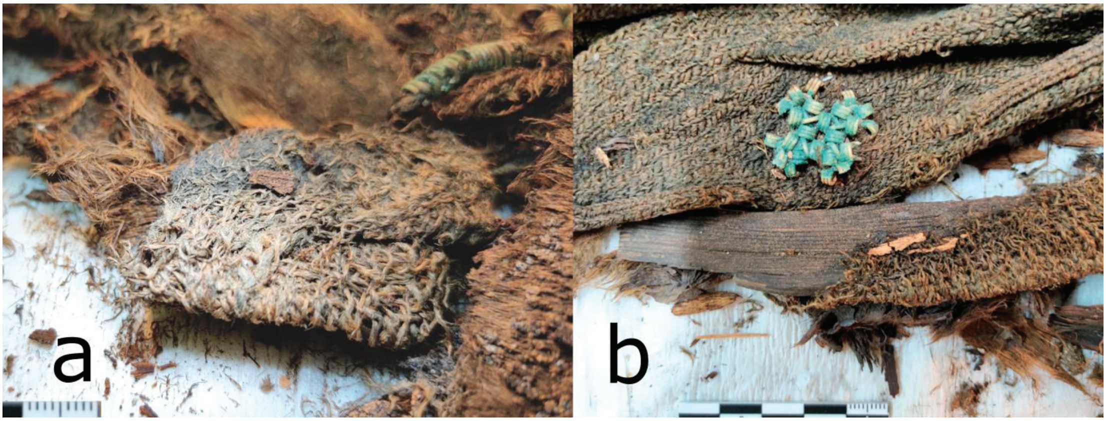


Figure 5. Twill fabrics. (**a**) Dress fabric with altering blue and undyed yarns. (**b**) Shawl, decorated with bronze spiral ornaments and bordered with a tubular tablet-woven band.

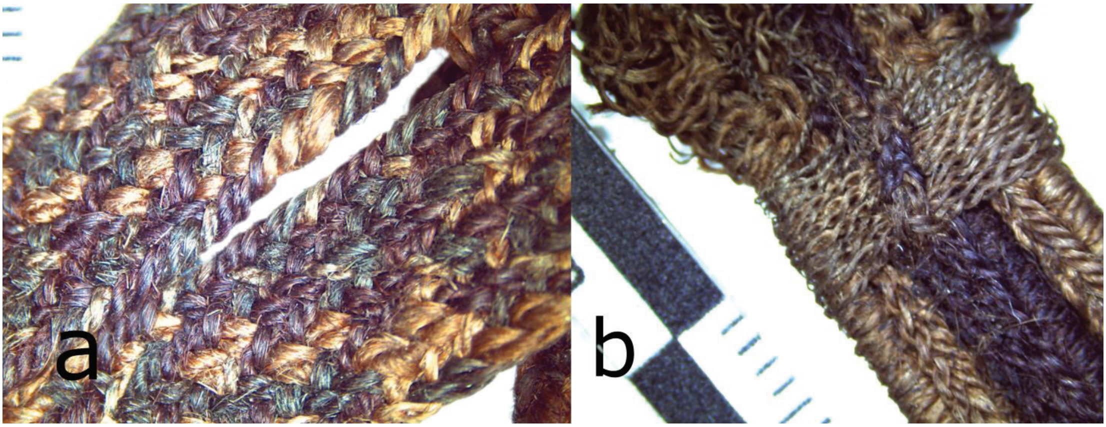


Figure 6. Three-colored bands. (**a**) Diagonally plaited apron band. (**b**) Plaited tassel finishing of the band.

The orange tabby and twill were woven using single-plied s- and z-spun yarns (Figure 8a). These small fragments were found near the feet, and may be sock remnants. A unique find was a sprang-like textile, placed on the upper body. It was crafted using Sz-plied dark- and light-colored yarns, and bordered with a colorful tubular band (Figure 8b). Since there are no other archaeological sprang textiles from Finland, the structure of this textile was difficult to completely parse.

3.2. Chromatography

The analysis method used was high-pressure liquid chromatography and photodiode array detection (HPLC-DAD), made using Water's ACQUITY Arc system with a column heater/cooler and a quaternary solvent manager, a 2998 PDA with low dispersion flow-cell 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 3–29 min, and isocratic 23A/67B/10C from 30–35 min.

For the stationary phase, a temperature-controlled column of LiChrosorb RP-18 with a 125 mm × 4 mm diameter end cap with 5 µm particle size and 100 Å pore diameter was used.

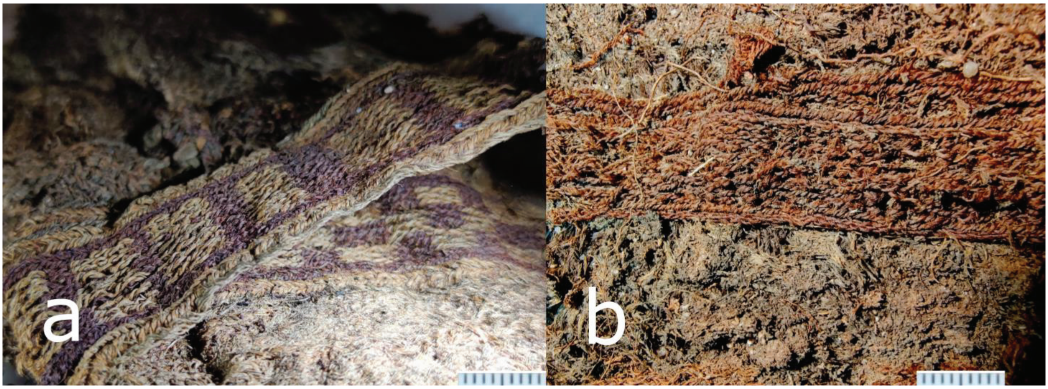


Figure 7. Tablet-woven bands. (**a**) Band with a square pattern. (**b**) Visually reddish tablet-woven band.

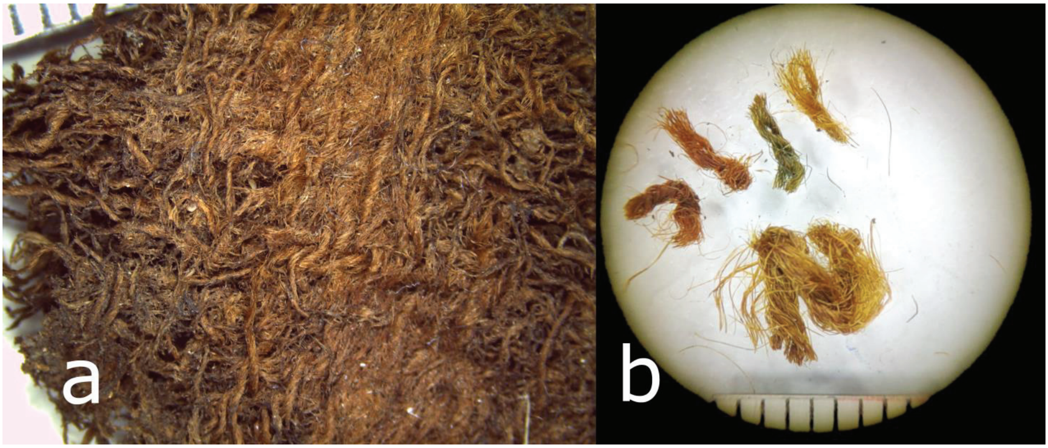


Figure 8. Visually orange and red yarns. (**a**) Orange twill fabric. (**b**) Yarn samples from the tubular band bordering the sprang-like textile.

3.3. Dye Extraction

Before analysis, the small 4 to 6 mm-long thread samples were examined under a Zeiss Stemi stereomicroscope to determine fiber type, morphology, color or hue, and sample condition. Where necessary and to the extent possible, surface contaminants were removed. The color extraction procedure was then chosen based on these initial observations. The dyes were extracted by treating the fibers in 250 µL water/methanol/37% hydrochloric acid (1/1/2, *v*/*v*/*v*) for 10 min at 105 °C in open Pyrex tubes in a heating block. The dye solution was further purified by adding 500 µL ethyl acetate. After a few minutes, the upper phase was decanted, and the ethyl acetate solution was dried in a vacuum evaporator. The dry residue was dissolved in 30/30 µL methanol/water, of which 20 µL was injected. [1]. If the initial sample size allowed for a second extraction, the remaining sample was analyzed after extraction in 250 µL water/methanol/37% hydrochloric acid (1/1/2, *v*/*v*/*v*) alone. After 10 min in open Pyrex tubes at 105 °C, the sample was filtered and vacuum evaporated. Hereafter, the residue was dissolved in 30/30 µL methanol/water, of which 20 µL was injected. Visually green and blue yarns (Samples 5, 8, 13, 22) were analyzed after extraction in dimethyl sulfoxide for 10 min at 80 °C, followed by immediate injection. When possible, the dry residue sample was subsequently extracted with hydrochloric acid and a second analysis performed on the solution obtained.

4. Results

Of the 30 analyzed yarns, colorants were present in 18 cases, either as dye or at the trace level. No dyes (NDD) were detected in 12 samples (Table 1) [45].

4.1. Indigoids for Blue

Indigoids (Figure 9A,B) were present in 11 samples: the detected compounds were indigotin (the main marker), indirubin (the isomer of indigotin), and /or isatin (a precursor). Indigotin was used to dye the border yarns blue in the tablet-woven band with square patterns (Sample 5; Figure 7a), to form a zig-zag pattern in the diagonally plaited band (Sample 8; Figure 6a,b) and in the warp yarn of the tubular tablet-woven band (Sample 13, Figure 5b). The threading yarn for the apron's bronze spirals (Sample 27) was dyed blue, as well as the green-looking warp yarn (Sample 22; Figure 8b) of the tubular band of the sprang-like textile. Minimal amounts of indigoids also occurred in the weft of the dress (Sample 2; Figure 5a), the light-colored yarn of the sprang-like textile (Sample 18), the tubular band's yellow weft (Sample 23, Figure 8b), both the warp and weft of the apron (Samples 25 and 26), and the shawl's warp (Sample 28; Figure 5b).

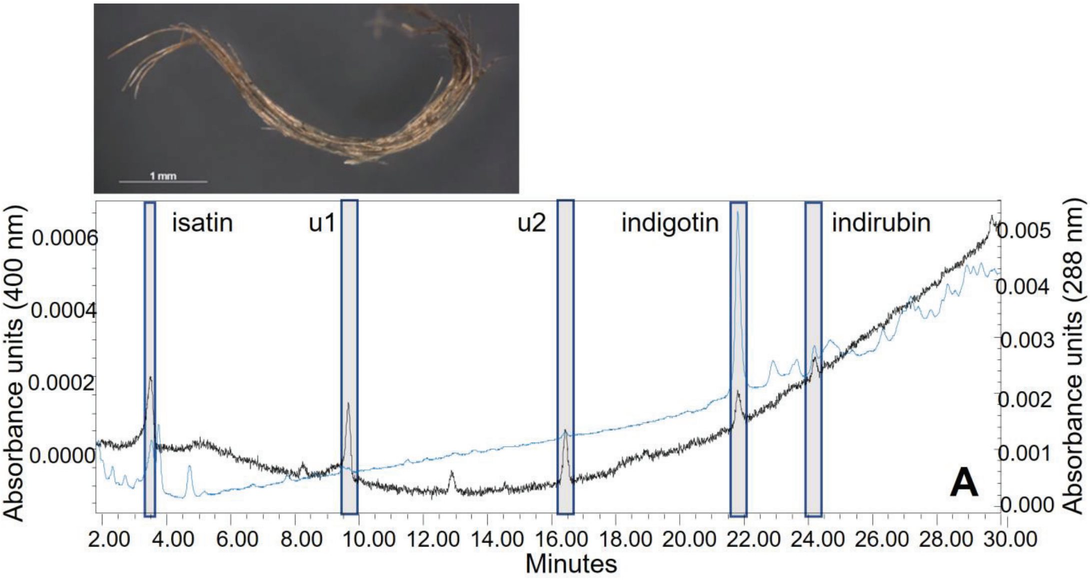


Figure 9. *Cont.*

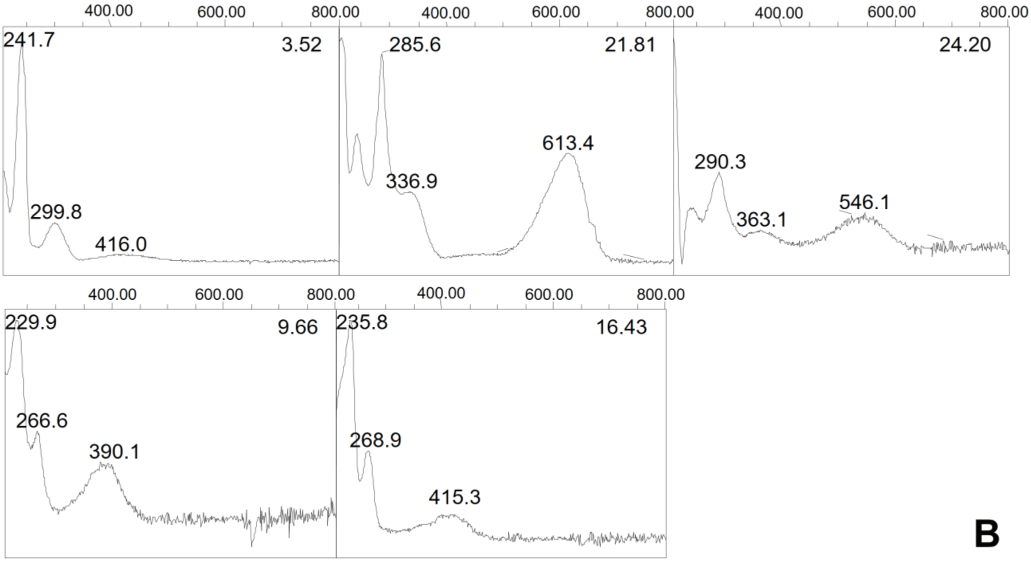


Figure 9. Indigoids and Compounds u1 and u2. (**A**) Chromatograms at 400 nm (black) and 288 nm (blue) of the dye extract obtained with hydrochloric acid and ethyl acetate from the blue yarn of a tablet-woven band (Sample 5) with (**B**) the absorbance spectra between 200–800 nm of the detected dye compounds isatin, indigotin, indirubin, and Compounds 1 and 2 (u1, u2).

4.2. Orange Compounds

In eleven of the thirty yarns analyzed, two chromophoric compounds were found (Compounds 1 and 2). They appeared at 9.6 and 16.4 min and had absorption spectra with a maximum absorbance in the visual light wavelengths at 390 and 415 nanometers, respectively, suggesting an orange-red color (Figure 10). In one sample (Sample 13), they were accompanied by a third, minor compound with a retention time of 19.5 min and absorption maximum at 390 nanometers (Compound 3). In this set of analyses, they were detected ten times in the presence of indigotin, isatin, or indirubin.

4.3. Anthraquinones for Red

Alizarin and purpurin, which are red anthraquinone colorants, were detected in both the wool tabby's (Sample 11) and orange twill's (Sample 30; Figure 8b) warp yarns. In both samples, the alizarin and purpurin were detected in relative peak area ratios of alizarin to purpurin of 72/28 and 89/11 (calculated at a wavelength of 255 nm), respectively (Figure 10A,B).

4.4. Yellow Colorants

The flavone dye molecules luteolin, and to a much lesser extent apigenin, were found in the dark (red) yarn of the tablet-woven band (Sample 16) (Figure 11A,B; Figure 7b). Minimal amounts of luteolin were also detected in three other cases, namely in the reddish yarn of the square patterned tablet-woven band (Sample 3; Figure 7a), in the dark red warp yarn of the tubular band of the sprang like-textile (Sample 20; Figure 8b), and in the yarn of the diagonally plaited band fragment (Sample 7; Figure 6a).

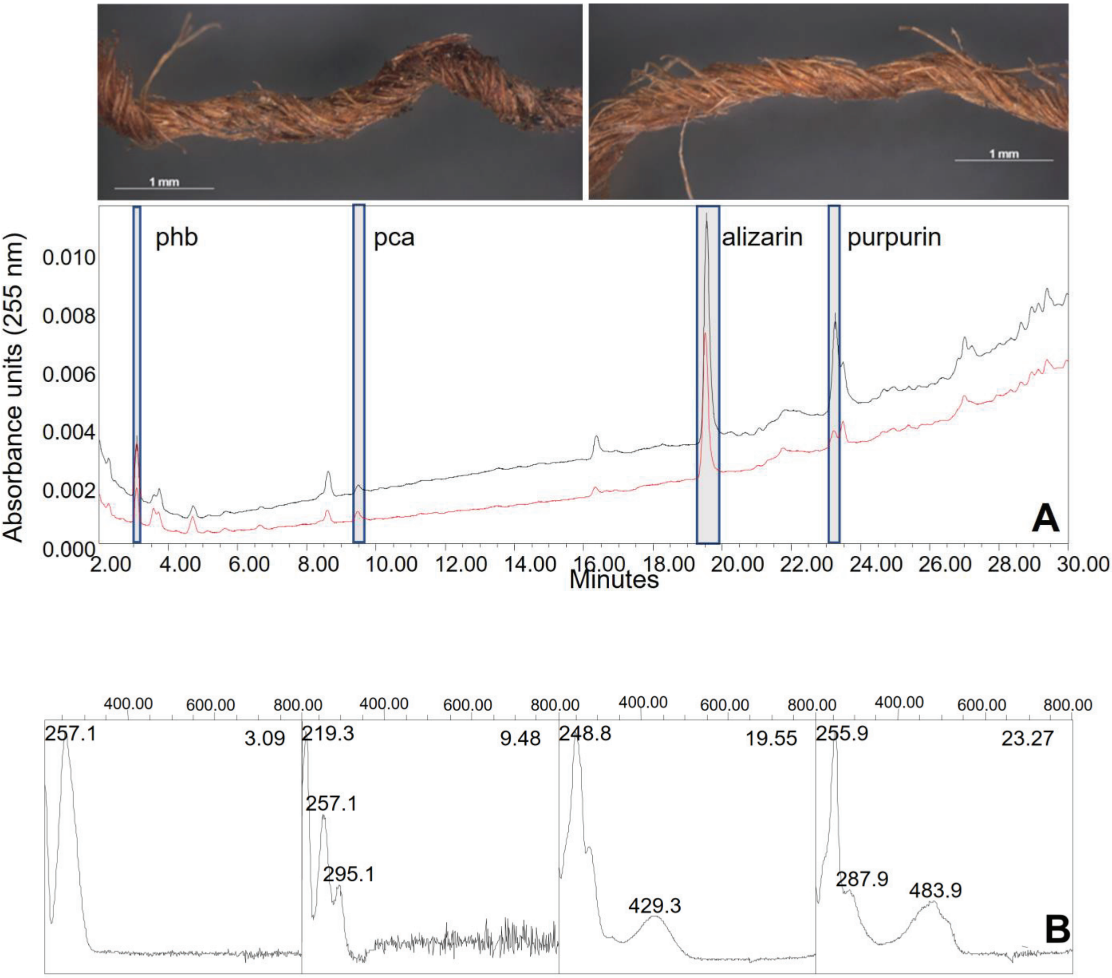
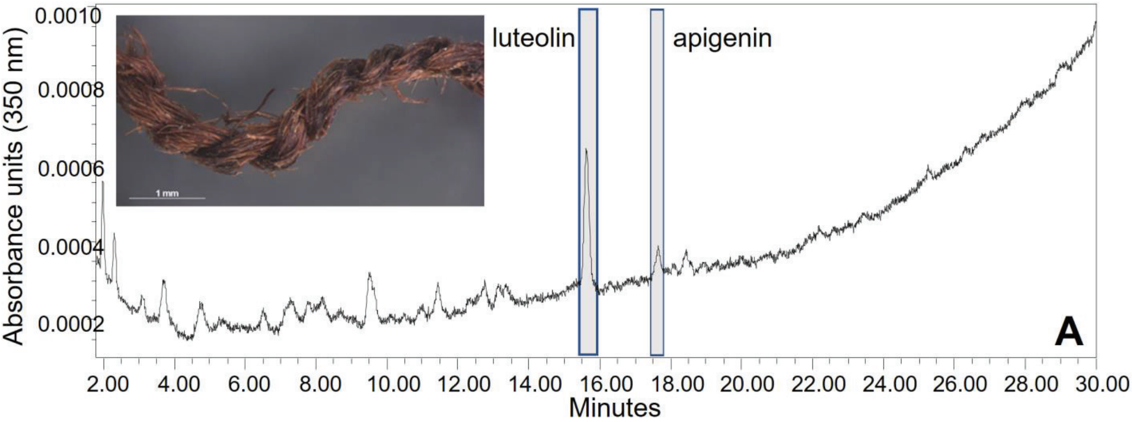


Figure 10. Anthraquinone reds and benzoic acid derivatives. (**A**) Chromatograms at 255 nm of the dye extract obtained with hydrochloric acid and ethyl acetate from the warp yarns of the orange tabby (Sample 11, in black) and the twill fabric (Sample 30, in red), with (**B**) the absorbance spectra between 200–800 nm of the detected benzoic acid derivatives (phb, pca), alizarin, and purpurin.

4.5. Other Compounds

Benzoic (phb, pmb, pca) and cinnamic acid (fea, phc) derivatives were detected in many samples. These are colorless compounds which cannot be related directly to any dye source. Their occurrence, in terms of the peak heights, was rather moderate.



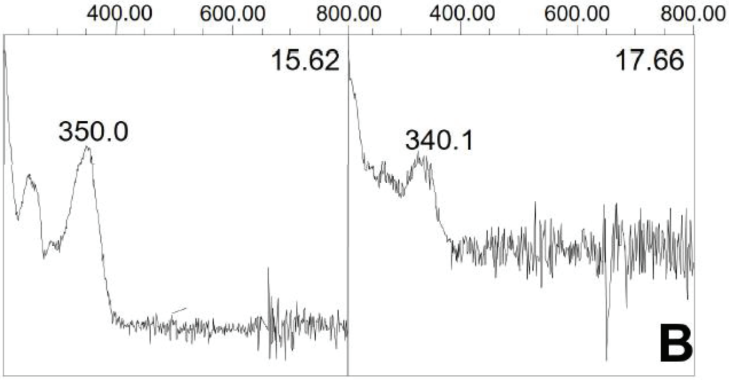


Figure 11. Yellow colorants. (**A**) Chromatogram at 350 nm of the dye extract obtained with hydrochloric acid and ethyl acetate from the dark (red) yarn of a tablet-woven band (Sample 16), with (**B**) the absorbance spectra between 200–800 nm of the detected dye compounds luteolin and apigenin.

5. Discussion

The dye composition found in the HPLC-PDA analysis of the Lieto Ristinpelto yarns does not distinguish between woad (*Isatis tinctoria* L.) or tropical indigo shrub (*Isatis Indigofera* L.). The geographical context (Northern Europe) and the date of the textiles (13th century AD) cannot be used to exclude the use of imported tropical indigo, since tropical indigo was already traded to Europe at this time [46] (p. 364). However, European woad is more likely: it has already been used in blue dyeing in Bronze Age to dye the Hallstatt textiles [47] and it was widely cultivated in at least in Germany by the Middle Ages, and traded all over Europe [16] (p. 368). Woad was probably never cultivated locally in Finland, even though it now grows wild along the sandy shores of Finland's southern coast. Woad was most likely traded to Finland as woad balls by the Iron Age [20,48].

Of the analyzed textiles, only four yarns were certainly dyed blue (Samples 5, 8, 22, 27), based on the clear presence of indigotin, indirubin, and isatin. The yarns were also in good condition, due to their placement in the grave. The tablet-woven band (Sample 5) with square patterns survived due to its direct contact with a bronze spiral rosette, while the diagonally plaited band (Sample 8) survived due its proximity to the apron's spiral bordering, as did the wool yarn threaded inside the apron's bronze spirals (Sample 27). The greenish warp yarn (Sample 22) of the tubular tablet-woven band survived inside the tightly woven band's wefts.

The dress fragments were very degraded, which can explain the trace level of indigoids detected in Sample 2. Additionally, the microscopic examination revealed that the twill dress was woven using plied blue yarns in every second warp, as well as single-plied blue yarns in every second weft. Every second yarn in both systems was undyed, like Sample 1. Similar-type twill, with two differently colored yarns in the warp and weft was recently found in Ravattula Ristimäki grave 41, although this example was woven by alternating naturally pigmented and white wool yarns [29,49]. The trace level of indigoids detected in the apron yarns (Samples 25, 26), as well as in the shawl's warp (Sample 28) and the sprang-like textile's lighter yarn (Sample 18) can be explained by the sampling location near the fragments' faded edges. TLM observations showed the fibers were very eroded, but some were blue in color. It is likely that indigotin was used to dye the shawl's warps, the sprang-like textile, and the apron, as well as the wrapping yarn of the tassel (Sample 10), following the pattern of utilizing blue in textiles in Finnish Late Iron Age attire [7,13,50,51]. The indigoids in the tubular band's yellowish weft (Sample 23) were most likely contaminated by the band's greenish warp (Sample 22), since no blue hue was found in TLM observation.

The orange-red colorants detected with indigoids in 10 samples indicate the use of a combined dyeing with an indigoid blue and another dye source, unidentified so far. These could possibly be lichens, but other dye sources with unknown or degraded dye components under the given environmental or analytical conditions cannot be ruled out. Lichen dyes that have been detected in woad-dyed Late Iron Age textiles found in Finland and Estonia [20,48]. This dye combination (woad and lichens) was also known elsewhere in the Medieval Europe [46] (pp. 499–501). In the weft yarn of the shawl (Sample 29) only orange-red dyes found, forming a vivid texture with the warp yarns that contained indigoids as well.

Orange dye components have been regularly found in Scandinavian archaeological textiles, but they not been identified or attributed to any dye class [1,19]. There is a lot of variation in absorption spectra and retention times which prevents further identification of the specific dye molecules. These are probably spectra of less stable dyes, which have degraded differently under the influence of the specific burial conditions. On the other hand, the mode of dye extraction and/or the chromatographic method may have caused changes in the composition and spectral characteristics of these (less stable) dye(s). The larger number of dye analyses performed on Finnish archaeological textiles during the last decade also bring up similarities; the orange dyes (Compounds 1 and 2) were previously found combined with dyes from indigo/woad in multiple samples from the cemetery of Ravattula Ristimäki near Turku, dated AD 1100–1250 [49], while also unknown orange-red compounds are reported in the presence of indigo/woad in samples from the contemporary sites Turku Kirkkomäki and Masku Humikkala [19,52]. Although the spectra from the latter unknown compounds (analyzed under slightly different extraction and analysis conditions) is not exactly the same as those from textiles found at the Ristinpelto and Ristimäki sites, the detection of such orange compounds together with indigotin might well indicate that it must have been a common dyestuff combination in that period.

The detected anthraquinones alizarin and purpurin indicate that the rhizomes of a plant from the Rubiaceae family were used for red dyeing (Samples 11, 30). Since alizarin was the predominant compound, the dye source was probably dyer's madder (*Rubia tinctorum* L.) instead of local bedstraws (*Galium* species) or woodruffs (*Asperula* species) [53]; the latter two were important local dye plants for stable red from the Late Iron Age to the 19th century, especially in the Nordic countries and Estonia [54]. Although madder dyed textiles were well-known in Scandinavia during the Early and Late Iron Age and the Early Medieval period [55–57], anthraquinone dyes are not commonly found amongst Finnish Late Iron Age or early Medieval textiles. Traces of alizarin was previously detected in the band of a leg wrap from the Turku Kirkkomäki inhumation cemetery, dated to the 11th–12th centuries AD [58]. This might be an indication of the use of dyer's madder. Additionally, local Rubiaceae dyes such as bedstraws (*Galium* sp.) or dyer's woodruff

(*Asperula tinctoria* L.) were detected in 11th century AD textiles from a female burial in the Eura Luistari inhumation cemetery, also located in southwest Finland [59].

In the Lieto Ristinpelto burial 86, dyer's madder was identified in two textile fragments. These were the visually orange tabby and twill fragments, located near the feet. These textile types are not common among Finnish archaeological textiles, which are usually twills with a plied warp yarn and single-plied weft yarn [7,13]. Madder dye, however, has been found in locally woven wool twill socks in Ravattula Ristimäki burial 41 [21,29]. Recent studies of the textiles from Turku, founded in the late 13th century [60], have provided new information of Medieval Finnish red dyes. Dyer's madder was identified in three imported textiles from a relic assemblage at Turku Cathedral. The items have been 14C dated to the 13th–14th centuries, and consist of one cotton and two silk fabrics, presumably of oriental origin [25]. Dyer's madder, bedstraw colorants, tannin, indigotin, and flavonoids of weld (*Reseda luteola* L.) have also been detected in urban textiles from Medieval Turku [23,24,30].

The presence of luteolin in four yarns (Samples 3, 7, 16, 20) indicate the use of a luteolin-based yellow dye source. Without other accompanying dye molecules, a wide range of yellow dye plants might have been used. Together with apigenin, the source of luteolin could be weld (*Reseda luteola* L.), dyer's broom (*Genista tinctoria* L.), chamomile (Anthemis species), and sawwort (*Serratula tinctoria* L.) [61] (pp. 346–357). These plants have a long tradition in the Central European textile dyeing from the Bronze Age [2,47] to the Medieval time [46] (pp. 168–180). In Scandinavian Iron Age textiles luteolin has been detected in several cases [1]. All these plants have luteolin as the main coloring component and some contain apigenin as a minor compound. None of these are native to Finland except scentless chamomile (*Anthemis arvensis* L.); dyer's chamomile (*Anthemis tinctoria* L.) arrived in Finland during the local Middle Ages.

In general, the preservation of flavone dye molecules in Finnish archaeological textiles is very exceptional. Previous research has found apigenin and luteolin only once in Late Iron Age textiles, namely in a three-colored imported textile found in the Mikkeli Tuukkala inhumation cemetery, dated to the early 14th century. Yellow dyes have been connected to the deep cultural changes in Finland at the beginning of the Medieval period due to Christianization and Swedish rule. New influences increased the import of new dye stuffs and alum that was not available in Finnish bedrock [20] (p. 63).

Surprisingly, luteolin-based dye was present in the square-patterned tablet-woven band's visually red warps (Sample 3), in the reddish warp of the diagonally plaited band (Sample 7), the dark red warp of the tablet-woven-band which rested on the chest (Sample 16), and in the dark red warp of the tubular band of the sprang-like textile (Sample 20). In two slightly differently colored visually red yarns, no dyes were detected (Samples 14 and 19). This suggests a colorant that cannot be detected using the HPLC method. Only parallel for these reddish yarns with a luteolin-based dye has been detected in a textile from a 11th century child burial from Turku Kirkkomäki [62]. According to the TLM examination, the wool in all these yarns was unpigmented, so a pigmentation cannot explain the shade of color in these yarns. Other warp yarns in these bands were undyed white wool (Samples 4, 9, 21) and blue dyed wool. When weaving colorful bands, it is mandatory to keep the yarns in order, to create certain patterns. With warps having only slight visual color differences, such as yellow and natural white wool, weaving becomes very demanding. Because of that, it seems unlikely that the reddish hue is the result of the burial context or degradation of yellow dyes.

The detected luteolin-based dye unfortunately cannot explain the several unknown red colorants in the visually red yarns, found in previous Finnish research of archaeological textiles. These compounds have appeared in HPLC analysis in Late Iron Age textiles from southern Finland, as well as in 18th century funerary textiles from northern Finland [19,27] with no parallels in other European archaeological finds. Alder buckthorn (*Rhamnus frangula* L.) bark has been suggested a source of the unknown red compounds detected in Finnish Iron Age textiles [20] while the unknown red colorants found in Medieval textiles from Turku have been connected to common alder (*Alnus glutinosa* L.) bark dye, which was used in conjunction with iron to produce a black dye [32].

The sprang-like textile's dark yarn and spiral rosette's construction yarn (Samples 17, 24) were undyed, naturally pigmented wool. The square-patterned tablet-woven band's light-colored warp (Sample 4), light warp of the tubular band of sprang-like textile (Sample 7), and the headband (Sample 6) were spun of undyed, white wool.

6. Conclusions

The dye analysis of the textiles in Lieto Ristinpelto burial 86, dating to the transition of the Late Iron Age to the Medieval period, identified several colorants in 18 of the 30 analyzed samples. Most textiles had natural dyed yarns. The headband was not dyed and contained only white wool, and the natural pigmented constructing yarn of a spiral rosette was also undyed.

Indigotin, indirubin, or isatin, likely originating from woad, were detected in 11 samples. This suggests that the bronze rosette decorated shawl was blue, as well as the apron and shawl's tubular tablet-woven band. Blue warps were also present in the diagonally plaited band, and the border warps of the tablet-woven band with a square pattern. The dress was woven with blue-dyed and undyed yarns in both the warp and weft. Blue colorants were accompanied by three orange-red compounds, indicating the use of woad with a second dye source, possibly lichen. Some other Finnish samples from other archaeological sites have contained these same colorants, suggesting a local dyeing tradition.

Dyer's madder was present in two samples, namely in the orange tabby and twill. As a rare dye finding in the Finnish context, this suggests imported textiles. In six visually reddish yarns originating from the bands, no red colorants were detected. Four of these contained the yellow colorant luteolin, once with apigenin. This suggests a luteolin-based dye source, and/or an unknown local dye source that cannot be detected by the HPLC-PDA method.

The textile and yarn structures originating from the Finnish Late Iron Age and present in the Lieto Ristinpelto shawl, apron, and diagonally plaited and tablet-woven bands indicate that locally spun wool yarns were used in these textiles. These were dyed with imported dyes, which may have been used alongside local colorants. The less common textile types, such as the orange tabby and twill, suggest that these madder dyed fabrics were imported. Woad and dyer's madder, along with weld, sawwort, and dyer's chamomile were widely used in Medieval Europe. These dye plants were not cultivated in Medieval Finland, but were already being traded during the late 12th and 13th century.

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Ethics: In this study: human bone was used for ^{14}C dating. It was treated with respect, although according to Finland's Antiquities Act, all materials over 100 years old (including human remains) are seen as objects.

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Heritage Science Contribution to the Understanding of Meaningful Khipu Colours

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Abstract: This work is the first scientific study of khipu dyes and inorganic mordants and auxiliaries, paving the way for a new approach to understanding khipus' meaningful materiality, technology, and colours. Khipus have usually been described as "Andean knotted records", but they are much more than complex knotted cords: a great part of the information encoded resides in khipus' incredible colours. The objects of this study are two Wari khipus, 1932.08.0001 and 1932.08.0002, now at the Museum of World Culture in Gothenburg, Sweden. After a morphological study of the khipus, the objects were imaged with multiband imaging (MBI) as an aid for the sampling decisional process. The khipus were then analysed non-invasively by X-ray fluorescence (XRF) spectroscopy on selected areas of particular interest. The khipus were consequently sampled for elemental characterisation by micro-XRF, and liquid chromatography coupled with high-resolution mass spectrometry (HPLC–HRMS) for characterising the organic dye composition. This paper presents a part of the results of the project "Meaningful materials in the khipu code", with the intent to shed light on the difficulties and possibilities of investigating khipu colours and dyestuffs. MBI and XRF revealed unforeseeable structural characteristics, such as remnants from a heavily degraded thread in an area of missing thread wrapping and a dual-coloured thread that was previously deemed single-coloured. The organic dyes identified by HPLC–HRMS comprised indigoids, cochineal, and an unknown flavonoid-based dyestuff. XRF of the inorganic components revealed associations of several elements with specific colours.

Keywords: khipu; Wari; textiles; dyestuffs; heritage science; multiband imaging; X-ray fluorescence; high-performance liquid chromatography; mass spectrometry

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1. Introduction

Khipus are a uniquely Andean three-dimensional communication medium made of colourful knotted cords. Khipus were interpreted through sight and touch. The Incas used them to encode information regarding the census, calendars, and accounting [1] using a decimal positional system of knots [2–4].

What is still missing is a full understanding of how the qualitative information was encoded (that is, "what are these numbers counting?"). Moreover, there are extensive chroniclers' testimonies that khipus were used for narrating stories and Inca history too: how narrative information was registered in the khipu code is still obscure [5–8]. With the advent of data science, urgent calls for digitisation and computational analysis of khipus are raised in order to decipher khipu writing [9].

The way the cords were manufactured and organised in relation to each other would convey meaning through fibre type and colour [10], ply direction [11], and possibly also knot attachment [12,13]. Recent research disclosed relational meanings of colourful cords

[6(165-166)-14-16], yet, prior to this study, no physical–chemical analyses of colourants had been conducted on Andean khipus. Colour remains largely uncharted territory: taphonomic processes and conservation practices have surely altered the original khipu colours, and, with that, our possibility to understand a vast part of khipus' meaning. No standard protocol for recording khipu colours has been developed to date that meets the extreme variability in khipu colours.

Chroniclers from the 16th and 17th centuries also often stress the importance of colour for recording qualitative information on Inca khipus [6] (pp. 165–166), [14–16] (pp. 359–361; 152; 155). However, we have no information about the dyestuffs and mordants for conferring meaningful colours to Andean khipus. Given the lack of this knowledge, many issues can be raised regarding the understanding of colour patterns and colour meaning of archaeological khipus. Factors such as soil composition, archaeological context, and later treatments in collection contexts have surely affected dyestuffs in different ways.

Knowing more about khipu dyes will enhance our understanding of meaningful khipu colours. By extension, it will also open new ways to investigate the meaning that may emerge from the process of khipu-making. What is more, dyes might have been relevant to the khipu code not only for the colourful result they produced on khipu cords but also for the socially produced significance of the dyestuff material and/or the potentially meaningful way of handling or processing required for colouring the threads (an example of this type of study in a Mesoamerican context can be found in [17,18]).

In this work, we will present the analyses carried out on two Wari khipus at the Museum of World Culture, Gothenburg. The Wari were a south-central Andean and coastal civilisation that flourished from about 500 to 1000 AD. Wari khipus are today believed to be the forefathers of the Inca khipu technological tradition, and they display unique features, such as thicker cords and smaller dimensions, no decimal organisation of knots, and, most importantly, complex and colourful thread wrappings, which are believed to store most of the Wari khipus' information [19–22]. Future comparisons of Wari and Inca khipu dyestuffs might tell more regarding the shared cultural trait of thread wrapping and the evolution of khipu technology.

The organic and inorganic components of khipu 1932.08.0001 and 1932.08.0002 were characterised following an analytical approach that implemented multiband imaging (MBI), X-ray fluorescence spectroscopy (XRF), and liquid chromatography coupled with high-resolution mass spectrometry (HPLC–HRMS).

2. Provenance

A collection of objects, including khipus 1932.08.001 and 1932.08.0002, arrived in Gothenburg in 1932. It was donated by Swedish consul Sven Karrel to the ethnographic department of the Gothenburg Museum, which, at that moment, was directed by Erland Nordenskiöld. In the catalogue, the only reference to provenance is "Nasca" [23] so far.

3. Description of the Khipus

In this section, khipus will be briefly described in order to present the key that is used to identify the areas where the analyses have been carried out. In Table 1, the colours of khipu 1932.08.0001 and 1932.08.0002 are listed. A Pantone® extended gamut coated guide has been used to classify khipu colours by juxtaposition of the chart to the khipu. A descriptive colour name is listed from the closest hexadecimal colour identified through the Encycolorpedia search engine [24]. For ease of legibility, short colour terms will be used in this article. Representation of the khipu cord structures is provided in the Supplementary Materials (Tables S1 and S2).

Table 1. Table of colours found on khipu 1932.08.0001 and 1932.08.0002.

Pantone® Colour Code	Closely Related Descriptive Colour	Short Colour Term	Material	1932.08.0002	1932.08.0001
*	Ivory	Ivory	Cotton	x	x
468	Durian white	Ecru	Cotton	x	x
4685	Manila		Cotton		
463	Violin brown	Brown	Cotton	x	x
7505	Coyote brown		Cotton		
464	Bronze	Light Brown	Cotton		x
465	Camel	Yellow	Cotton		x
467	Burlywood	Beige	Cotton		x
2311	Tumbleweed		Cotton		
201	Royal red	Red	Wool	x	x
7613	Old rose	Pink	Cotton	x	x
7612	Tuscany-Antique brass		Cotton		
442	Ash grey	Blue	Cotton	x	x
5497	Morning blue		Cotton		
7538	Dolphin grey		Cotton		
455	Antique bronze	Green	Cotton	x	
*	Black	Black	Cotton	x	x

* no correspondence found.

Registering visually perceived colours is a qualitative process subjected to several influential factors, such as light source, background, eye tiredness, and cultural conceptualisation of colour [25]. For this reason, the specific hues do not have to be considered absolute and are only meaningful in the context of this specific study. Even though the same colour chart was used to register colours of other khipus in different museums, visually perceived colours registered in different environmental conditions can only be compared on an approximate and qualitative level but not for quantitative or statistical studies. This is also why study of khipu colours needs to be sustained by dye analysis.

4. Khipu 1932.08.0002

Khipu 1932.08.0002 presents a loop and branched Wari khipu morphology (for a description of morphological Wari khipu types, see [21]) (Figure 1). To a primary cord looped in a circle, only one pendant (P_1) is attached. P_1 hosts eight subsidiary cords (P_1s_1–P_1s_8), the last of which also hosts eight subsidiary cords of second level ($P_1s_8s_1$–$P_1s_8s_8$). P_1s_6, P_1s_7, $P_1s_8s_7$, and $P_1s_8s_8$ also host one subsidiary cord each. All twenty-two cords are made of cotton except the red threads, which are made of animal fibre. Colour patterns on this khipu include solid (monochrome) cords, mottled, and typical Wari-style segmented cords—which means that one cord starts solid and ends barber pole [21].

Figure 1. Khipu 1932.08.0002. The scale bars in the colour chart are 5 cm. The khipu as laid out in this photograph is approximately 30 cm × 15 cm.

Similar colours are present on the thread wrappings around P_1 and P_1s_8. The wrapping on P_1 presents eight distinct bands, while the wrapping on P_1s_8 has six bands (Figure 2).

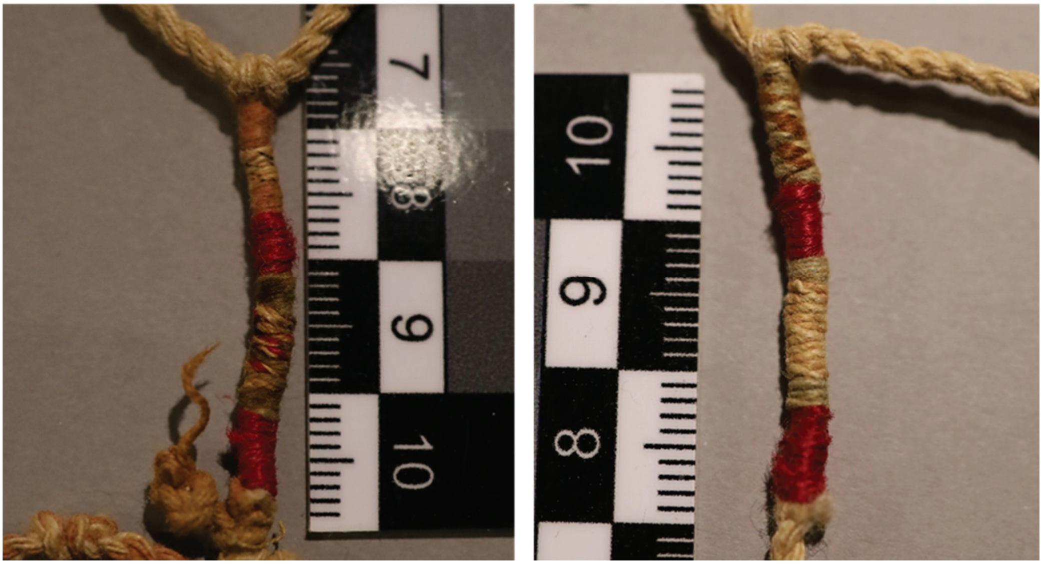

Figure 2. **Left photo**: wrapping on 1932.08.0002 P_1; **right photo**: wrapping on 1932.08.0002 P_1s_8.

5. Khipu 1932.08.0001

Khipu 1932.08.0001 also presents a loop and pendant Wari khipu morphology (Figure 3). To a primary cord looped in a circle, four pendants (P_1–P_4) are attached. While the first two pendants host, respectively, eight and nine subsidiaries, the last two pendants do not have any subsidiary cord at all.

Figure 3. Khipu 1932.08.0001. The scale bars in the colour chart are 5 cm. The khipu as laid out in this photograph is approximately 42 cm × 35 cm.

The khipu is made of a total of thirty-three cords (pendants and subsidiaries), all of which are made of cotton.

The colour patterns on this khipu include solid (monochrome), mottled, barber pole, and segmented cords.

Only two subsidiaries are segmented ($P_2s_8s_1$, $P_2s_9s_1$), and both are segmented in Wari style. The first one is highly deteriorated right after the segmentation, which makes it possible to see the structure of Wari segmentation's construction (Figure 4).

Figure 4. 1932.08.0001 $P_2s_8s_1$, segmentation structure visible due to cord deterioration. The upper half of the cord (right) is monochrome. Half-way through the cord, a brown thread is attached. This allows to obtain the lower half with barber pole pattern. The cord length in this photograph is approximately 2 cm.

On khipu 1932.08.0001, there are eight sequences of thread wrappings: four almost identical sequences are on top of the four pendant cords; two similar ones are on the second-to-last subsidiary cords of P_1 and P_2 (P_1s_7 and P_2s_8); another pair of similar thread wrappings are on P_1s_8 and P_2s_9; and one is on P_1s_5 in correspondence to the first simple knot (Figure 5).

Figure 5. 1932.08.0001 $P_1s_5K_1$, wrapped single knot with red dyed animal fibre thread. The knot is approximately 8 mm in length.

All the wrappings on cords begin right below the point of attachment of the cord, with two interesting exceptions: P_1s_7 and P_2s_8. The wrapping sequence is ecru–pink–ecru in the first one and ecru–pink in the latter. It is likely that the wrapping on P_2s_8 would have had the same sequence as P_1s_7 because the loose ends that both wrappings terminate with are a sign of unravelling. Careful morphological study noticed some black material at the top of both thread wrappings (Figure 6). We hypothesise, and will confirm later in this article, that other extra bands were present at the top (and possibly also at the bottom) of these two thread wrappings so that the band sequence for each of them would originally have been black–ecru–pink–ecru–black. The questions raised by the observation of the black material at the top of these two thread wrappings guided the research team in mapping P_2s_8 by XRF.

Figure 6. Black material visible at the very top of 1932.08.0001 P_1s_7 (**left photo**) and 1932.08.0001 P_2s_8 (**right photo**). The wrapping sections in the photographs are approximately 1 cm to 1.5 cm long.

6. Sampling

Investigation of the thread wrappings, the most meaningful aspect of Wari khipus, was at the centre of this research. However, it was not possible to take samples from thread wrappings because this would have heavily compromised the structural stability of the khipus. Samples for colour analysis were only taken from khipu 1932.08.0002. This is because, compared to 1932.08.0001, 1932.08.0002 has more pendants presenting colours corresponding to those in the thread wrappings. The assumption is that, by studying the colours of the pendants in 1932.08.0002, we can also expand our knowledge about thread wrappings on the same khipu. Given the shared origin of the two khipus, the analyses of samples from pendants of 1932.08.0002 are also considered to shed light on the thread wrappings on pendants of khipu 1932.08.0001. See Supplementary Materials Table S3 for a list of the wrapping bands from the two khipus with colours corresponding to the samples taken in this study.

Samples were cut off by pendant cords in areas with loose ends. On some occasions, pendants can terminate both with loose ends and with loops, which are the result of the multiple plies of threads the cord has been manufactured with. Cutting out the looped segments of a khipu pendant end prevents observation and study of the cord structure, and, for this reason, this option is not desirable from a conservation ethics point of view. The sampling areas were selected based on the morphological study, as well as the observations we could make on account of what emerged from the technical photography executed on the whole khipus.

Seven samples were taken from khipu 1932.08.0002; each one is between 6 and 10 mm (Figure 7 and Supplementary Materials Table S3). These samples were then photographed again in comparison to other khipu samples within the broader research project "Meaningful materials in the khipu code".

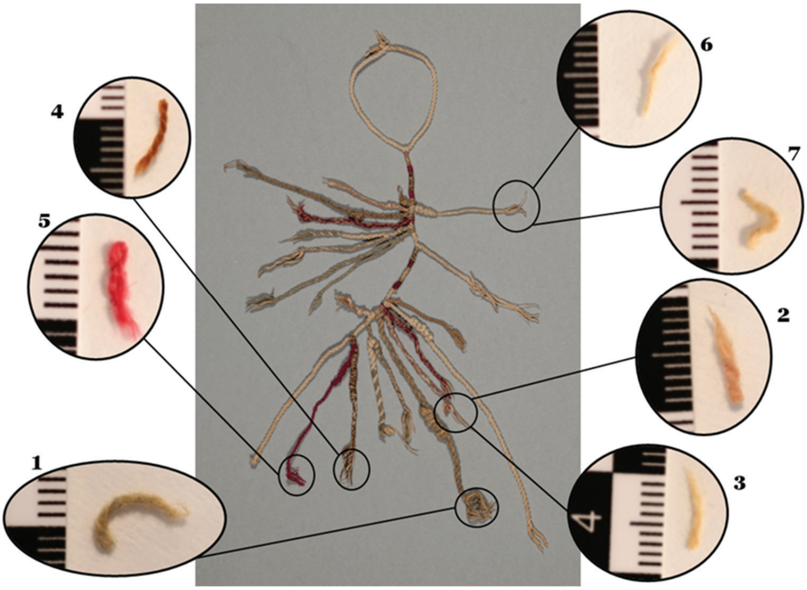

Figure 7. Samples (1–7) collected from khipu 1932.08.0002. The khipu as laid out in this photograph is approximately 30 cm × 15 cm.

Both khipus contained small areas or remnants of black threads, which could not be sampled. Furthermore, various shades of ecru, light brown, yellow, and green were also not sampled.

7. Materials and Methods

7.1. Multiband Imaging

Multiband imaging (MBI) is a photographic method that encompasses a set of light and filter combinations to spatially visualise the different components of an object. Depending on the chemical nature of a material, its reflection and luminescence behaviour will generate different responses in the created images. Use of MBI can be especially helpful when designing a sampling strategy. Other useful aspects can be visualising surface coatings, staining, restorations, or patterns. Multiband imaging is an indicative method, and interpretation should be completed with the knowledge that mixtures of dyes, different mordants, or residues from soil or dirt can affect the results. However, even if MBI needs to be accompanied by other analytical methods, it provides initial insight and imagery that can guide the sampling process and be of great use to communicate and visualise results from the accompanying methods.

A crucial part of creating photographic material that can be referenced and compared to other work outside this study was to employ a systematic approach. Therefore, the setup and postprocessing follow the guidelines described in "Multispectral Imaging in Reflectance and Photo-induced Luminescence modes: a User Manual" [26]. In this study, the khipus and samples were imaged with visible (VIS), infrared (IR), and ultraviolet (UV) light. Using filters, either UV or IR reflectance, and luminescence were registered (UVL, UVR, and IRR). By combining VIS with IRR, false colour (IRFC) images were created [26,27]. Multiband reflectance subtraction (MBR) was used to investigate the presence of indigo; the method encompasses capturing two images at narrow bandwidth and calculating the difference [28].

The main purpose of using MBI on the khipus was to investigate the different visual responses from different dyes and colourants. Using photographic techniques on archaeological or historical textiles has previously been shown to be successful [29–31].

The khipus were photographed in situ at the magazine storage area of the Museum of World Culture in Gothenburg to guide the sampling decisions. In order not to stress the junctions of the khipus, they were left on their original paperboard support. Unfortunately, the paperboard had inherent luminescence in the ultraviolet region, therefore not providing the best visualisation of the khipus in their entirety. A filter paper could be slid under a smaller specifically interesting area to improve visualisation. In addition, the khipus were not flat, but, again, the decision was made not to interfere with the khipu structure, for example, by using pins to flatten the objects, and, therefore, some shadows in the images had to be accepted. Despite these practical difficulties arising from the real-life situations that now and then appear in this field of research, imaging the objects provided useful guidance for the study.

All images were acquired using a modified full spectrum Nikon D810 camera (IR-UV-blocking filter removed) with a Nikon AF Nikkor 50 mm lens. The objects were placed approximately 100 cm (whole khipu) or 50 cm (sections and samples) from the camera. Two identical light sources were placed symmetrically at approximately 45 degree angle toward the objects. Depending on the image, different light sources were used, and filters were mounted on the camera lens (Table 2). All filters used were from the Cultural Heritage Science Open Source (CHSOS) Technical photography Robertina filter set [32] or Multispectral Antonello filter set [33]. An X-rite Macbeth chart and a white Spectralon diffuse reflectance standard (99%) were used for image calibration. A white non-luminescent homogeneous paper board was used for flat-fielding. Postprocessing was completed following the guidelines proposed in the user manual and by using nip2 software [26]. The method for infrared false colour was adapted to Adobe Photoshop from the principles in the manual [26] following personal communication with J. Dyer (12 October 2022).

Table 2. Summary of light sources and filters used for different images. See Supplementary Materials for specifications.

Image	Light Source (Set of Two)	Filter in Front of Camera
VIS	Godox LED1000 II	UV-IR blocking bandpass, c. 400–700 nm
UVL	Engelbrecht UVA-366 black lights	UV-IR blocking bandpass, c. 400–700 nm
IRR	IR LED Synergy 21 M30205	IR cut-on, c. 800 nm cut-on, 25% transmittance at 900 nm
MBR	Kaiser Studiolight 1000 with an Osram halogen Superphot 1000 W bulb	Bandpass, 630 ± 5 nm + 740 ± 5 nm

7.2. XRF

The two khipus, 1932.08.0001 and 1932.08.0002, were analysed at the magazine storage area of the Museum of World Culture in Gothenburg. XRF point analysis and maps were collected using a Bruker Artax 800 instrument with molybdenum tube at 50 kV and 600 µA in air atmosphere. A capillary lens provided a spot size of <100 µm. A stack of at least four pure cellulose filter papers was slid under each area of analysis, which provided a blank background of Bremsstrahlung. Software Bruker ARTAX version 7.8.2.0 was used to control the XRF instrument as well as to evaluate the data. Automatic corrections were performed for escape peaks and background using cycle setting 1. Details of the analysed areas, scan time per point, number of measurement points, spot distance, scan area, and total scan time are listed in Supplementary Materials Table S4. Selected results are discussed in this manuscript, and a report of all XRF results from the in-situ analyses is available from Zenodo [34].

The samples collected from khipu 1932.08.0002 were analysed at Fort Cumberland laboratories, Historic England (Portsmouth, UK). The samples were mounted on filtered paper and covered with a nylon net to fix them to the support. The area was mapped by micro-XRF using a Bruker M4 Tornado µ-XRF spectrometer. Elemental maps were collected at 50 kV and 200 μA with a vacuum, spot distance 50 μm, measure time 5 mm/s for three cycles. Cotton fibres (samples 1, 2, 3, 4, 6, and 7) and animal fibre (sample 5) were analysed in 2 distinctive maps. Separate accumulated spectra were collected from each thread from an area of about 4.5 mm^2. The intensity and net area of the peaks and the maps provide semi-quantitative data about the elements detected, assuming constant thickness of the threads across the investigated areas. Software Bruker M4 Tornado was used for data processing.

7.3. HPLC–HRMS

HPLC-ESI-Q-ToF MS analyses were carried out using an Agilent 1200 Infinity HPLC with a Quadrupole-Time of Flight tandem mass spectrometer 6530 Infinity Q-ToF detector with a Jet Stream ESI interface (Agilent Technologies, Santa Clara, CA, USA). The ESI operating conditions were the following: drying gas (N2, purity >98%): 350 °C and 10 L/min; capillary voltage 4.5 KV; nebuliser gas 35 psig; sheath gas (N2, purity >98%): 375 °C and 11 L/min. The nozzle, skimmer, and octapole were set at 1000 V, 65 V, and 750 V, respectively. High-resolution MS and MS/MS spectra were acquired both in negative and positive mode in the range 100–1000 m/z with a scan rate of 1.04 spectra/sec, employing AutoMS/MS acquisition mode (1 precursor per cycle, CID voltage for tandem mass spectra 30 V, collision gas N2, purity 99.999%, FWHM (full width half maximum) of quadrupole mass bandpass used during MS/MS precursor isolation 4 m/z). The mass spectrometer was calibrated daily using Agilent tuning mix HP0321. MassHunter® Workstation Software (B.04.00) was used to carry out mass spectrometer control, data acquisition, and data analysis.

For the chromatographic separation, an Agilent Poroshell 120 EC-C18 was used (3.0 × 75 mm, particle size 2.7 μm,) with a pre-column Zorbax (4.6 × 12.5 mm, particle size 5 μm), both Agilent Technologies (Palo Alto, CA, USA). The injection volume was 5 μL for the extracts of samples 4 and 5 and 15 μL for the extracts of samples 1, 2, 3, 6, and 7.

The two eluent solutions were: A: formic acid (FA, 0.1% *v*/*v*) in bi-distilled water; B: FA (0.1% *v*/*v*) in acetonitrile (ACN, HPLC grade). The elution program started at 15% B, held for 2.6 min, and then a linear gradient to 50% B was applied in 13 min, then to 70% B in 5.2 min and to 100% B in 0.5 min and then held for 6.7 min; re-equilibration time took 11 min. The flow rate was 0.4 mL/min.

Details on chemicals and sample treatments can be found in the Supplementary Materials section on HPLC–HRMS.

Data interpretation was based on comparison with reference materials available in the laboratory and literature data on chromatographic analyses of Peruvian textiles and dyestuffs.

8. Results and Discussion

The results are organised showing first the results of the multiband photography, then discussing the XRF mapping and then the organic dyes.

A summary of the results is reported in Table 3.

Table 3. Summary of all results from XRF, MBI, and HPLC–HRMS analyses. XRF results in bold indicate significant levels of the element associated with the colourant and are confirmed by both XRF of samples and XRF in situ. All samples are made of cotton, with exception of sample 5, which is made of wool.

Colour	Sample	XRF Areas In Situ 1932.08.0002	XRF Areas In Situ 1932.08.0001	MBI Samples and In Situ	XRF Samples and In Situ	HPLC–HRMS Samples
blue	1	P_1s_8—Band 1, 3, 5	P_1_Band 3, 5, 6 P_2s_9—Band 1	UVL-dark MBR-bright IRRFC-red	**Ca**, **Cl**, Fe, Cu	Indigo
pink	2	P_1_Band 1, 2, 3 P_1s_8—Band 4	P_1_Band 1 P_2s_8_Band 2 P_2s_9_Band 3	UVL-dark IRRFC-orange–yellow	Fe, Cl, K	Cochineal
ivory	3	P_1_Band 2 P_1s_8—Band 4	P_1_Band 1, 3, 6 P_2s_8—Band 1 P_2s_9—Band 2	UVL-light IRRFC-white		Blank
brown	4	P_1s_8—Band 1		UVL-very dark IRRFC-orange	**K**	Cochineal (very weak)
red	5	P_1s_8—Band 2, 6	P_1_Band 4, 6	UVL-very dark purple IRRFC-orange UVFC-green	Ca	Cochineal (most intense) plus unknown anthraquinone
ivory	6	P_1_Band 2 P_1s_8—Band 4	P_1_Band 1, 3, 6 P_2s_8—Band 1 P_2s_9—Band 2	UVL-light IRRFC-white		Blank
ecru	7	Point analyses P_1s_2	\	UVL-dark IRRFC-yellow	Ca, Cl, Fe, K	Flavonoid dye based on rutin, luteolin, and luteolin-O-glucosides
black		P_1	P_2s_8		**Fe**, **Mn**, **K**	
pink			P_2s_8_Band 2		S, Sn	

8.1. Multiband Imaging

Multiband imaging provided useful documentation of the objects. The techniques that specifically contributed to the sampling strategy and understanding of the khipus during this study were UVL, IRRFC, and MBR (for indigo). Some complementary images are included in the Supplementary Materials (Figures S1–S8).

In visible light, some cords of khipu 1932.08.0002 appear undyed. The UVL image, however, revealed P_1s_2 as a two-coloured cord (Figure 8). Consequently, XRF point analysis was performed on this cord and one sample from each of the two different coloured threads was taken. One of the threads (sample 7) was shown by HPLC to contain a flavonoid-based dye-stuff. The UVL image overall improved visualization of two-coloured threads, enhancing the difference between the colours.

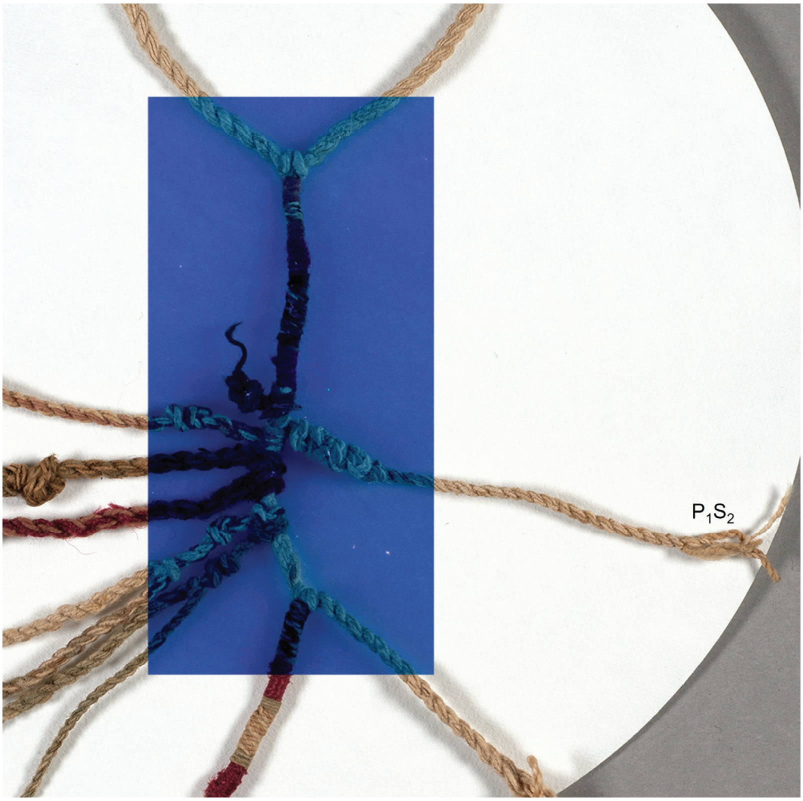

Figure 8. Section of khipu 1932.08.0002 in VIS and UVL (overlay) where UVL helps to visualise the differently coloured threads. Cord P_1s_2￼appears undyed in visible light, but UV light clearly shows there are two different threads. The khipu section is approximately 11 cm × 11 cm.

The transparent and loose structure of the samples imposed some difficulty in interpretation as shadows and reflected luminescence in some respect hindered clear visualisation.

Infrared false colour images (IRRFC) can be helpful to differentiate colours that look similar in visible light (Figure 9). Samples 2, 3, 6, and 7 are all similar with different tints in the VIS image: 2 is slightly pink; 7 is slightly ecru. In the false colour image, these samples become more distinguishable. Sample 2 becomes light orange–yellow, 3 and 6 become white, and 7 becomes light yellow. Samples 3 and 6 had the same beige tint in the visible image and were rendered white in the false colour image. HPLC indicated that both samples were undyed. Samples 2, 4, and 5 were all found to be dyed with cochineal but have different colours in the visible image—pink, red, and brown. In the false colour image, sample 2 turns orange–yellow and 4 and 5 turn orange. Even though this might imply that these samples have something in common, this also highlights that one needs to be careful in interpretation. HPLC and XRF showed that, even though these samples all contain cochineal, there are differences in elemental composition. In addition, sample 5 contains an unknown anthraquinone. Sample 1 goes from blue to red in the infrared colour image, implying that it could have been dyed with indigo. Indigo can also be visualised in the MBR image, where the presence of indigo appears bright. In Figure 9, all samples that contain indigo are marked with "*" for clarity, but only samples 1–7 from khipu 1932.08.0002 are discussed in this manuscript. Indigo in sample 1 was also confirmed by HPLC.

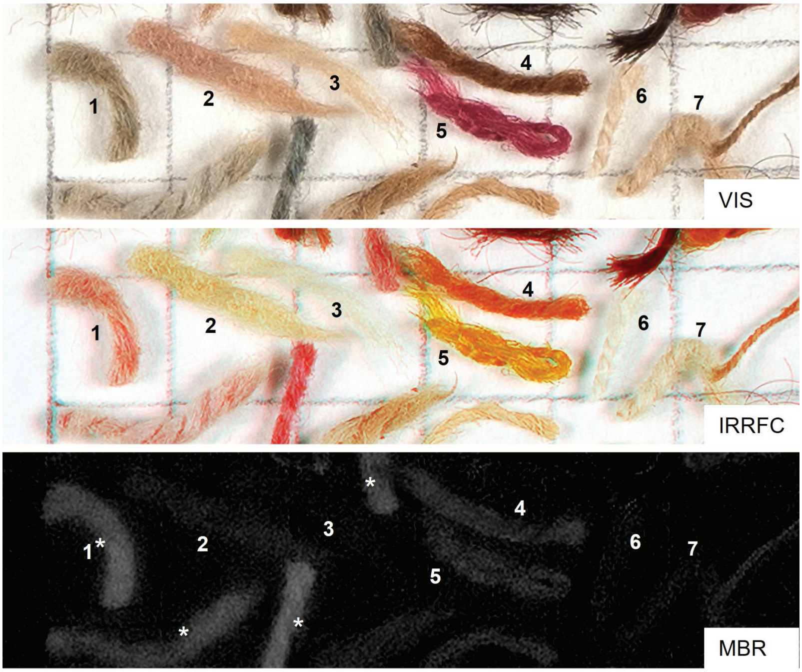

Figure 9. Samples 1–7 from khipu 1932.08.0002 in VIS, IRRFC, and MBR placed on a 5 × 5 mm grid. The MBR image shows the difference between reflectance at 630 and 740 nm; bright areas suggest the presence of indigo. Asterisk marks are placed on samples where indigo was identified by HPLC; for clarity, also samples not discussed in this manuscript are marked.

8.2. Analysis of the Inorganic Components

Elemental maps were acquired by portable micro-XRF to evaluate the distribution of inorganic components used as colorants, mordants, or dyeing auxiliaries in proteinaceous and cellulosic fibres. Evaluation of the presence of mordants and dyeing auxiliaries in archaeological textiles is complex as elemental contamination can generate misleading results.

The greyscale maps show the distribution of each element in the samples. The areas where an element is present in highest concentration (high peak area in the spectrum) are bright, while, in dark grey or black areas, the element is in low concentration or not present (low peak area in the spectrum or absence of the peak).

The XRF instrument used in the magazine storage area of the Museum of World Culture in Gothenburg for in situ mapping on khipu areas has the limitation that elements of relatively light atomic weight may be missed due to the air gap between the analysed area and the detector. This means that the instrument cannot reliably inform on the presence or absence of aluminium. Detection of alum, being historically the most important mordant, is of special interest. The benchtop micro-XRF instrument used for mapping khipu samples has the advantage that measurements can be carried out in a vacuum, thereby enabling detection of lighter elements.

XRF maps on the khipus in situ reveal the presence of several elements, such as S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, Hg, and Br (Figure 10). The XRF spectra in vacuum show several additional elements of lighter atomic weight: Al, Si, and P (Figures 11–13). The following paragraphs discuss each of the detected elements to place the results obtained from XRF in situ on khipu areas and XRF of khipu samples in a context of possible auxiliaries and mordants used in conjunction with textile dyes.

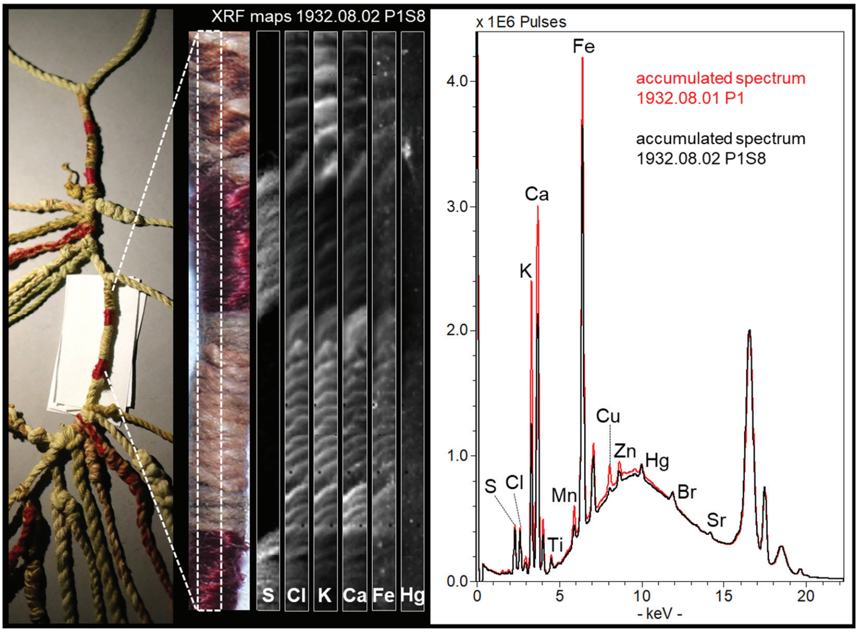

Figure 10. XRF maps of elements that showed differences in distribution from area P_1s_8 on khipu 1932.08.0002. Map size is 24 mm × 0.9 mm. Accumulated spectra of the XRF maps of the comparable wrappings (see Figure 2) from the two different khipus, 1932.08.0001 P_1 and 1932.08.0002 P_1s_8. The similarity between the two accumulated spectra provides further evidence that the two khipus are a pair and that results from one can inform on the other (see Supplementary Materials Table S3).

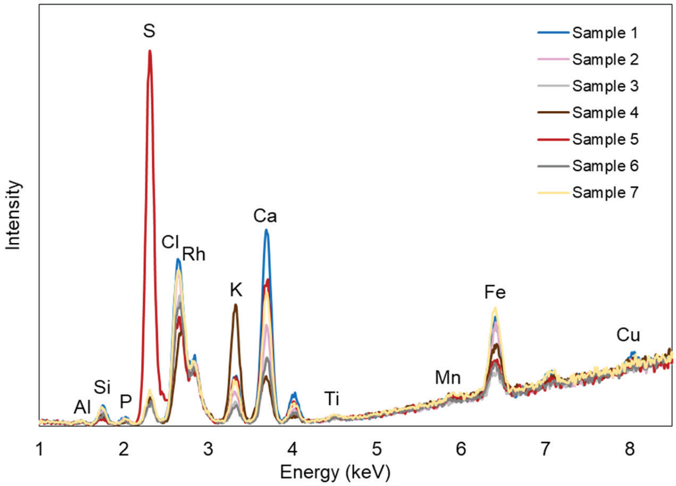

Figure 11. Accumulated spectra collected from an area of about 4.5 mm2 from each thread sample of khipu 1932.08.0002.

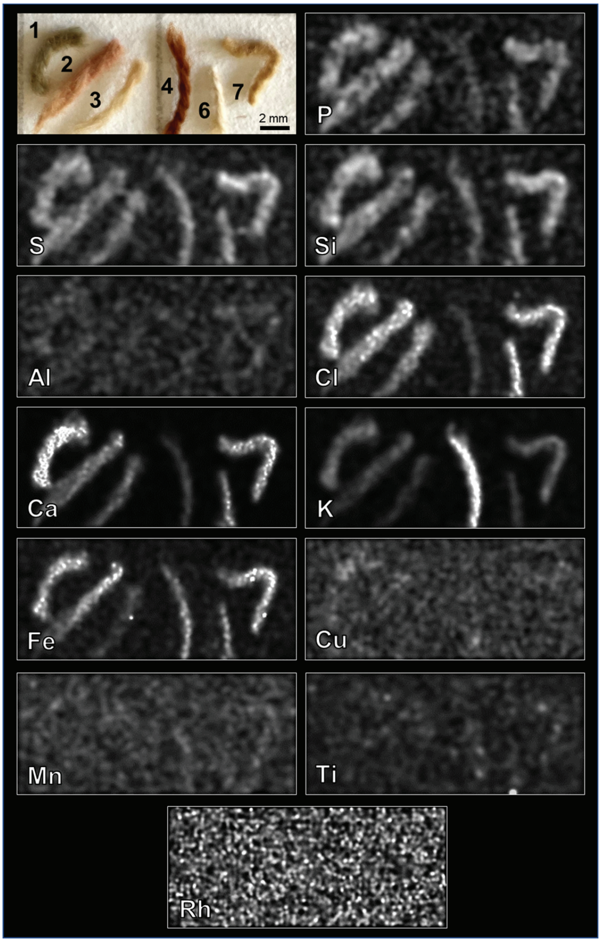

Figure 12. XRF maps of phosphorous, sulphur, silicon, aluminium, chlorine, calcium, potassium, iron, copper, manganese, titanium, and rhodium (rhodium anode of the X-ray tube) measured in the cotton samples (from left to right: sample 1–sample 7) from khipu 1932.08.0002.

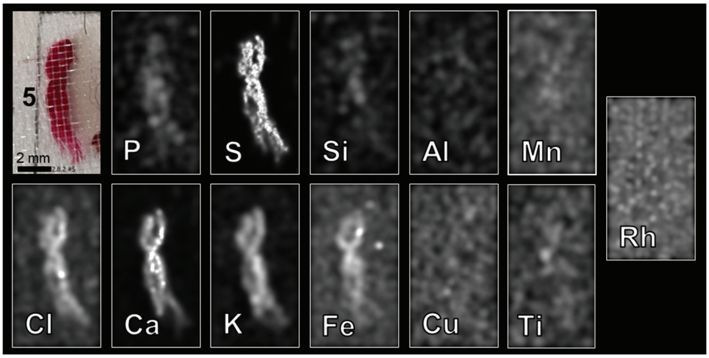

Figure 13. XRF maps of phosphorous, sulphur, silicon, aluminium, manganese, chlorine, calcium, potassium, iron, copper, titanium, and rhodium (rhodium anode of the X-ray tube) measured in the animal fibre sample from khipu 1932.08.0002.

8.2.1. Aluminium

Aluminium was not detected by XRF in situ on khipu areas, while the analysis in vacuum carried out on thread samples allowed its detection. The accumulated spectra of all the threads exhibit the peak for aluminium; however, no differences in intensities between the undyed and dyed threads were shown (Figure 11).

Aluminium is found in alum salts, which are the most common mordants for textiles. According to the literature, considering that silicon is the most common contaminant when the ratio between the heights of Al and Si signals is higher than 0.5, alum salts were probably used as mordants [35,36]. In these thread samples, the Al/Si ratio was too variable, preventing conclusive information from being obtained.

Peru has natural resources of alum salts (e.g., aluminium potassium sulphate) [37,38], and the hypothesis is that they were used as mordants in the highly advanced textile technologies of the pre-Columbian civilisations. This was proven analytically in 1913 by ashing samples of Paracas textiles [39]. Valette found silicates of lime and aluminium associated with cochineal dyed fibres. Other inorganic elements identified by Valette were significant amounts of lime in the ashes of blues and greens dyed with indigo, ferruginous clay (yellow ochre) for some yellow fibres, and notable amounts of iron in some browns. Valette suggested that the mordanting may have been carried out by suspension of aluminium-containing clay in water. Fester, instead, identified sulphate ions in the fibres (analytical method not stated), suggesting that the mordant was more likely in the form of aluminium sulphate or aluminium potassium sulphate [38].

It Is known that alum was used as a mordant In ancient Egyptian and also Roman textiles and the processes and effects of alum and other mordants were described by Pliny the Elder [40] (pp. 183–186). The history of alum in Europe, Asia Minor, and the ancient Roman and Egyptian empires has been described by several authors [41–44], but historical accounts of the use of alum in the Americas are scarce. Nevertheless, Fester [38] reports that 17th-century chronicler Bernabé Cobo provides an account of several kinds of alum present in Peru ([38] citing Antonio Raimondi, who wrote about alum sources in Minerales del Perú, Lima 1939, supplement to first edition 1878). However, contrary to what Fester reports, Cobo mentions use of alum for dyeing purposes only with reference to Mesoamerica: «De Piedra alumbre se hallan en estas Indias cuatro ó cinco especies. En la Nueva España lo hacen muy blanco, lúcido y trasparente, del cual usan los tintoreros en sus tintes [. . .] («In these Indies [Peru] there are four or five types of alum stones. In New Spain [which included contemporary central and south USA, Mexico and most of Mesoamerica until Costa Rica. The author most likely refers to the Mesoamerican area] they make it very white, shiny and transparent, [. . .]». Translation of the author) [45]. In the extensive work by Ana Roquero "Tintes y tintoreros de America", she mentions "kollpa", the Quechua name for aluminium potassium sulphate ("Piedra alumbre" in spoken Spanish), but there is no mention of chroniclers that refer to Viceroyalty of Peru ([46] (p. 91).

8.2.2. Silicon and Phosphorus

Silicon and phosphorus were not detected by XRF in situ on khipu areas. XRF in vacuum on khipu samples enabled detection of silicon and phosphorus, where the maps for each element showed comparable signal intensities among the samples.

8.2.3. Sulphur

Sulphur was detected by both XRF techniques and is always highest in animal fibres due to the presence of sulphur in the proteins of the fibres (red areas in Figure 10 and sample 5 in Figure 11)

XRF mapping of khipu areas or samples of cotton allowed some differences in sulphur content to be detected between differently coloured threads (Figure 12).

8.2.4. Chlorine

XRF maps of the khipu areas in situ indicate that chlorine is generally higher in cotton compared to wool and is often highest in blue areas. The chlorine signal in analysis of thread samples is also highest in the blue (sample 1) and significant in the pink (sample 2). The other dyed and undyed samples all contain chlorine but at lower levels (Figure 11).

Chlorine can be associated with use of a salt as mordant or alkaline additive to the dyeing bath. The fact that the undyed samples contain chlorine may indicate that they were treated with a salt but left undyed or that they were dyed with a fugitive dye or that chlorine is inherently present in the cotton source fibres.

8.2.5. Potassium

The signal for potassium was relatively high for all khipu areas and the khipu samples. Figure 14 shows that potassium was highest in the yellow and pink areas; the same observation was made for the ecru threads in the map on 1932.08.0001 P_2s_2 blue-ecru cord. Figure 15 shows that the pink threads in map 1932.08.0001 P_2s_8 ivory–pink wrapping are higher in potassium than the ivory threads. The pink threads are also higher in sulphur, tin, and manganese. No sample was available for dye analysis. Figure 10, the XRF map of 1932.08.0002 P_1s_8 multicoloured wrapping, shows potassium levels that are highest in the brown threads at the top of the map; these are equivalent to sample 4. Potassium levels were also slightly elevated in the pink when compared to the blue. Potassium was lowest in the red animal fibres in Figures 10 and 14.

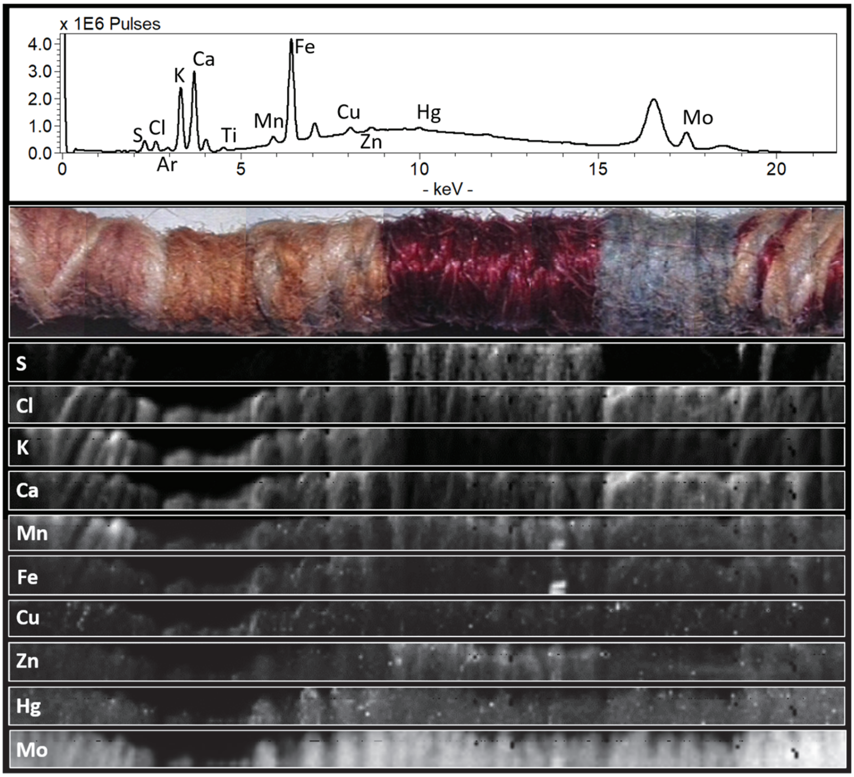

Figure 14. XRF maps from 1932.08.0001 P1 multicoloured wrapping bands 1–6. Map size is 1 mm × 22.95 mm.

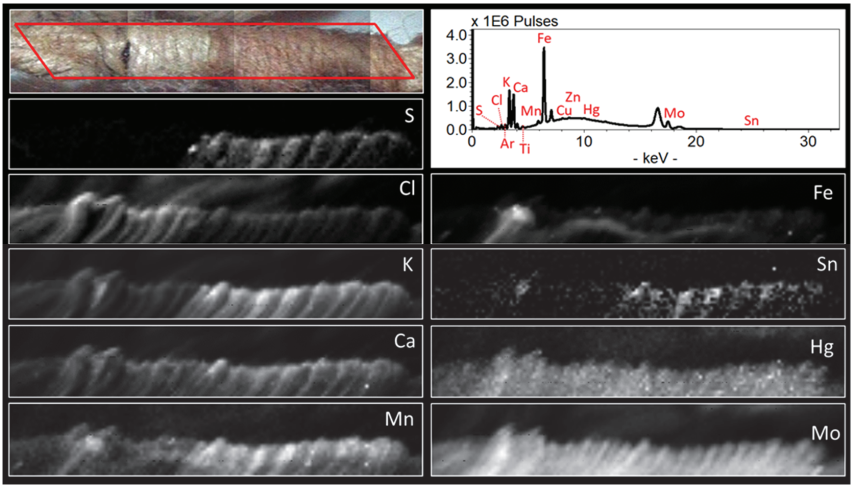

Figure 15. XRF maps from 1932.08.0001 P_2s_8 ivory-pink wrapping. Map size is 2 mm × 11.79 mm.

For the khipu samples, the potassium signal was significantly higher in brown sample 4 compared to any other sample (Figures 11 and 12). The intensity of the potassium signal was lowest in undyed samples 3 and 6.

The presence of potassium in dyed threads possibly indicates use of potassium carbonate, in the form of wood ash, to alkalise the bath. It is known that ashes were used as auxiliaries to darken the colour of dyebath in several American cultures, including the Navahos and many Native American peoples of the Wisconsin and Great Lakes region [47–49]. Although we are not aware of use of saltpetre for dyeing purposes, we know that Peruvian natives knew about this material since "zuca", the indigenous name of saltpetre, is reported by Bernabé Cobo [46] (p. 91).

Calcium was present at relatively high levels on all khipu area maps. Generally, the highest levels were associated with blue areas, as in 1932.08.0001 P_1 multicoloured wrapping band 1–6 map (Figure 14), 1932.08.0001 P_2s_2 blue–ecru cord map, 1932.08.0001 P_2s_9 blue–ivory–pink wrapping map, and 1932.08.0002 P_1s_8 multicoloured wrapping map (Figure 10).

The XRF map of thread samples also showed that calcium is present in every sample, especially in the blue one (sample 1). It is also distributed in the red (sample 5) and ecru (sample 7) samples, and it is lowest in the brown (sample 4) and undyed samples (samples 3 and 6) (Figures 11–13). The fact that calcium is highest in the blue sample, which was dyed with indigo, indicates that it was probably added as an auxiliary reagent to create an alkaline dyeing bath. Burned shells, limestones, or lime could have been used for this purpose. This result is consistent with data collected from Paracas textiles dyed with indigo [50,51] and confirms the early results obtained through ashing analysis [39].

8.2.6. Titanium

Titanium was present in all accumulated spectra from the XRF analysis on khipu areas but never showed a coherent distribution in the XRF maps. Titanium is most likely present as a contaminant from dust or sand.

8.2.7. Iron and Manganese

The XRF map on 1932.08.0001 P_2s_8 ivory–pink wrapping shows an iron-containing thread that is running under the ivory and pink wrapping (Figure 15). It emerges on the left side of the mapping area and becomes visible as the end of a black thread, indicating a now missing area of black wrapping from the top of the wrapping and possibly from the bottom too. A further thread that was high in iron was identified in the XRF map of

1932.08.0002 P_1 pink–ivory wrapping, where a black thread was interspersed in the ivory area, creating, therefore, a mottled band in the thread wrapping instead of a solid ivory colour band. The black threads from both khipus showed similar compositions as they also contain potassium, manganese, and possibly tin. XRF mapping of the areas that did not contain black threads showed that iron is distributed everywhere and is most likely present as a contaminant. However, some variations between colours were noted, and, in general, the undyed areas and the red animal fibres were lower in iron than any of the dyed cotton threads (Figure 10).

In the XRF analysis of thread samples, iron is distributed in every thread, especially in the coloured ones (Figures 11–13). The ecru (sample 7), blue (sample 1), and pink (sample 2) samples exhibit the highest iron content, suggesting use of iron mordants. Alternatively, an explanation for iron in the blue sample could be use of iron sulphate as a reducing agent in the indigo vat, as suggested by Fester [38]. The relatively high iron content in sample 7 is somewhat puzzling as an iron mordant on a yellow flavonoid dye would normally result in a darker shade than this very-light-coloured ecru sample. Alternatively, iron may be present as an ochre (iron oxide), as previously identified in Paracas textiles by Valette [39]. This was not investigated here. All three cochineal dyed samples, pink (sample 2), brown (sample 4), and red (sample 5), also contained iron, but the red animal fibre sample shows a lower iron signal, close to those of undyed samples 3 and 6. This may indicate that the detected iron is a general background contamination and not related to the dye. Alternatively, the varying iron levels in the three cochineal dyed samples could point to different recipes, in terms of source and concentration of iron in the bath, when dyeing animal or plant fibres. Iron was also found in red and yellow areas of Paracas textiles [50,51] and in purple Peruvian textiles [52]. Low signals of manganese are found in the samples, and they appear to be associated with iron. Manganese is a common impurity in sources of iron. Natural deposits of iron were mined in the Andean region, and stagnant mud was also used to turn textile dyes darker or even black [49]. Roquero reports that the Quechua term “kollpa” was used to indicate both iron sulphate and aluminium, with the only distinction that the first was “kollpa negra” and the second one was “kollpa blanca”. She reports Cobo mentioning use of iron sulphate mixed with tannins to obtain black dyes [46(92)].

8.2.8. Copper and Zinc

Copper and zinc are present in every accumulated spectrum of the analysed areas but are not resolved in the XRF maps. For the XRF analysis of samples, copper was found only in the blue sample (sample 1) (Figures 11 and 12), but, in the map, its distribution is less clear (Figures 12 and 13). Whether copper or zinc were employed as mordants is, therefore, uncertain, although similar results were obtained in analysis of Peruvian textiles where copper was also detected in a blue indigo-dyed sample [50–52].

8.2.9. Mercury

Mercury is present in every accumulated spectrum of the analysed khipu areas, and an uneven, speckled distribution can be discerned on most maps. The presence of mercury on these objects is interpreted as originating from a biocide treatment, for example, from brushing with so-called sublimate, a solution of mercury (II) chloride [53]. Mercury was not present in the spectra of khipu samples, possibly due to uneven application where the ends of the cords were missed.

8.2.10. Tin

In Figure 15, the pink area was higher in sulphur than the white area. In this khipu area, the signal for tin coincides with the signal for sulphur and may indicate a tin mordant used on this pink thread. Unfortunately, a sample for dye analysis from this thread was not available, and the analyses of other pink areas did not show the same results. The only other colour where tin was also detected were the black threads mapped in situ.

8.3. Analysis of the Organic Dyes

All the samples collected from khipu 1932.08.0002 were treated for extraction and determination of organic dyes. The chromatographic profiles of the extracts of ivory cotton samples 3 and 6 were both superimposable to the procedural analytical blank and can thus be considered undyed. Blue cotton sample 1 features indigotin and indirubin as the colouring components (Figure S9), well-known molecular markers of indigo-producing species; in the Peruvian area, the most common are Indigofera suffruticosa and Cybistax antisyphilitica [54].

The extracts of pink cotton sample 2, brown cotton sample 4, and wool bright red sample 5 contained the main molecular marker of cochineal dyestuff, namely carminic acid (Figures S10, S11 and Figure 16, respectively). Cochineal dye extracted from Dactylopius coccus is a very well-known Peruvian dyestuff, which began to appear more frequently in ancient Peru in the Wari and Tiwanaku period (700–1100 AD) [54,55]. In addition, samples 2 and 5 also contained further molecular markers of cochineal dcII, kermesic acid, flavokermesic acid, dcIV, and dcVII. Sample 5 was indeed the most intensely coloured of the three yarns dyed with cochineal; besides the known markers of this dye, a further unknown anthraquinone was detected in its extract, eluting shortly after carminic acid, whose spectrum features maximise at 279, 515, and 551 nm (Figure 16, inset C).

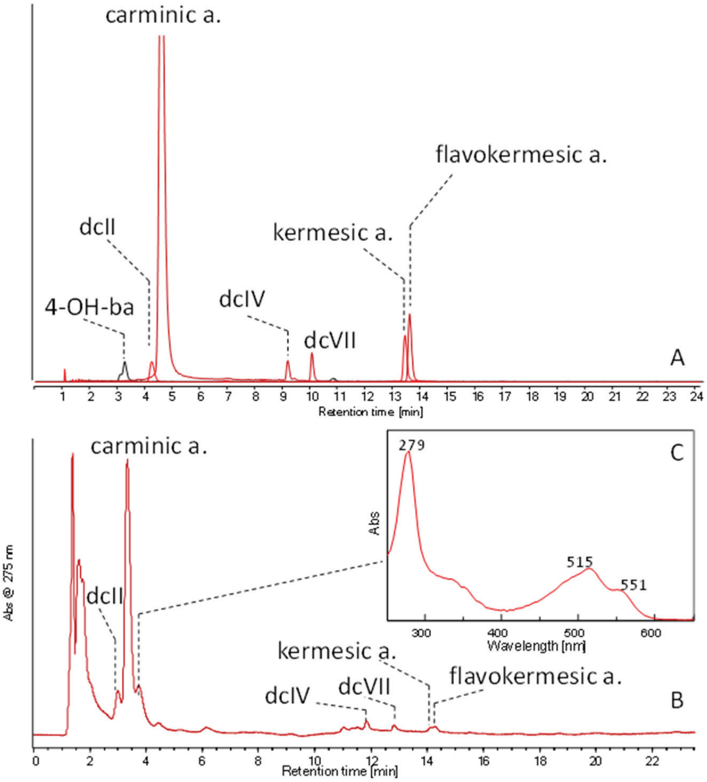

Figure 16. Chromatograms obtained for the extract of sample 5. (**A**): HPLC(-)ESI extracted ion chromatograms corresponding to the molecular ions of carminic, kermesic, and flavokermesic acids, Dactylopius coccus markers dcII, dcIV, and dcVII, and 4-hydroxybenzoic acid (4-OH-ba); (**B**): HPLC-DAD chromatogram extracted at 275 nm; (**C**): UV-Vis spectrum acquired in correspondence of the unknown peak at 3.9 min in the HPLC-DAD chromatogram.

The brown colour of sample 4 cannot be explained by the nature of the dyestuff, which is present in very low concentration (see the chromatogram in Figure S11); possible hypotheses entail use of mordants or modifiers in the dye bath, or an originally darker cotton, as discussed below.

Finally, the extract of ecru cotton sample 7 contained several flavonoids, such as rutin, luteolin, and two luteolin-O-glucosides. The detected profile, unfortunately, does not match any of the available reference materials or composition reported in the literature; moreover, both quercetin and luteolin are extremely common in plant extracts and thus quite unspecific. Nonetheless, their detection proves that the yarn was actually purposefully dyed in yellow with a flavonoid-based dyestuff (Figure S12).

All the samples were investigated for presence of polyphenols related to use of tannins as dyes or plant-based mordants. No specific marker for tannins was found (e.g., ellagic or gallic acid, or their glycosides). Sample 5 contained 4-hydroxybenzoic acid, which is a common plant metabolite but also a known molecular marker related to ageing of protein-based fibres, such as wool [56]. This compound is also present in the extract of sample 7 (Figure S12), most probably as a component of the flavonoid dyestuff or produced by photo-degradation [57]. Finally, 4-hydroxybenzoic was also unexpectedly detected in traces in the extract of sample 4 (Figure S11). Its presence may suggest that, in this case, the cochineal dye was applied to an originally brown cotton sample since 4-hydroxybenzoic acid was detected in the extract of Peruvian brown cotton reference material.

9. Conclusions

Multimodal analysis, where archival, morphological, non-invasive, and invasive/destructive scientific methods have been employed to examine the two Wari khipus, 1932.08.0001 and 1932.08.0002, proved to be effective. Provenance and meticulous morphological study enabled improved understanding of khipu structure and to select areas of interest for more detailed study. Together with multiband imaging, they provided essential guidance for designing an effective and ethical sampling strategy. XRF in situ was fundamental to disclose information on areas where sampling was not possible (thread wrappings). It also revealed unforeseeable structural characteristics that produced a new understanding of these khipus' structure and revolutionised our idea of the affordances of khipu morphological study. Identification of an iron-mordanted thread in the wrapping of 1932.08.0002 P_1 allowed us to label the second band as mottled and not solid. Mapping of an iron-mordanted thread running beneath 1932.08.0001 P_2s_8 thread wrapping allowed us to virtually reconstruct the pattern of the thread wrappings on P_2s_8 and, by analogy, P_1s_7. These were likely to present five bands instead of two and three, respectively. The extremities of these wrappings were constituted by an iron-mordanted and now lost thread.

XRF in a vacuum on khipu samples revealed mordants and other inorganic auxiliaries. Calcium- and potassium-based compounds were used as alkaline agents in the dyeing bath. The signal of calcium was particularly high in the sample dyed with indigo, and potassium compounds (such as ashes) were probably added to darken the colour of the dyebath. These results were entirely consistent with XRF results obtained in situ from various areas on the khipus. The results of XRF on samples also indicated use of iron mordants for variously dyed cotton samples, especially blue, pink, and ecru, while the distribution of iron in the XRF maps in situ was less clear and pointed mainly to general high background contamination with iron.

HPLC revealed that cochineal was used for dyeing pink (sample 2), brown (sample 4), and red (sample 5). It proved that samples 3 and 6 were undyed and that the blue (sample 1) was dyed with indigo. Additionally, it confirmed the hypothesis proposed based on multispectral imaging that sample 7 was indeed dyed in yellow. This implies that P_2 of 1932.08.0002 was not a solid colour cord but a mottled ivory-yellow cord. It is possible that this also applies to other cords on the same khipu, as Figure 8 suggests. This finding, together with the new structural understanding provided by XRF in situ, puts into question current practices of khipu morphological analysis and colour notation. It goes without saying that it also undermines the affordances of using these data for statistical comparative purposes. By reporting the first dye analyses ever conducted on a khipu, as well as a new understanding of khipu morphological study, this research paves the way for deeper understanding of meaningful khipu colours and possibly to socially constructed meanings associated with the dyes and dyeing practices.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/heritage6030124/s1, Table S1: Representation of khipu 1932.08.01 cord structure [58], Table S2: Representation of khipu 1932.08.02 cord structure, Table S3: Samples, colours and corresponding areas of wrapping on both khipus, Figure S1 Overview VIS image of Khipu 1932.08.0002, Figure S2. Overview UVL of Khipu 1932.08.0002, Figure S3. Overview VIS image of samples from the "Meaningful materials in the khipu code" project, Figure S4. Irradiance of Godox LED 1000 II measured with an Ocean Optics Flame spectrometer at 100 cm distance, Figure S5. Irradiance of Godox LED 1000 II measured with an Ocean Optics Flame spectrometer at 100 cm, Figure S6. Irradiance of Kaiser Studiolight 1000 fitted with an Osram Halogen Superphot 1000W bulb measured with an Ocean Optics Flame spectrometer at 100 cm, Figure S7. Irradiance of Engelbretcht UVA-366 black lights measured with an Ocean Optics Flame spectrometer at 100 cm, Figure S8. Transmission of CHSOS Robertina Technical Photography filter set [32], Table S4. XRF positions and measurement details, Figure S9. Chromatograms obtained for the extract of sample 1, Figure S10. Chromatograms obtained for the extract of sample 2, Figure S11. Chromatograms obtained for the extract of sample 4, Figure S12. Chromatograms obtained for the extract of sample 7.

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The Unexpected Discovery of Syngenite on Margarito d'Arezzo's *The Virgin and Child Enthroned, with Scenes of the Nativity and the Lives of the Saints* (Probably 1263–4) and Its Possible Use as a Yellow Lake Substrate

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Abstract: The oldest painting in the National Gallery collection, *The Virgin and Child Enthroned* by Margarito d'Arezzo (NG564), dated to about 1263–4, depicts the Virgin and Child in a mandorla, surrounded by scenes of the Nativity and lives of the saints, set within red and decorative black borders, against a gilded background. The materials and technique were investigated using a combination of non-invasive techniques, such as Fibre Optic Reflectance Spectroscopy (FORS) and macro X-ray fluorescence scanning (MA-XRF), and the analysis of a small number of paint samples using energy dispersive X-ray analysis in the scanning electron microscope (SEM-EDS), High-Performance Liquid Chromatography (HPLC), Attenuated Total Reflectance—Fourier transform infrared spectroscopy (ATR-FTIR) and micro X-ray Diffraction (micro-XRD). The results provided evidence for the use of a number of organic colourants, with both indigo and red lake pigments identified. The finding of an unusual compound, syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$), is here postulated as a potential substrate for an organic yellow lake pigment. In addition, reference pigments were prepared to explore this hypothesis. Although documentary evidence confirms that yellow lakes were being produced from an early date, there is very little direct evidence for their use in 13th-century panel paintings.

Keywords: syngenite; yellow lake; safflower; organic colourants

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1. Introduction

The Virgin and Child Enthroned by Margarito d'Arezzo (NG564), dated to about 1263-4, is the oldest painting in the National Gallery collection. It is of considerable interest since the technique and materials of the Gallery's paintings of this period have not so far been studied in any depth. The panel shows the Virgin and Child in a mandorla, surrounded by scenes of the Nativity and lives of the saints, set within red and decorative black borders, against a gilded background (Figure 1).

The recent conservation campaign of this altarpiece focused on the reassessment of a past intervention on the painting, mainly the re-gilding of the original frame and overpainting of the adjoining red and black border. This work was probably undertaken by the Florentine restorer Ugo Baldi in preparation for the panel's sale in the mid-19th century.

Investigations undertaken during the conservation treatment used a combination of non-invasive techniques, such as Fibre Optic Reflectance Spectroscopy (FORS) and macro X-ray fluorescence scanning (MA-XRF), together with the analysis of a small number of paint samples using energy dispersive X-ray analysis in the scanning electron microscope (SEM-EDS), High-Performance Liquid Chromatography (HPLC), Attenuated Total Reflectance—Fourier transform infrared spectroscopy (ATR-FTIR) and micro X-ray Diffraction (micro-XRD). The results provided evidence for the use of a number of inorganic pigments, such as orpiment, azurite, vermilion and red and yellow earths, as well as the organic colourants indigo and lac lake in the original painting. As expected, analysis of several samples indicated an egg tempera medium (ATR-FTIR and transmission FTIR).

Figure 1. *The Virgin and Child Enthroned* by Margarito d'Arezzo (92.1 × 183.1 cm). NG564, after conservation. © The National Gallery, London.

The presence of indigo was identified non-invasively (using FORS) at various locations on the panel. It is present in the inscriptions above the narrative scenes, for example, and, perhaps most notably, was used for the blue sea in the scene depicting *The Miracle of Saint Nicholas*. This paint layer now appears very dark and opaque and conceals the details of sea creatures, probably painted in carbon black, and known only from the infrared reflectogram (IRR) (Figure 2). The use of indigo in paintings of this period is not unusual and has been confirmed in other 13th-century works, including the *Madonna and Child* from Arezzo, for example, where it was used as an underpaint for azurite [1].

Organic colourants such as red and yellow lake pigments rarely survive on paintings of this date and have been successfully analysed even less frequently. Their identification generally requires the analysis of small samples to detect both the organic dye components and the inorganic substrate onto which the dye molecules were precipitated or adsorbed. Furthermore, the pattern of major and minor dye components identified can, in favourable circumstances, provide details of the precise biological source from which they were extracted. One such paint sample was removed from the Virgin's skirt, next to an area of existing damage in the central motif, where the modelling of the fabric relies on the application of a red lake pigment over the top of a vermilion underlayer. Analysis by High-Performance Liquid Chromatography (HPLC) confirmed the dye source of the pigment to be lac, made from the dyestuff extracted from the lac insect *Kerria lacca* Kerr, while analysis by SEM-EDS indicated that it had been precipitated onto a hydrated alumina substrate. Although similar analyses have not yet been conducted on any comparative material from the National Gallery collection, lac lakes have been identified by HPLC in a number of English and Norwegian panel paintings, wall-paintings and sculptural polychromy from the mid-13th to the early 14th centuries [2].

The identification of yellow organic ("lake") pigments on paintings from this period is particularly rare, partly because few have been studied in-depth, but also because of the light-sensitive nature of many of the yellow dye sources. Thus, the detection of the inorganic substrate is often the only remaining clue that a yellow organic pigment might once have been present. There are few early recipes, but those that do exist generally suggest the use of a white substrate, perhaps a local white earth or a calcium salt, to adsorb (rather than precipitate) the dye molecules and produce the yellow pigment (see discussion in Section 4.1). It is in the context of a substrate for a yellow organic pigment that the identification of syngenite in a yellow glaze layer on *The Virgin and Child Enthroned*, described below, is significant. While no evidence for the presence of organic dyes was obtained, the identification of syngenite, together with additional contextual information, strongly suggests a yellow organic pigment was used as a glaze on the decorative border of the painting.

Figure 2. Detail of *The Miracle of Saint Nicholas.* Infrared reflectogram (IRR) revealing the sea creatures. © The National Gallery, London.

The removal of 19th-century overpaint from the decorative border revealed an original foliate decoration, painted in a fairly opaque, strong yellow over an (original) red background (Figure 3).

Close examination of the paint surface revealed what appeared to be a translucent yellow paint or glaze layer surviving on the surface of the yellow foliate design (Figure 4), perhaps applied to enhance the yellow colour or to imitate the type of gold foliate border seen in contemporary paintings, such as Guido da Siena's *Virgin and Child with S. Francis, John the Baptist, John the Evangelist and Mary Magdalene* (Siena Pinacoteca).

This paper details the analytical investigations undertaken to establish the presence of syngenite in the glaze layer on the surface of the yellow foliate design. In addition, reference organic pigments were prepared to explore the hypothesis that syngenite is present as a substrate for a yellow organic lake pigment.

Figure 3. Detail of Figure 1 showing: part of the angel in the scene of *St. John the Evangelist in a Cauldron of Boiling Oil*; the inscription above this scene contains indigo; and the newly revealed border with a yellow foliate design painted on the red background. The inset shows a detail of this border. © The National Gallery, London.

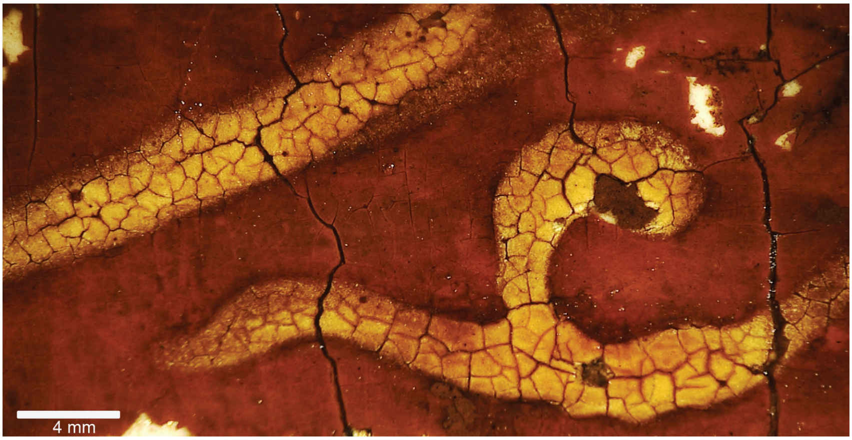

Figure 4. Hirox microscope image of a detail of the yellow border showing craquelure of the yellow paint layer/s. © The National Gallery, London.

2. Materials and Methods

2.1. Analytical Techniques

2.1.1. HPLC

The lake samples were extracted using 4% BF_3 in MeOH (*ca.* 3–6 µL). The solutions were left overnight, before being centrifuged for 1 min at 3000 rpm and the supernatant collected and analysed using a standard protocol developed at the National Gallery for the analysis of lake pigments extracted from historical paint samples. An Agilent Technologies High-Performance Liquid Chromatography system, comprising a 1200 series capillary pump and vacuum degasser and an HP 1100 series column oven and Photo Diode Array (PDA) detector, was used. The samples were injected manually via a Cheminert Valco low-dispersion 6-port injector with a 2 µL sample loop. Agilent OpenLab CDS (Chemstation edition) was used to control the equipment and process the data. The flow cell path length was 10 mm (0.5 µL volume) and the bandwidth (resolution) of the detector was 8 nm. The method used a Phenomenex LUNA C18(2) reverse phase column, 5 mm particle size, 150 × 0.5 mm (length × i.d.). The total run time was 80 min (+15 min post-run at initial conditions) at a flow rate of 10 μL min^{-1} and the column was maintained at a temperature of 40 °C. A binary solvent system was used; A = 0.1% aqueous trifluoroacetic acid, B = 94.9% acetonitrile, 5% methanol, 0.1% trifluoroacetic acid. The elution program was a linear gradient from 95A:5B to 70A:30B (0 to 25 min), followed by a linear gradient to 5A:95B (65 min). Isocratic conditions were maintained (75 min) before a linear return to the starting conditions, 95A:5B (80 min).

2.1.2. (ATR) FTIR

Spectra were acquired using a Bruker Tensor 27 FTIR Spectrometer connected to a Hyperion 3000 Series microscope, fitted with a mid-band MCT detector (range = 12,000–600 cm^{-1}) and a 64 × 64 (4096 pixels) FPA detector (range = 4500–900 cm^{-1}). Both detectors were cooled with liquid nitrogen. The microscope was fitted with a CCD camera, x-y stage (adjustment accuracy of 0.1 μm), knife-edge apertures and two glass objectives (4× and 20× magnification), a 15× Cassegrain objective and a dedicated ATR objective (20× magnification). The ATR had a germanium crystal with a tip size of 250 μm. Both the spectrometer and microscope were purged with water- and CO_2-free air. For transmission measurements, samples were compressed between the windows of a Spectra-Tech micro-compression diamond cell, then spectra acquired with the uppermost window removed. Bruker Opus software, version 8.7 was used to control the equipment and process the data. Spectra were collected with 4 cm^{-1} spectral resolution and were the sum of 128 scans.

2.1.3. XRD

Five small fragments from a sample taken from the glaze layer on the yellow foliage design on the red border of the painting were mounted on carbon fibres using small drops of epoxy. The mounted samples were fixed on a goniometer head in the XRD instrument. XRD measurements were carried out using a Rigaku Dmax Rapid II Micro-XRD. The samples were analysed using copper radiation at 40 kV and 36 mA. The X-ray beam was conditioned to a size of 300 μm. The samples were moved during the measurements along two axes (omega and phi-rotation) to improve particle statistics. Measurement times varied between 1 and 5 h.

The collected 2D data were converted to conventional 1D XRD patterns using the DP software (Rigaku). Phase identification was carried out using HighscorePlus (Panalytical) in combination with the PDF-2 database from ICDD. The XRD patterns were background subtracted before phase identification.

2.1.4. SEM-EDS

Samples were mounted as paint cross-sections and analysed in a Zeiss EVO MA10 variable pressure scanning electron microscope (VPSEM) with Oxford Instruments X-max large area Energy Dispersive X-ray Spectroscopy (EDS) and Silicon Drift Detector (SDD) at 25 keV, 200 pA, 44 Pa (Air) working distance 8.48 mm.

2.1.5. MA-XRF

MA-XRF scanning was undertaken using a Bruker M6 Jetstream macro X-ray fluorescence (MA-XRF) scanner which allows paintings to be scanned while secured on an easel in front of the scanner, with no contact being made with the paint surface. The measuring head consists of a 30 W Rhodium-target microfocus X-ray tube with a maximum voltage of 50 kV and a maximum current of 0.6 mA. With the Bruker M6, only elements heavier than silicon can be detected. The painting was scanned in 6 sections with acquisition parameters: Tube, 600 μA, 50 kV: detector, 275 kcps; spot size, 580 μm; step size, 580 μm; dwell time 10 ms; number of cycles, 1.

2.2. Synthesis of Syngenite

Syngenite was first synthesised using gypsum and potassium sulfate following an adapted version of a published method [3]. Gypsum ($CaSO_4{\cdot}2H_2O$; 12.1 g) was added to an aqueous solution of potassium sulfate (K_2SO_4; 14.2 g in 100 mL) at room temperature with constant stirring. After 3 h, the suspension, which had become noticeably "fluffy", was filtered under vacuum, and the resulting solid dried in an oven at 80 °C overnight. Syngenite was then synthesised in an identical manner using gypsum ($CaSO_4{\cdot}2H_2O$; 12.1 g) and an aqueous solution of potassium carbonate, K_2CO_3 (9.7 g in 100 mL) following an adapted version of a published method [4]. In both cases, analysis of the dried powder by FTIR confirmed the absence of gypsum (no bands present at 3560 and 3430 cm^{-1}) and indicated the presence of syngenite ($K_2Ca(SO_4)_2{\cdot}H_2O$; signature absorption bands at 758 and 658 cm^{-1}) [5], with chalk ($CaCO_3$; signature absorption bands at 1430 and 877 cm^{-1}) also present in the second sample (Figure 5).

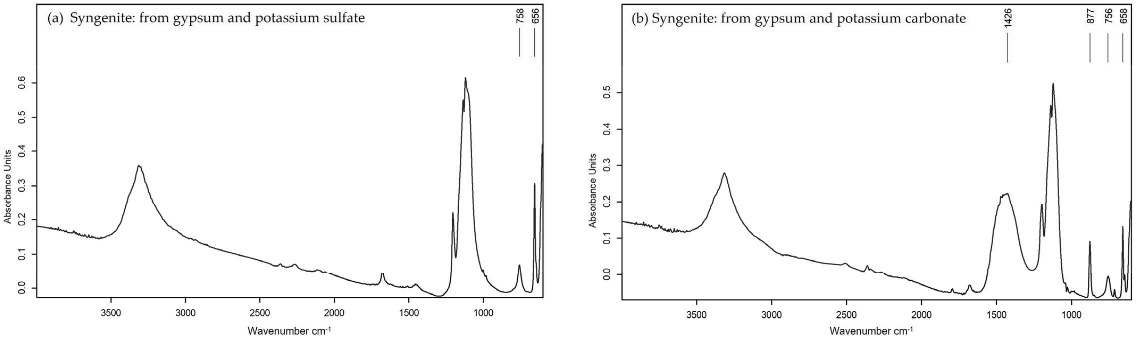

Figure 5. FTIR absorbance spectra indicating the presence of syngenite, synthesised from (**a**) gypsum and potassium sulfate and (**b**) gypsum and potassium carbonate (also containing chalk).

2.3. Preparation of Reference Organic Pigments

2.3.1. Weld on Gypsum Support

The dried weld (2.5 g) was placed in distilled water (250 mL) and left to soak for *ca*. 48 h. The solution was then heated to between 60 °C and 80 °C for 30 min before being left to cool for another 30 min, then filtered. One aliquot of the filtered solution (100 mL) was used for the syngenite experiment (see Section 2.3.2), while a second aliquot (100 mL) was placed in a beaker and gypsum (1.2 g) added. This was left for *ca*. 24 h (with occasional stirring) before the solid, now slightly yellow in colour, was removed and placed on a watch-glass to dry in a desiccator. To increase the amount of dye adsorbed onto the surface and produce a more intensely coloured pigment, a portion of the pale-yellow solid (0.7 g) was then placed in a second weld dye solution, prepared in a similar fashion to the first, and left for *ca*. 24 h (with occasional stirring) before being removed and placed on a watch-glass to dry in a desiccator. The same procedure was then repeated with a portion of the solid from the second immersion (0.4 g), thus producing three separate pigments which had been immersed in one, two and three fresh dye solutions, respectively.

As expected, immersion in successive dye solutions produced pigments with slightly deeper shades of yellow, however, all three pigments were still relatively pale in colour, so a further experiment was conducted using a more concentrated weld solution. In this case, the dried weld (15 g) was placed in distilled water (200 mL) and left to soak for *ca*. 24 h. The solution was then heated to boiling for 60 min before being left to cool for another 30 min, then filtered. The filtrate was placed in a beaker and heated, allowing the solution to evaporate until only *ca*. 10 mL remained. The resultant solution, slightly syrupy in consistency, was left to cool for *ca*. 30 min before an aliquot (5 mL) was removed and added to a beaker containing gypsum (1.2 g). This was left for *ca*. 24 h (with occasional stirring) before the solid was removed and placed on a watch-glass to dry in a desiccator. This produced a yellow pigment, deeper and darker in shade than those produced previously.

2.3.2. Weld on Syngenite Support

An aliquot (100 mL) of the weld solution prepared above (Section 2.3.1) was placed in a beaker and syngenite (prepared using gypsum and potassium sulfate in Section 2.2; 4.0 g) was added. This was left for *ca*. 24 h (with occasional stirring) before the solid, now slightly yellow in colour, was removed and placed on a watch-glass to dry in a desiccator. Analysis by FTIR confirmed the substrate, now slightly yellow in colour, had remained as syngenite and had not decomposed back to gypsum.

In an identical manner to that described in Section 2.3.1, a second pigment was prepared with the aim of increasing the amount of dye adsorbed onto the surface. However, when a portion of the solid from the first immersion (1.9 g) was added to an aliquot of the second weld solution and left for *ca*. 24 h (with occasional stirring) then removed and placed on a watch-glass to dry in a desiccator, it became apparent that it had decomposed. Analysis by FTIR confirmed the substrate was now gypsum.

In order to produce a more intensely coloured pigment with only one immersion, a further experiment was conducted using a more concentrated weld solution. An aliquot of the concentrated weld solution described in Section 2.3.1 (5 mL) was left to cool for *ca*. 30 min before adding syngenite (prepared using gypsum and potassium sulfate in Section 2.2; 2.3 g). This was left for *ca*. 24 h (with occasional stirring) before the solid was removed and placed on a watch-glass to dry in a desiccator. While analysis by FTIR confirmed the presence of syngenite, it was no longer the only component within the substrate. It is therefore apparent that although, in principle, syngenite can be used as a substrate for a yellow organic pigment, it remains as a pure substrate only under certain conditions.

2.3.3. Safflower

Safflower petals contain two dyes; the water-soluble yellow dye is generally washed out before the red dye (soluble in alkali) is extracted (see discussion in Section 4.1). However, the use of an alkali in the preparation of the dye solution makes safflower a particularly interesting dye source to consider in the present study as it provides a compelling reason for the addition of an alkali to the dye solution. It perhaps offers an explanation as to how a substrate such as syngenite might be produced from gypsum and an alkali such as potassium carbonate (following a synthetic route such as that outlined in Section 2.2) or potassium hydroxide. This first exploratory experiment was unsuccessful and did not produce syngenite, but the method is reported here nevertheless.

Safflower petals (10 g) were washed in distilled water and left to soak for 1 week to remove a large proportion of the yellow dye. They were then washed again five times with distilled water (the first and second washes used 500 mL and the petals were left to soak for *ca*. 1 h, then the third and fourth washes used *ca*. 250 mL before a final wash using *ca*. 200 mL). Approximately half the petals were then placed in a desiccator and the other half added to a potassium carbonate solution (100 mL; 9.7 g), warmed slightly, and left for one hour. The gypsum was then added (12.1 g) and the mixture stirred for *ca*. 30 min before being left overnight. The following day, the solution was stirred for several hours before citric acid (10%; 10 mL) was added and the solid, now yellowish-orange in colour, removed and placed on a watch-glass to dry in a desiccator. Before addition of the acid, a small sample of the solid was removed and allowed to dry in a desiccator. FTIR analysis indicated the presence of syngenite together with gypsum and chalk. However, analysis of the dried solid after the addition of citric acid indicated that syngenite was no longer present.

The second portion of washed and dried safflower petals (*ca*. 5 g) was mixed with solid potassium carbonate (0.64 g) in a process based on historical methods for testing or extracting the red dye (see Section 4.1) and then transferred to a Buchner funnel with filter paper. Deionised water (50 mL) was gradually added and allowed to drip through (not under vacuum). The same liquid was collected and allowed to drip through the petals again before a second portion of distilled water (50 mL) was gradually added and allowed to drip through. Any remaining liquid was collected by filtration under vacuum and the combined filtrate (*ca*. 80 mL) split into two equal portions. Citric acid (10%; 5 mL) was added to the first portion until a fine precipitate appeared, indicating that safflower red pigment was indeed present and had been soluble in the alkaline solution. The pigment was left to settle and then removed from the solution and allowed to dry in a desiccator. It is very possible that such a pigment could have been manufactured then ground with a suitable white substrate, such as gypsum or syngenite. However, another possibility is that the white material was added to the dye solution, thus syngenite (prepared from gypsum and potassium sulfate in Section 2.2; 1.0 g) was added to the second portion, followed by citric acid (10%; 5 mL). The mixture was stirred for *ca*. 30 min, then the solid, now red in colour, removed and placed on a watch-glass to dry in a desiccator. However, FTIR analysis of the dried solid confirmed that the syngenite had decomposed and was no longer present.

3. Results

The analytical investigations undertaken to establish the presence of syngenite in the glaze layer on the surface of the yellow foliate design are presented below.

3.1. Analysis of Layer Structure of Yellow Foliate Pattern of Border

A cross-section prepared from a paint sample taken from the yellow foliate pattern revealed the following stratigraphy (Figure 6a,b). Directly on top of the red earth paint of the background (1) is an opaque yellow paint layer (2) containing bright yellow particles with thin tabular and foliated fragments. These are clearly visible in the back-scattered electron (BSE) image (Figure 7) and SEM-EDS analysis of these yellow pigment particles confirmed the presence of arsenic (As) and sulfur (S), suggesting the presence of the arsenic sulfide pigment orpiment (Figure 8), and this was confirmed by micro-XRD. A few particles with similar characteristics and elemental profile were also found to be present in the overlying semi-translucent yellow layer (3). In UV illumination (Figure 6b), the substantial translucent yellow glaze layer seemed, in addition to the few inclusions of orpiment, to also contain other particles. There was also a thin fragmentary layer on the surface which fluoresced a milky white in UV; this was most probably varnish (4).

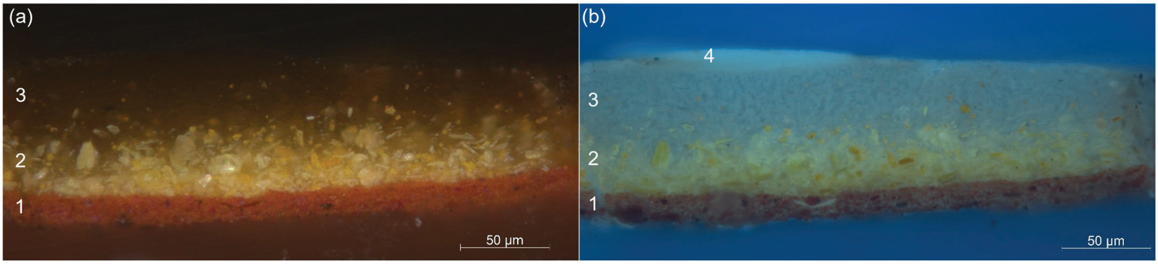

Figure 6. (**a**) Paint cross-section taken from the yellow border design in dark field-reflected light. Stratigraphy from the bottom upwards: 1. Red iron earth paint layer; 2. orpiment 3. yellow glaze layer with a few particles of orpiment present, particularly in the lower portion where layers 2 and 3 are intermixed. (**b**) Paint cross-section in 5a photographed in ultraviolet light (excitation filter 340–380 nm). 1. Red iron earth paint layer; 2. orpiment; 3. in UV illumination a particulate structure is visible in the yellow glaze layer; 4. trace of early/original varnish which remains on the surface of the sample. © The National Gallery, London.

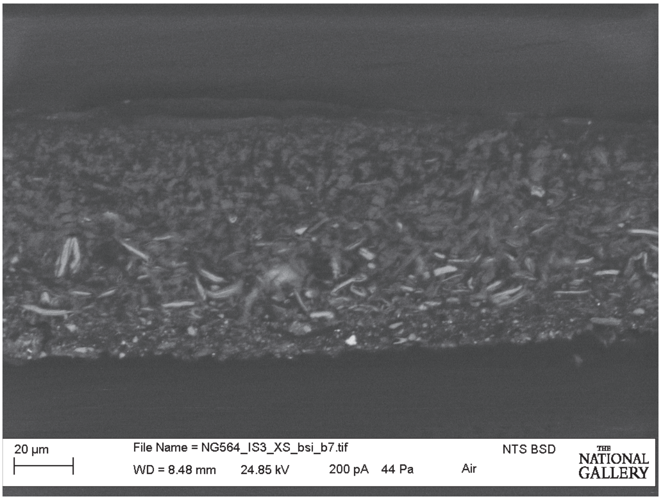

Figure 7. Back-scattered electron (BSE) image of the paint cross-section in Figure 6, clearly showing the particles present within the glaze layer.

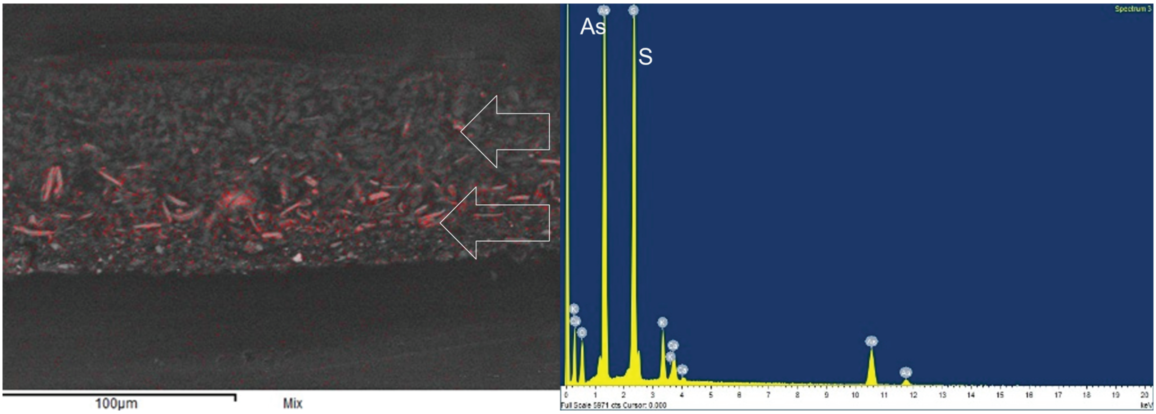

Figure 8. (**Left**) Back-scattered electron image of the paint cross-section with X-ray map for arsenic (As) in red, indicating the presence of particles of orpiment in the yellow paint layer and also a few within the overlying glaze. (**Right**) SEM-EDS spot spectrum confirming the presence of arsenic (As) and sulfur (S). This spectrum is representative of a large number of particles that were analysed in the sample.

To gain a clearer idea of the structure and composition of the particles visible under UV illumination in the translucent glaze layer and in the BSE image, SEM-EDS analysis was undertaken. This indicated the presence of sulfur, potassium and calcium, suggesting a complex potassium sulfate salt within the layer (Figure 9). ATR-FTIR analysis indicated that the inorganic component was homogeneous in composition and excluded the presence of either calcium sulfate or indeed chalk (data not shown). It also confirmed that the egg tempera binder was present in both the upper and lower layers, suggesting that the upper yellow layer was a paint or glaze layer rather than a degradation crust or discoloured varnish. Thus, it seems likely that the inorganic material within the upper layer is the substrate for a yellow organic “lake” pigment, which would have been used to produce a yellow glaze paint over the yellow foliate pattern painted in orpiment.

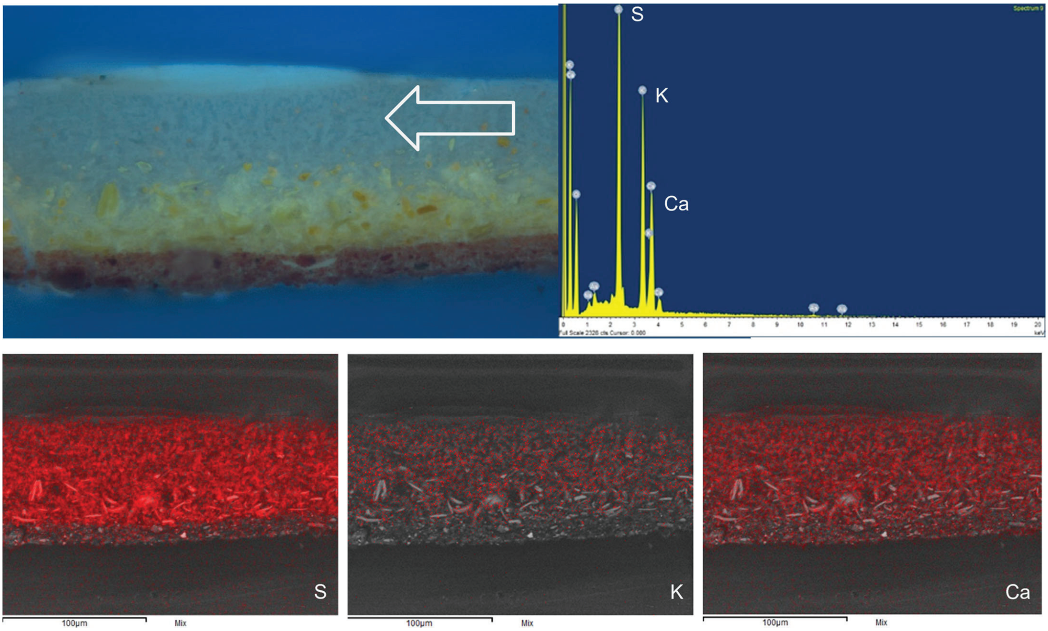

Figure 9. Image of the cross-section as shown in 6b with an SEM-EDS spot spectrum from a representative particle within the glaze layer showing the presence of sulfur (S), potassium (K) and calcium (Ca). **Below** (**from left to right**) are back-scattered electron images with X-ray maps (in red) for sulfur, potassium and calcium.

MA-XRF mapping provided further evidence for the painting technique used for the foliate perimeter border. The arsenic map (Figure 10) clearly shows the location of the yellow, orpiment-rich (As_2S_3) paint of the foliate pattern painted over the red iron oxide background. The foliate pattern is also visible in the potassium map (present in syngenite), which shows where the yellow lake glaze was applied over the orpiment paint along the entire length of the border design. The foliate design is visible as a negative in the iron (Fe-KA) map because the signal for iron is masked by the arsenic from the orpiment-containing yellow paint on top.

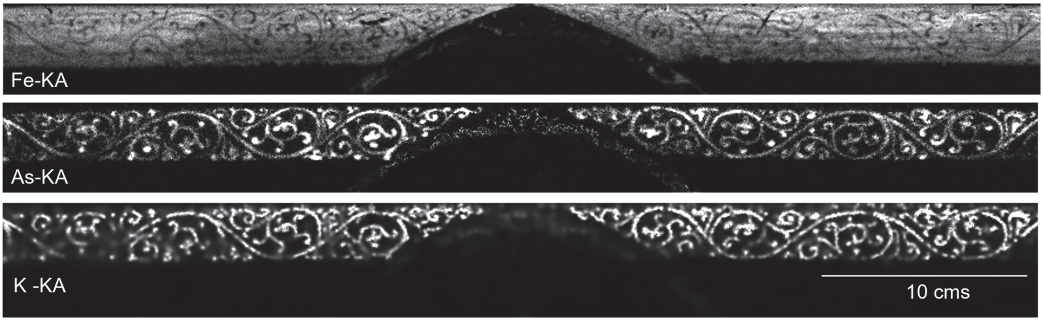

Figure 10. MA-XRF scanning: (**top**) iron distribution map (Fe-KA) showing the red iron earth paint of the background; (**centre**) arsenic distribution map (As-KA), showing the location of the arsenic sulfide pigment orpiment; (**below**) potassium distribution map (K-KA), showing the location of potassium present in syngenite from the yellow glaze layer along the whole length of the border design on the upper edge of the painting. © The National Gallery, London.

3.2. Identifcation of Syngenite (Micro-XRD Analysis)

In order to precisely identify the complex sulfate indicated by SEM-EDS and FTIR analysis, micro-XRD was undertaken. The major phase present in all the sub-samples from an unmounted fragment of the glaze layer was confirmed to be syngenite, $K_2Ca(SO_4)_2{\cdot}H_2O$. The XRD pattern for one of these sub-samples (IS3-5) is shown in Figure 11. The major and minor phases identified in all sub-samples are summarised in Table 1.

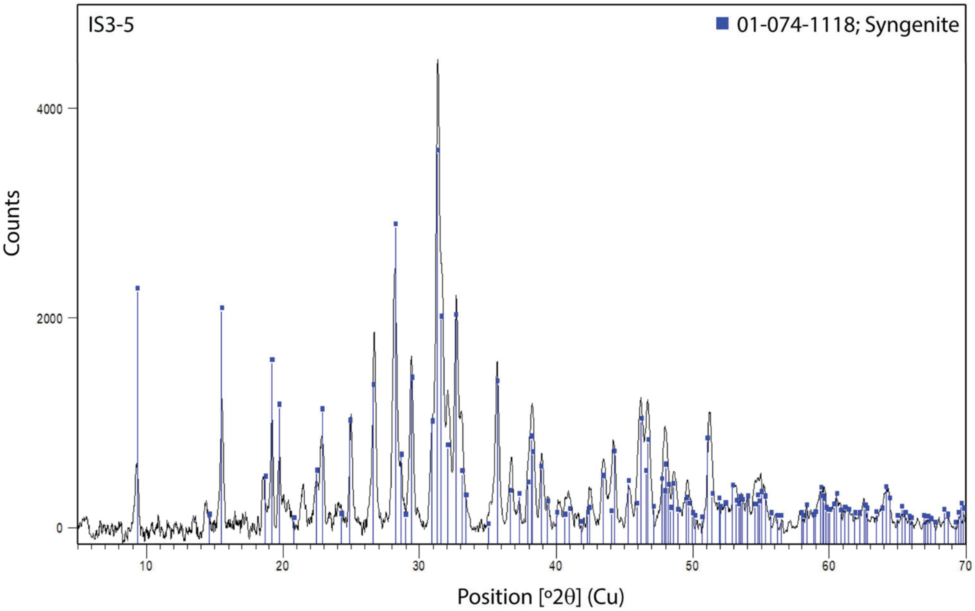

Figure 11. Micro-XRD pattern of an unmounted fragment (sub-sample IS3-5) from the glaze layer, confirming the presence of syngenite as the major phase.

Table 1. Phases identified from micro-XRD patterns of the unmounted sub-samples from the yellow glaze layer.

Sample ID	Major Phase	Minor Phase/s
IS3_1	syngenite	weddellite; calomel or polyhalite
IS3_2	syngenite	weddellite; calomel or polyhalite; anhydrite
IS3_3	syngenite	calomel or polyhalite; possibly trace of weddellite
IS3_4	very weak diffraction signal indicating the presence of amorphous material	
IS3_5	syngenite	Calomel or polyhalite

There is no doubt about the identification of the major phase syngenite in all fragments from the sample. The minor phases are harder to confirm, but the results suggest small quantities of weddellite (calcium oxalate) in three of the five fragments from IS3. The presence of small amounts of oxalate is not unusual in very aged paint layers, particularly at or near the surface. A trace of anhydrite was also suggested in one sample, while an unassigned peak with low intensity at 21.5° in four of the fragments could be explained with calomel (Hg_2Cl_2) or with polyhalite $K_2Ca_2Mg(SO_4)_2{\cdot}2H_2O$, which has a similar composition to syngenite.

4. Discussion

4.1. Organic Lake Pigments: Recipes and Possible Dye Sources

By the mid-13th century, the method of making red lake pigments by extracting the dye from the raw material using alkali and precipitating the pigment by the addition of potash alum had been known for several hundred years [6] (for lac and kermes, see nos. 174A–6, pp. 52–53, for example or for madder, nos. 188–9, p. 54). The deep-crimson lac lake in particular has been identified quite frequently in 13th- and 14th-century works [7] (pp. 89–95), and the way this translucent pigment has been used to paint the shadows in the folds of the Virgin's skirt is very characteristic. Yellow organic pigments seem to have been used as glazing pigments less frequently; in fact, they are rarely identified in paintings of this period, perhaps partly because they are not lightfast, and analytical evidence is thus lacking. They have, however, been identified in 14th-century Italian (Tuscan) paintings used in mixtures: for example, with blue pigments, such as azurite, to give greens, and with rather muted yellow ochres to give a brighter, more vibrant yellow [8]. In the present case, HPLC analysis was undertaken on a small paint sample taken from the foliate design in an attempt to identify any remaining dyestuff in the glaze layer, but no result was obtained. This is probably due to the very tiny sample size and perhaps also because yellow dye components are notoriously light-fugitive [9].

Yellow lake pigments are not well-documented: there are very few recipes for them dated before the late 14th century. Those that are known indicate that the pigments were made by precipitation or adsorption onto a suitable white substrate, which could include a local white earth or limestone, gesso, marble chips, lead white or even white flour, sometimes with the addition of alum to the dye solution. The earliest pigments based on organic dyes were made in this way and examples are recorded in Classical Roman sources: in *De architectura* (c. 30–20 BCE), Vitruvius describes how to make a yellow ochre-coloured pigment by heating dried violets in water and grinding the coloured solution with chalk [10]. Pigments were also made from flower petals directly, expressing the juice and mixing it with a suitable white substance. This, too, was a very old method, described in the first book of the so-called *De coloribus et artibus romanorum*, attributed to Eraclius (or Heraclius). This text consists of three books, the first two of which are in verse form. These probably date from around the 10th century and the author is believed to have been Italian. In a recipe from the first book, fresh flowers were ground on a smooth stone with raw gypsum, giving a pigment that could be stored dry. The third book, which is a prose text probably dating from the 13th century and by a French author, contains similar instructions to those described by Vitruvius centuries earlier [11] (vol. 1, no. II, pp. 184–185, no. LV (245) pp. 250–251. These methods were often used to make pigments from blue flowers, such as cornflowers (adding lime if a green was required) and are repeated in later sources. It is worth noting that these pigments probably were intended for use in aqueous media on parchment or paper.

It was only towards the end of the 14th century that recipes incorporating alum as an ingredient, together with a white material as substrate, began to appear, although in practice, pigments of this sort were probably used considerably before this. The 15th-century *Segreti per colori*, better known as the Bolognese manuscript from its publication by Mrs Merrifield in 1849, contains instructions for a bright yellow for use on paper made with saffron and lead white and a more familiar yellow, named *arzica*, made using a concentrated solution of the dye from weld (*Reseda luteola* L.) to which alum and either finely ground marble or lead white were added [11] (vol. 2, nos. 184, 194, pp. 480–483). Similar instructions occur in other 15th-century Italian sources. Alkali is rarely mentioned as an ingredient, although one example is a recipe for a yellow described as 'finer than orpiment or German giallolino', made using a strong extract of ripe buckthorn berries (*Rhamnus cathartica* L.) to which is added a solution of strong alkali mixed with alum. This gives a green solution, which is mixed with a fine white earth, repeating this several times to build up the colour [11] (vol. 2, no. 105, pp. 428–429). It is slightly surprising that this recipe should give a yellow as the ripe berries are the source of the pigment sap green; unripe berries are generally used for yellow pigments. Yellow pigments made from buckthorn berries are notably warmer in colour than those given by weld, which can be cool and acidic-looking.

The absence of alum from the yellow lake pigment found over the orpiment used to paint the decoration on the red border suggests that the yellow pigment was made in the simplest way, mixing a concentrated solution of yellow dye extracted from a plant source with the white material forming the substrate, repeating this process to build up the colour as required. If the pigment was a warm yellow colour, buckthorn could be a source of the dye, although other sources such as sawwort or weld are also possible.

Although there is no evidence at all for the use of alkali in making such a pigment at a date as early as the 13th century (required if it is assumed the syngenite substrate was unexpectedly synthesised during the lake-making process), there is no reason against this being done either; the use of alkali to extract flavonoid dyes such as these does result in more intense colours, and this might have been observed by dyers [12]. However, the possible identification of safflower red in the trace of red glaze on the border of the Virgin's veil in a damaged 13th-century painting of the Virgin and Child in the Istituto Santa Caterina in Arezzo suggested that safflower red was worth studying: this is unusual in that alkali must be used for extraction of the dye [1].

As mentioned above (Section 2.3.3), safflower contains two dyes, a red and a yellow, neither of which is lightfast; the water-soluble yellow dye must be washed out before the red can be extracted. The use of safflower in Europe as early as the 13th or 14th centuries is not well-documented, least of all in painting; the tentative identification of the pigment used as a glaze over gold in the 13th-century painting in Arezzo by Daveri and co-workers is a rare example [1] (pp. 401–402), [13]. By contrast, it was quite regularly used in 14th-century Middle Eastern manuscript production for illumination over gold, exactly as seen in the Arezzo painting, and was also used to dye paper [14,15]. It seems likely that, like several other dyes, the extraction and use of the safflower red dye in Italy had its origins in Arabic practice spreading across Mediterranean regions and then further north; certainly early descriptions of the dye and its extraction are found in 10th- and 11th-century Arabic sources [16] (see p. 195, attributed to Abū Mūsā Jābir ibn Ḥayyān, died around 806–816 CE), [17] (pp. 30–31, 44–45; al-Mucizz ibn Bādīs, written in about 1025 CE). By the first decade of the 14th century, its use in dyeing was well-understood and is, for example, recorded in Lucca [18]. A few years later in 1316, also in Lucca, dyeing equipment sold to Landino Parpaglioni by the merchant Ranieri Malisardi included two presses of some description, a wide, shallow vessel and a sieve, all for working with safflower [18] (p. 170). That safflower was a regular item of trade is also indicated by the description of how to test its quality by the Florentine merchant Francesco Balducci Pegolotti in *La pratica della mercatura*, a handbook compiled between about 1320 and 1340. Pegolotti describes how the sample of safflower to be assessed is tested in a way very similar to the manner described in Section 2.3.3 above, washing out the yellow dye and then obtaining the red by mixing the washed petals with dry wine lees, pouring water through the mixture, and finally acidifying with strong vinegar. If a good vermilion red colour is produced, with very little effervescence, the sample is of good quality; if the solution becomes white, with a lot of effervescence, the safflower is of bad quality [19].

Pegolotti's description matches the few extant dyeing recipes from this period very closely [20,21]: if he had put a piece of textile into the final solution the red colour would have been precipitated onto it. To make a pigment, the red material could be allowed to settle, collected, and ground with a suitable white substrate. Alternatively, the white material (gesso, for example) could be present in the vessel so that precipitation took place onto it. However, not enough is known about workshop practices at this time to provide a firm indication of how such a pigment would have been made and, without positive identification of any dye components from HPLC analysis, the dye source remains unknown for the presumed organic pigment on the yellow foliate design on the border of *The Virgin and Child Enthroned* by Margarito d'Arezzo.

4.2. Syngenite and Its Possible Use as a Substrate for a Yellow Organic Lake Pigment

Syngenite has previously been identified on paintings, but it has generally been found only in very small amounts and usually as a degradation product [22–24]. For example, syngenite was identified in an orpiment-containing paint layer, applied in imitation of gold, on a 13th-century painting by Cimabue [22]. The authors suggest that syngenite is present as a secondary mineral following the degradation of the orpiment-containing paint layer. Similarly, syngenite was identified together with schultenite, mimetite and palmierite in areas originally painted with orpiment in a 17th-century Dutch painting [23]. It is also suggested that these secondary minerals formed as a result of the degradation of orpiment.

However, in the sample taken from the Margarito painting under discussion, no evidence of orpiment degradation was found by SEM-EDS analysis and no arsenolite was identified during XRD analysis. Arsenolite is usually the starting point for deterioration of orpiment via light-induced photooxidation and its absence in the samples under investigation is significant. Indeed, the syngenite observed on the painting by Margarito is homogeneously present within an apparently continuous glaze layer over the yellow foliate design of the border (Figures 6–10). This is puzzling and requires explanation. It is our hypothesis that its presence is most likely explained as the substrate of a yellow organic "lake-type" pigment which, when applied over a layer of orpiment (see Figure 6) must have produced a rich and intense yellow or orange-yellow colour (depending on the dye source used), perhaps intended to imitate the appearance of gold.

Assuming the syngenite does indicate the presence of a yellow organic pigment, the question then arises as to whether the syngenite itself was used as a white substrate on which to adsorb a yellow dye (see discussion in Section 4.1) or whether it is an alteration product of some kind. While it is impossible to come to any definitive conclusions in this regard, some possible scenarios are outlined below.

The syngenite may have been found, either in mineral form or precipitated from solution (perhaps accidentally) and used in the lake-making process as a convenient white substrate. Although rare in absolute terms, syngenite can be found in marine and volcanic deposits [25,26], and this would be the simplest and most straightforward explanation. In Italy, for example, deposits are known in the Campania, Piemonte, Lazio and Apulia regions. However, the particles in the cross-section are relatively small and fairly uniform in size and do not have the appearance of having been ground from a mineral source. In addition, although exploratory experiments using syngenite to adsorb a yellow dyestuff (in this case, extracted from weld) were partially successful (Section 2.3.2) they also indicated that syngenite is prone to decomposition and only remains as a pure substrate during the pigment-making process under certain conditions.

Syngenite can be prepared relatively easily by stirring stoichiometric amounts of gypsum with potassium sulfate [3], and much of the modern scientific literature on this topic is focused on trying to avoid its formation during the production of the relatively useful potassium sulfate from industrial waste streams containing phosphogypsum [27]. Although potassium sulfate is unlikely to have had any technological uses in the 13th century, if it was known at all, the extremely low solubility product of syngenite means that it will readily precipitate from a solution containing the correct proportion of calcium, potassium and sulfate ions. It is therefore possible to imagine an alternative scenario, avoiding the need to collect the syngenite, whereby it was unexpectedly synthesised during the manufacture of the organic pigment itself, perhaps from a 'standard' white substrate such as gypsum.

Preliminary experiments exploring the possibility of syngenite production during the lake-making process indicated that it could be formed by the addition of gypsum to a solution containing potassium carbonate—a substance that would have been available in the 13th century, either converted from cream of tartar, or in the form of wood ash alkali (Section 2.2). The use of potassium carbonate (or any other alkali) when preparing a yellow organic pigment is unusual, but would have been necessary when using a dye source such as safflower (see discussion in Section 4.1). A more pressing problem in this case, however, is that calcium carbonate (chalk) is also formed during the reaction and no chalk was observed in the syngenite-containing layer in the cross-section from the Margarito painting. The recipe for the preparation of safflower pigments requires the addition of acid (in the form of citric acid from lemon juice or acetic acid from vinegar) and while this has the potential to remove the chalk, preliminary experiments were unable to produce a syngenite-containing substrate (Section 2.3.3). Another possibility, not yet explored, is the use of a strong alkali, potassium hydroxide, made by putting wood ash ley over quick lime.

It should be acknowledged that when making pigments of this type, the process of adding the substrate to a strongly coloured solution was often repeated to build up the colour and this repetition (and the exact conditions in the dye solutions) are particularly difficult to recreate. Thus, while it is entirely possible that syngenite, either collected or unexpectedly synthesised, was used as the white substrate on which to adsorb a yellow dye, there is currently no specific evidence for this. The alternative possibility, whereby the syngenite is a degradation product, formed within the paint due to degradation of a 'standard' yellow lake substrate such as gypsum, is also worth considering but is similarly speculative and is perhaps the least likely scenario. Firstly, there is no obvious source of potassium ions within the paint layers, nor any indication of how they would have migrated throughout the paint to create such a uniform layer of syngenite. It is possible that a harsh cleaning of the painted surface using alkali may have provided such an environment; however, the relatively low density of syngenite compared to gypsum would presumably result in a significant dimensional change to the paint layer during any such transformation. The paint layer containing the syngenite is still intact, following closely to the yellow orpiment lines of the design and does not appear to have been disrupted in this way.

5. Conclusions

A multi-analytical approach has provided evidence for the use of several types of organic colourant on *The Virgin and Child Enthroned* by Margarito d'Arezzo, with both indigo and a red lake pigment unequivocally identified. Micro-XRD analysis confirmed syngenite ($K_2Ca(SO_4)_2{\cdot}H_2O$) was present in a translucent paint layer on top of a yellow scroll design on the border, and it is argued that this is likely to be the substrate for an organic yellow lake pigment. Exploratory experiments to investigate whether the syngenite itself may have been used as a white substrate on which to adsorb a yellow dye or whether it might represent an alteration product of some kind were inconclusive, but documentary evidence confirms that yellow organic pigments were being produced from an early date and several possible dye sources suggested. Since there is very little direct evidence for the use of yellow organic pigments in 13th-century panel paintings, the identification of syngenite as a possible substrate or alteration product is both an unusual and an important observation.

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Mapping Materials and Dyes on Historic Tapestries Using Hyperspectral Imaging

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Abstract: Hyperspectral imaging has emerged as a promising analytical method of artwork due to its potential in combining non-invasive analytical capabilities and imaging allowing the survey of the entire (or of a large area of the) surface of an artwork, which is a highly significant application for historic tapestries. This project deployed a high-resolution ClydeHSI Art Scanner, which was used with both a push-broom visible to very-near infrared (VNIR; 400–1000 nm) and near infrared (NIR; 900–1700 nm) hyperspectral cameras. Initial testing focused on the characterisation and mapping of the different materials used on historic tapestries (wool, silk, metal threads). To facilitate the dye characterisation, a collection of wool and silk samples dyed with recipes based on medieval practices was used. The samples measured using the system and the data collected formed an external reference library including the type of the natural dyes and mordants used during their production. The outcomes of the on-site deployment of this analytical instrumentation for the characterisation and analysis of 16th century tapestries on display at Hampton Court Palace will be discussed.

Keywords: Flemish tapestries; textiles; natural dyes; hyperspectral imaging; non-invasive dye analysis; brazilwood; yellow dyes; fading

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1. Introduction

Historic tapestry collections have been considered among the most significant forms of art from the 15th to 18th century in Europe. Historic Royal Palaces (HRP) is the custodian of Hampton Court Palace in London, UK, and its important tapestry collection, developed primarily by Cardinal Wolsey (1475–1530) and Henry VIII (1509–1547), which is part of the Royal Collection [1]. The characterisation of tapestry materials is crucial for assessing the condition and formulating suitable conservation treatment strategies for these nationally significant large-scale textiles.

Tapestry is a 'weft-faced' woven textile where the coloured weft threads carry the pictorial intricate design while contributing to the physical weave structure of the textile. Materials used for the weft are primarily wool and silk dyed in a wide range of colours with natural sources (plants and insects). In the most expensive tapestries, metal threads, comprising gold, silver or silver gilt wrapped around a silk core, were also used.

Micro destructive chromatographic methods have been commonly used for dye analysis as they allow the different molecular components to be separated and then characterised. High-performance liquid chromatography (HPLC) has enabled the identification of a large number of dyes used in textiles [2,3]. However, this requires sampling usually from the reverse of the tapestry, which is not always feasible and the results are limited to the sampled area [4]. The development of non-invasive analytical approaches for the identification of tapestry materials or the analysis of the natural dyestuffs has progressed over the last few years, including Fourier-transform infrared spectroscopy (FTIR) and fibre optics reflectance spectroscopy (FORS) [5–8]. Raman spectroscopy is another method which can be deployed for the analysis of dyes in particular surface-enhanced Raman spectroscopy (SERS); however, it requires a small sample (approximately 80 µg); therefore, it is a micro invasive technique [9]. X-ray fluorescence spectroscopy is also useful for analysing metallic mordants [10,11]. However, these non-invasive analytical techniques also provide limited information on the spot analysed.

Hyperspectral imaging (HSI) has emerged as a promising analytical method for works of art [12,13]. The systems used in cultural heritage are usually operated in reflectance mode and cover the visible (Vis), near infrared (NIR) and short-wave infrared (SWIR) spectral regions depending on the type of sensor their cameras have [14]. This technique produces high-quality optical spectral signatures in reflectance at each image pixel position, providing the ability to identify the materials used for the artwork and map their spatial distribution over the object surface. The method has been used primarily in paintings [15–17] and manuscripts [18,19]. Other applications include prints [20], ethnographic collections [21,22], murals [23], photographs [14] and archaeological objects [24].

During the deployment of this method, spectral data are acquired at each spatial position across a measurement line and the spectral cameras are scanned to create a data cube that can be formed into x, y and spectral axes. The processing of these large data sets has been an active area of research particularly for the identification of pigments, lakes and other materials used in the construction of paintings such as binders [16–18,25–31]. Another application of automated classification techniques is related to the authentication of artworks [32].

HSI has also been applied to the examination and analysis of textiles [33]. Zhao looked into the use of a portable spectroradiometer with a range from 2500 nm to identify and characterise textile fibres [34], while another interesting application successfully deployed HSI combined with FORS in the visible to very near infrared range (VNIR 400–1000 nm) for the characterisation of twelve dyestuffs and three mordants [35]. Finally, Vermeulen was successfully deployed a range of non-invasive analytical techniques including HSI to characterize organic colorants used in 20th-century traditional textiles from Mexico [36].

HSI allows the survey of the entire (or of a large area of the) surface of an artwork, which is beneficial for the analysis of historic tapestries; however, there are limited studies related to this application. Delaney deployed an hyperspectral camera (NIR 967–1680 nm) combined with FORS to map the different materials (wool, silk and metal threads) on a 16th century tapestry using the spectral regions between 1500 and 1600 nm and 2100 and 2400 nm [37]. De la Codre investigated the materials used in three 18th century Royal tapestry manufactories Abusson, Gobelins and Beauvais using HSI (400–2500 nm). In this research, dyed samples were used as reference materials and two different classification methods were compared for data processing and material identification [38]. Furthermore, the characterisation of yellow dyes in the tapestries and the influence of the composition and degradation on analysis were also studied [39]. This research has also been included as a case study in a paper exploring the applications of a small hyperspectral camera operating in the visible–near infrared range (VNIR) [24].

This collaborative research considers the advantages and potential limitations of HSI applied to the study of historic tapestries deploying a high-resolution ClydeHSI Art Scanner. Initial testing focused on the characterisation and mapping of the different materials used on historic tapestries (wool, silk, metal threads). To facilitate the dye characterisation, a collection of wool and silk samples were used which had been dyed during the Monitoring of Damage in Historic Tapestries (MODHT) EU research project using recipes based on medieval practices [40]. The samples were measured using the system and the data collected formed an external reference library, including the type of the natural dyes and mordants used during their production. Finally, the analytical instrumentation was deployed on site for the characterisation and analysis of several 16th century tapestries on display at Hampton Court Palace.

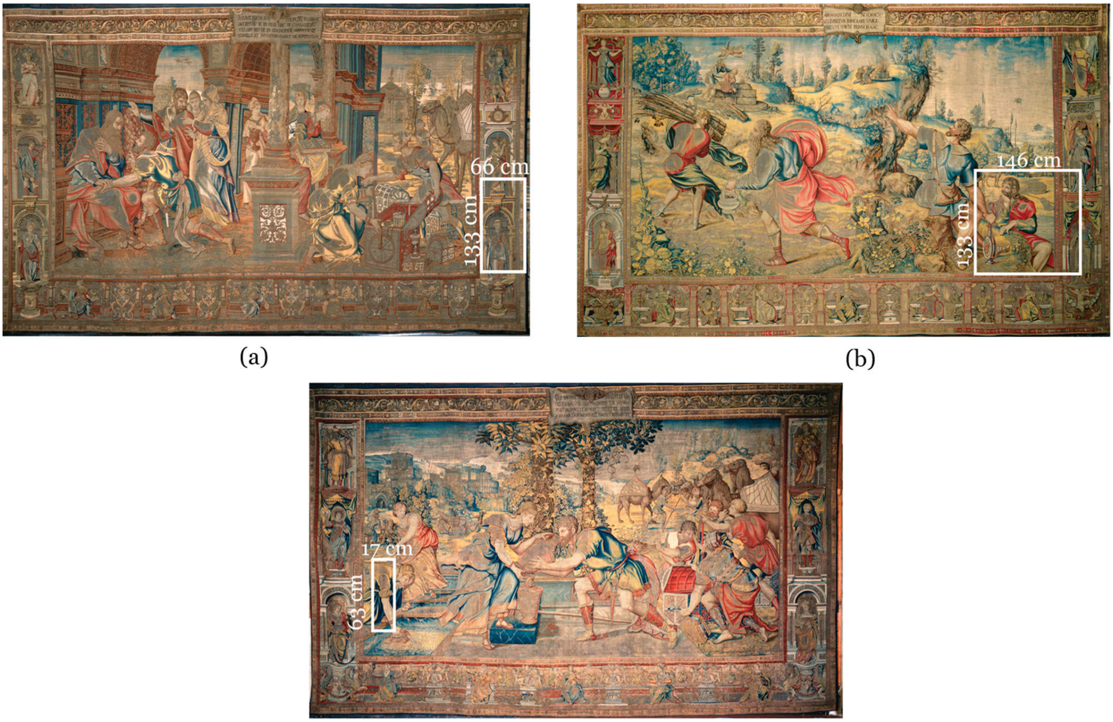
2. Materials and Methods

2.1. Historic Tapestries

The *Story of Abraham* is a set of ten Flemish tapestries depicting scenes from the Old Testament. The tapestries, each measuring approximately eight meters across by five meters high, were constructed from dyed wool and silk yarns, while large areas were decorated with precious gold and silver metal threads. The *Story of Abraham* is considered the most artistically and historically significant set of tapestries in the UK's Royal Collection, and have hung in their original location in the Great Hall at Hampton Court Palace since the early 1800s (Campbell 2007). The tapestries are likely to have been commissioned by King Henry VIII, their design is attributed to Pieter Coecke van Aelst and they were constructed in the workshop of Willem de Kempeneer in Brussels (c.a. 1541-43) [41].

In this study, three tapestries of the *Story of Abraham* set were analysed (Figure 1). Details of the tapestries and the size of the areas scanned are listed in Table 1.

This research builds on the Henry VIII's Tapestries Revealed project, which focused on virtual restoration of the original colour palette of the *Oath and Departure of Eliezer* tapestry. As part of this research, spectral imaging technology was used for the first time to accurately assess the impact of fading, and develop a model which, when projected on the tapestry, produced the recoloured effect [42].



(a) (b) (c)

Figure 1. The three tapestries from the *Story of Abraham* set analysed in this project: *Oath and Departure of Eliezer* (**a**), *Sacrifice of Isaac* (**b**) and *Eliezer and Rebekah at the Well* (**c**). The white rectangles indicate the areas scanned on each tapestry (Royal Collection Trust/© His Majesty King Charles III 2022).

Table 1. Details of the *Abraham* tapestries and the areas of investigation.

Tapestry Name	Inventory Number	Area of Analysis	
		Height (cm)	Width (cm)
Oath and Departure of Eliezer	1046.8	133	63
Sacrifice of Isaac	1046.9	133	146
Eliezer and Rebekah at the Well	1046.5	63	17

2.2. Reference Samples

Tapestry samples created during the European Commission-funded project Monitoring of Damage in Historic Tapestries (MODHT) were used in this research [40]. The samples were woven from wool and silk yarns representative of historic tapestry materials and dyed using medieval natural colourant formulations that would have been used in 16th century tapestry weaving [43].

Dye analysis of European tapestries showed that a limited number of dyes from natural sources such as plants and insects were used to create a wide palette of colours. This was achieved by deploying different mordants (inorganic salts for bonding the dye to the fibre), adding chemicals, or overdyeing a colour with another one (yellow with blue for green) [4,40,43]. Table 2 summarizes the information on the materials, dyestuff and mordant combinations used for the production of the MODHT model tapestry samples. Details of the actual recipes and the testing of the samples are available in publications developed as outputs of the MODHT project [40,43]. In this paper, the same abbreviation codes are used.

2.3. Hyperspectral Imaging

The hyperspectral imaging system deployed in this research was a high-resolution ClydeHSI Art Scanner, with both a push-broom visible to very near-infrared (VNIR; 400–1000 nm) and near infrared (NIR 900–1700 nm) hyperspectral cameras. The cameras were mounted on a stage providing the capability for the instrument to scan large areas of 1.5 × 1.5 m. Tapestry fragments from the Historic Tapestry Fragments Collection housed at the HRP Heritage Science Laboratory were initially tested using the scanner to define the operational conditions to ensure the best signal to noise ratio and initial analytical protocol. The instrument was then carried into the Great Hall where, over a period of one day, areas on three Abraham tapestries were analysed (Figure 2). A line scan, push-broom, spectral camera creates a two-dimensional image by scanning its field of view across a measurement line and then moving the camera to create additional lines in the scan direction. This gives a field of view in the across track direction, the measurement line, and an image in the along track which forms a data hypercube. There is a trade-off between field of view and spatial resolution. This means that for high resolution scanning, the field of view is narrow and in order to image large areas in high resolution, multiple image strips need to be measured. These strips are measured with a spatial overlap so that they can be stitched together using feature mapped procedures. Table 3 summarises the number and size of the individual image strips as well as information on the resulting composite images for each tapestry. The initial tapestry analysed was the *Oath and Departure of Eliezer*, where an area of approximately 1 m^2 was scanned in seven strips. The largest area was captured on the *Sacrifice of Isaac tapestry*, which was about 2 m^2 and consisted of 17 strips. On the final tapestry, *Eliezer and Rebekah at the Well*, due to time limitations, only one strip was captured, measuring 0.1 m^2.

Table 2. MODHT samples material, dye and mordant information.

Weft Fibre	Name	Code	Dyestuff	Mordant
Silk	Red/Brazilwood	RS1a	Brazil wood	Alum
Silk	Red/Brazilwood	RS1b	Brazil wood	Alum
Silk	Red (pink)/Brazilwood with lye	RS1c	Brazil wood	Alum
Silk	Red (dark pink)/Brazilwood with lye	RS1d	Brazil wood	Alum
Silk	Red/S2a, Madder	RS2a	Madder	Alum
Silk	Red/S2b, Madder with lye	RS2b	Madder	Alum
Silk	Red/S2c, Madder with lye	RS2c	Madder	Alum
Silk	Red/Cochineal	RS3	Cochineal	Alum
Silk	Blue light/Woad	BS1a	Woad	-
Silk	Blue dark/Woad	BS1b	Woad	-
Silk	Green/Woad-Weld	GS1b	Woad/weld	Alum
Silk	Green light/Weld-Woad	GS2b_L	Weld/woad	Alum
Silk	Green dark/Weld-Woad	GS2b	Weld/woad	Alum
Silk	Yellow/Weld	YS1b	weld	Alum
Silk	Yellow/Greenweed	YS3	Greenweed	Alum
Silk	Black/$FeSO_4$	BlkS1_a	$FeSO_4$	Oak gall
Silk	Black/$FeSO_4$	BlkS1_b	$FeSO_4$	Oak gall
Silk	undyed	CON S	-	-
Silk	Alum	Alum S	-	Alum
Silk	Oak gall	Oak gall S	-	Oak gall
Wool	undyed	CON W	-	-
Wool	Red/Madder	RW1	Madder	Alum
Wool	Red/Madder with lye	RW1_wl	Madder	Alum
Wool	Red/Madder	RW2	Madder	Oak gall/Alum
Wool	Red/Madder with lye	RW2_wl	Madder	Oak gall/Alum
Wool	Red/W3, Brazilwood	RW3	Brazil wood	Alum
Wool	Red/Brazilwood with lye	RW3_wL	Brazil wood	Alum
Wool	Red/Cochineal	RW4	Cochineal	Alum
Wool	Red/Cochineal	RW5	Cochineal	Alum
Wool	Blue/Woad	BW1	Woad	-
Wool	Green/Weld-Woad	GRW1	Weld/woad	Alum
Wool	Green/Woad-Weld	GRW2	Woad/weld	Alum
Wool	Yellow/Weld	YW1	Weld	Alum
Wool	Yellow/Greenweed	YW2	Greenweed	Alum
Wool	Black/$FeSO_4$	BLKW1	$FeSO_4$	Oak gall
Wool	Black/$FeSO_4$	BLKW2	$FeSO_4$	Oak gall
Wool	Black/$FeSO_4$	BLKW3	$FeSO_4$	Alder bark
Wool	Black/W4, Cu+$FeSO_4$	BLKW4	$FeSO_4$/$CuSO_4$	Oak gall
Wool	Undyed	CON W	-	-
Wool	Alder bark tannin	Alder W	-	Alder bark
Wool	Alum mordant	Alum W	-	Alum
Wool	Oak Gall mordant	Oak gall W	-	Oak gall

Table 3. Specifications of the hyperspectral analysis on the tapestries.

Tapestry	Number of Strips	Size of One Strip (Pixels)	Size of Composite Image (Pixels)
Oath and Departure of Eliezer	7	VNIR; 640 × 4552 NIR; 320 × 3400	VNIR; 2797 × 4552 NIR; 1971 × 3400
Sacrifice of Isaac	17	VNIR; 640 × 4690	VNIR; 6484 × 4690
Eliezer and Rebekah at the Well	1	VNIR; 640 × 2411	

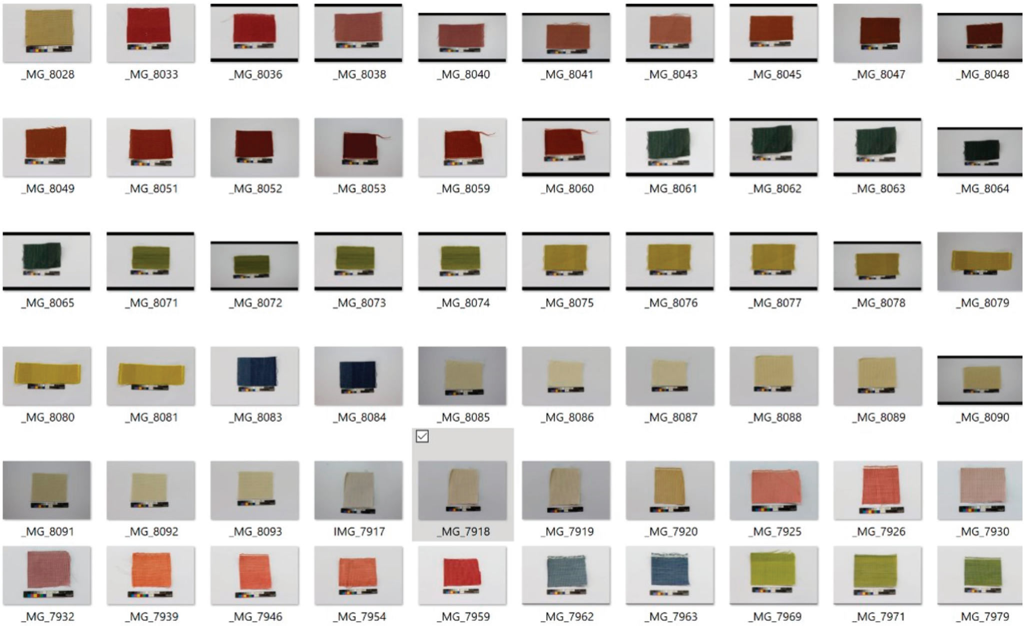
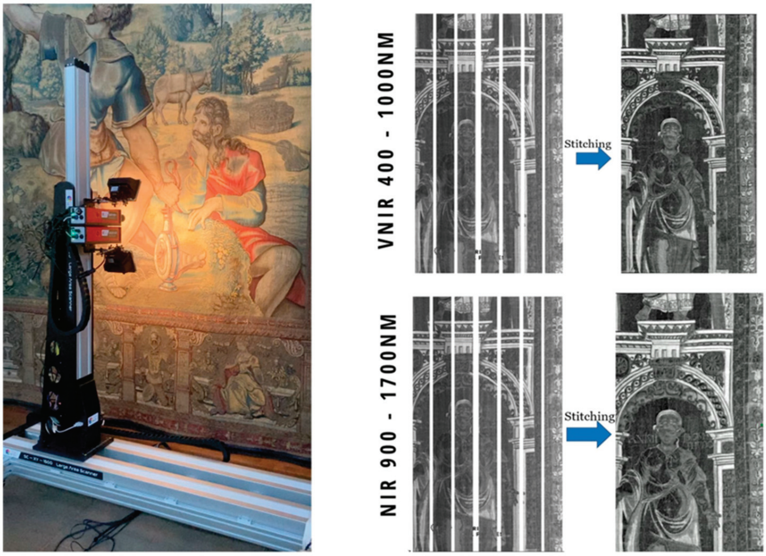


Figure 2. The MODHT samples representing a wide range of natural dyes used in the manufacture of 16th century historic tapestries.

The tapestries were scanned vertically; the acquisition time for one strip was 15 s with a spatial resolution of 0.25 mm/pixel. Two halogen light sources positioned at 45° with respect to the cameras were used for illumination of the scanned area; the light exposure level in the visible spectrum was ca. 2000 lx. This illumination level was measured under static conditions and, as a result, when line scanned measurements are performed, the speed of acquisition means the illumination of a measurement area occurs for a fraction of a second. The estimated light dose of exposure for one second is 0.5 lux hours, a minor contribution to the 150,000 lux hours threshold adopted as an acceptable annual dose in the course of usual display. The system was set up to allow an overlap of 15% between consecutive strips to facilitate the stitching at the post-processing phase and to combine them into one composite hyperspectral image (Figure 3c, Table 3). At the start and end of each scan, a reflective white Polytetrafluoroethylene block was measured to record the instrument spectral/spatial response function to provide the reference for converting the raw data of the composite hyperspectral image signal into reflectance data. The reflection data were calculated from the measurement of the instrument response using a white tile reference and a dark noise reference with the camera shutter closed. Further details on the hyperspectral cameras specifications and the scan parameters are indicated in Table 4.

For the operation of the cameras and spectra acquisition, as well as the processing of the hyperspectral data, the SpectraSENS Clyde HSI software was used. The composite hyperspectral reflectance image was initially processed with an unweighted smoothing average before using principal components analysis (PCA) and spectral angle mapping (SAM) algorithm to achieve the distributions of the material across the tapestry areas analysed and identify the dyes used for their manufacture.



(a) (b) (c)

Figure 3. The hyperspectral imaging scanner set up in front of the *Sacrifice of Isaac* tapestry in the Great Hall, Hampton Court Palace, UK (**a**) The hyperspectral image strips from the VNIR and NIR cameras (**b**) The composite hyperspectral images in VNIR (top) and NIR (bottom) (**c**).

Table 4. Hyperspectral camera specifications and scan parameters.

Parameter	VNIR	NIR
Spatial Resolution (mm)	0.25	0.25
Spectral range (n)	400–1000	900–1700
Lens focal length (mm)	50	50
Aperture (f/#)	2.5	2.5
Working distance (mm)	700	700
Scan speed (mm s^{-1})	25 mm/s	25 mm/s
Acquisition time (s/line strip)	15	15
Frame rate (fps)	88.40	88.40
Number of bands	306	240

PCA is a statistical tool that represents data using uncorrelated variables named principal components (PC). PCA is used to reduce variables, detect general patterns in the data and identify outliers. As a result, the hyperspectral cube is reduced in dimension and the clustering is taking place according to a number of components. In unsupervised deployment, the clustering algorithm automatically detects patterns which are useful for initial processing of the data [14,27,32]. PCA was performed independently on the VNIR and NIR data sets to identify spectral outliers and reduce the number of dimensions in the hyperspectral cubes to less than 10 PC dimensions. The resulting false colour images from this processing indicated the mapping of the different dyes across the area of analysis based on their spectral responses.

SAM is a classification algorithm commonly used in the processing of hyperspectral imaging data. This algorithm assesses the angle between each spectrum at each pixel with the spectra of a reference library (endmembers) [25,26,29,35,38]. In this project, an external library was used with spectra acquired from the MODHT tapestry model tapestries where the dyes and mordants are known (Appendix A Table A1). The SAM algorithm then proceeds in the classification of each pixel of the reflectance hyperspectral image and produces an endmember classification map showing the distribution of each dye on the area of analysis. The map is associated with a list of the identified endmembers and shows their distribution on the area under investigation.

3. Results

3.1. PCA Analysis

PCA was applied to the VNIR and NIR reflectance hyperspectral cubes of the tapestries. The results produced detailed mapping of the dyes based on their spectral responses where the design of the tapestry was reproduced in high resolution but in false colour. Figure 4 shows the *Oath and Departure of Eliezer* tapestry area analysed with HSI (Figure 4a) and the false colour images following PCA analysis of the VNIR (Figure 4b) and NIR (Figure 4c) hyperspectral cubes.

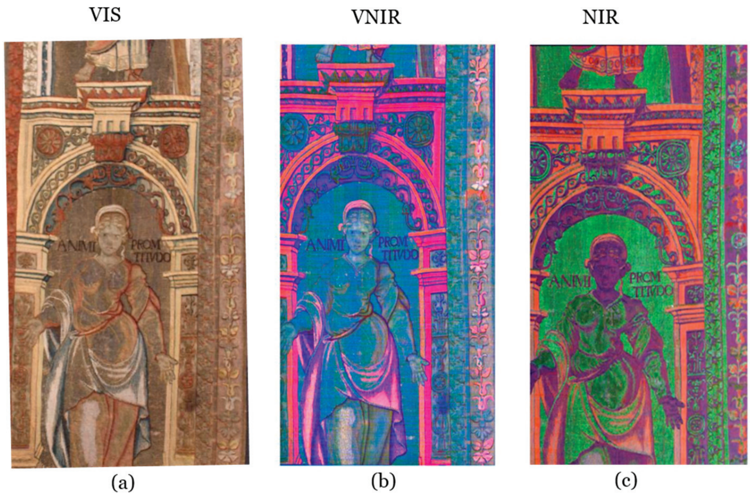


Figure 4. The *Oath and Departure of Eliezer* tapestry area analysed with HSI. (**a**) False colour images following PCA analysis of VNIR (**b**) and NIR (**c**) reflectance hyperspectral cubes.

Following closer interrogation of the PCA images, some interesting observations could be reported. For example, on the section of the border of the *Oath and Departure of Eliezer* tapestry, which seems relatively uniform under visible light, the PCA false colour images highlighted an area of restoration with a bright orange/red colour (Figure 5a). Furthermore, on the architecture, although the visible image has the same beige colour, the mapping of the dyes in the VNIR PCA image suggests the use of different dyes (Figure 5b). Moreover, the PCA NIR image shows that the dye highlighted in purple has most likely been used on the sleeve of the figure as well as the design of the architecture (Figure 5b).

3.2. SAM Analysis

The SAM algorithm was applied in the processing of the VNIR reflectance data cubes of the three Abraham tapestries for the identification and mapping of the dyes used in their manufacturing. The non-invasive classification of the dyes was achieved with the use of a spectral reference library based on the HSI analysis of the MODHT model tapestry samples. The spectra range used for this analysis was between 500 and 920 nm in order to reduce poor noise to signal ratios. Furthermore, a high tolerance angle of 1.5 rad was applied to facilitate the characterisation of dyes. Previous research has suggested that SAM analysis using high tolerance angle (2.56 to 1.81 rad) resulted in the identification of four yellow dyes (weld, safflower, chamomile and turmeric), while these were not able to be characterised using their reflectance spectra [35].

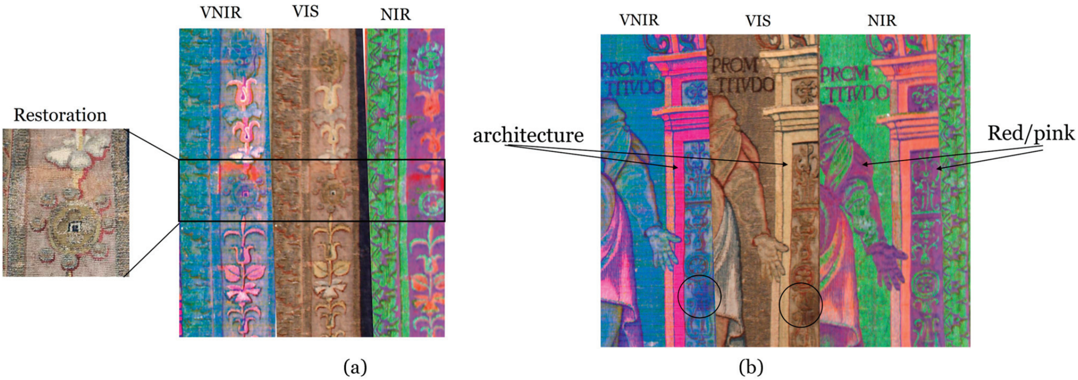


Figure 5. (**a**) Section of the border of the *Oath and Departure of Eliezer* tapestry area analysed with HSI. Following PCA analysis. the mapping of the dyes revealed a restored area. (**b**) The PCA VNIR mapping indicates the use of different dyes.

3.2.1. MODHT Samples Analysis and Compilation of Endmember Library

Forty-two MODHT samples were analysed with HSI VNIR (400–900 nm) and NIR (900–1700 nm) cameras, and the resulting reflectance spectra were used as the spectral reference library for performing SAM analysis on the HSI data collected from the Abraham tapestries.

Figure 6 shows four MODHT replica tapestry samples representing yellow (YW1), red (RW1), green (GRW1) and blue (BW1) colours (Figure 6a) and their respective reflectance spectra in VNIR and NIR (Figure 6b). Details of the endmember library are summarized in Appendix A Table A1, including the dyestuff, mordants, visible images and reflectance spectra for forty-two MODHT samples. This table also includes the colours attributed to the endmembers in the SAM classification. These digital colours were selected as an approximation of the original colour group of the MODHT sample such as pink, red, light and dark green, light and dark blue, brown, beige and black, while grey indicated metal threads.

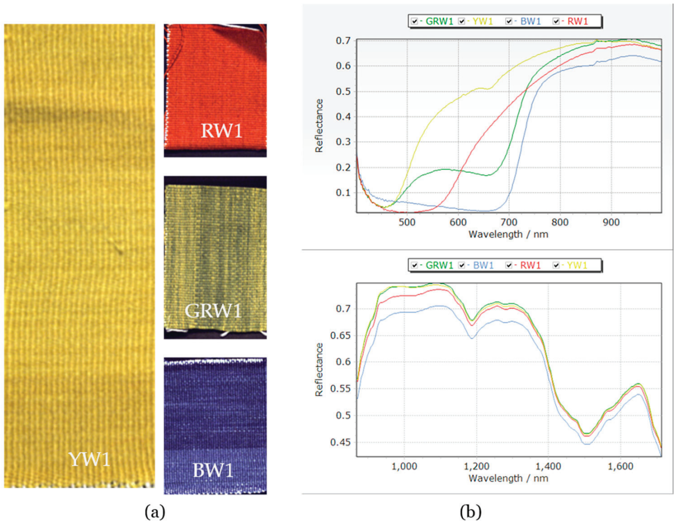


Figure 6. MODHT replica tapestry samples (**a**) and their respective reflectance spectra in VNIR (top) and NIR (bottom) graphs (**b**).

The classification of the dyes used in this section of the *Oath and Departure of Eliezer* tapestry indicated the use of brazilwood with lye treatment for the pink (RS1c) or dark pink, brown/red (RS1d) silk areas, while there is also a smaller amount of the brazilwood dye RS1a. In wool, the only red dye identified was madder (RW2); however, this was in traces. The blue areas were dyed with woad (BS1a), while a darker shade (BS1b) was produced with a longer dyeing time. The yellow silk areas were dyed with both greenweed (YS3) and weld (S1b); however, for wool, greenweed (YW2) was primarily used, while weld (YW1) had a much lower quantification value. Green in the silk areas was produced with threads dyed first with weld and then with woad (GS1a); however, threads which were dyed first with woad and then with weld (GS2b) were also identified in two different shades, light and dark. On the wool green areas, only threads dyed first with weld and then woad (GW1) were identified. Oak gall was classified in silk and wool areas, while Alder bark and Alum mordanted threads were identified only in wool. Black was limited to wool threads and was produced primarily with BLKW4, which was produced with a combination of iron sulphate and copper sulphate mordant.

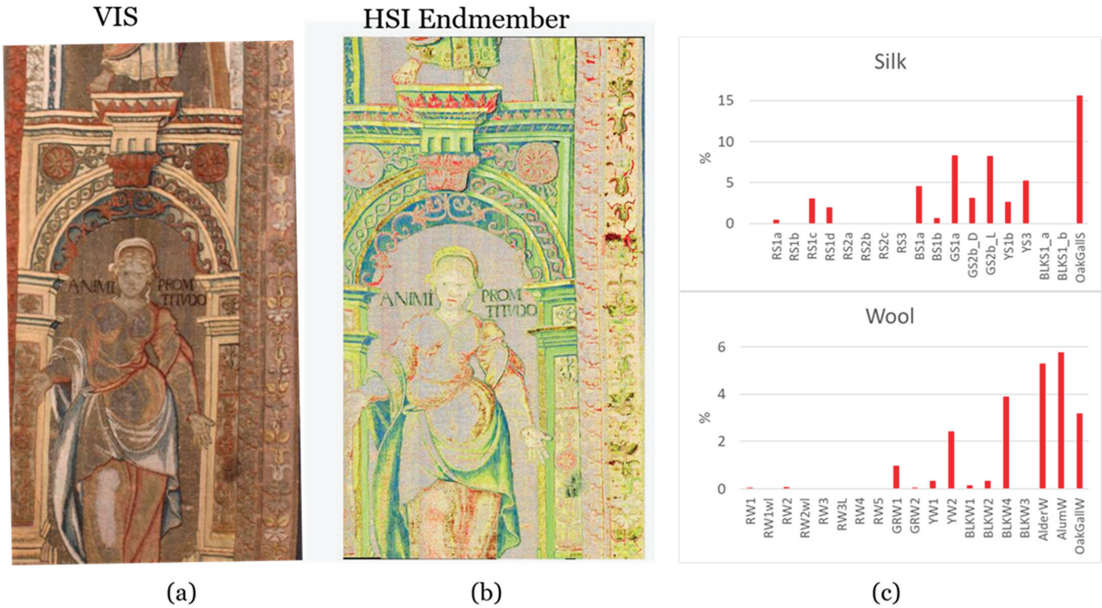
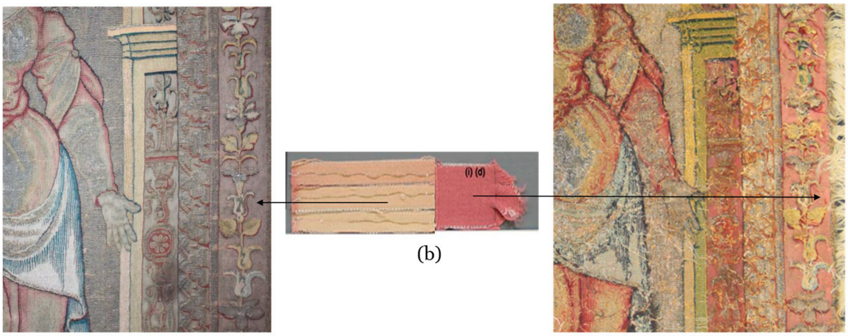


Figure 7. The *Oath and Departure of Eliezer* tapestry area analysed. (**a**) The SAM analysis with the identified endmember mapping. (**b**) The graphs summarize the silk (top) and wool (bottom) dyes identified after SAM analysis (**c**).

The *Oath and Departure of Eliezer* as part of previous research was recorded in high-resolution imaging in both obverse and reverse [42]. Figure 8a shows the detail of the area analysed with HSI, while Figure 8c shows the same area in reverse where the tapestry was protected from light exposure and the original colour palette has been preserved. Visual examination of the reverse image confirmed the use of green and yellow dyed yarns on the architecture. However, most significantly, the use of brazilwood was also indicated in the background of the border following a comparison with the brazilwood dyed sample (Figure 8b). During this research project, samples were exposed to a xenon arc lamp in an accelerated light ageing chamber (Xenotest 150S) with an IR and UV filter system intended to replicate sunlight through window glass and following the conditions set in BS EN ISO 105-B02. The relative humidity was controlled by the apparatus to 65 ± 2%, and the temperature was 20 ± 2 °C. Trial samples showed that a total exposure of 60 Mlx h (megalux hours) was a suitable dose, producing a significant and measurable difference in physical properties, and approximating the light exposure which may have been received by a 400-year-old tapestry, based on archival research and current illumination levels. These accelerating ageing experiments confirmed that brazilwood is one of the most fugitive dyes [42].

The *Oath and Departure of Eliezer* was also used in this research to map the different materials used for the weaving of the tapestry, wool, silk and metal threads. For this purpose, the SAM algorithm was applied in the processing of the NIR reflectance data cube of the tapestry and the endmember library included the undyed silk and wool MODHT samples spectra.1500 to 1600 nm of the wool and silk reflectance spectra can be used in reflectance imaging spectroscopy to map these fibres [37] therefore, the spectral range used for this analysis was between 1497 and 1567 nm. Furthermore, a high tolerance angle of 1.5 rad was applied. The results are shown in Figure 9b, while the percentage of area coverage for each endmember is presented in Figure 9c. This analysis reproduced the design of the tapestry in high resolution, providing a clear understanding of the distribution of the materials. In almost 50% of this area, the weft threads used silk in the head and parts of the dress of the figure, as well as the architecture and the border. Wool yarns covered approximately 20% of this area and they were deployed in specific areas of the design. Finally, about 30% of the area was covered by metal threads; this included part of the figure's dress as well as the background of the architecture and the decorative border.



(b)

(a)

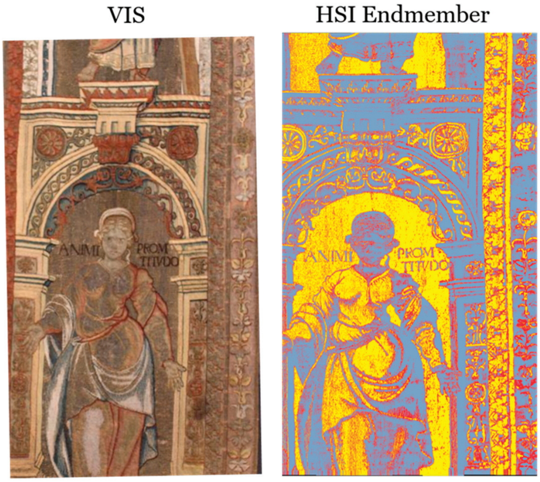
(c)

Figure 8. The *Oath and Departure of Eliezer* tapestry obverse (**a**) and reverse (**c**) The brazilwood dyed sample in the middle before (right) and after (left) light ageing (**b**).

3.2.2. Sacrifice of Isaac

The scanned area from the *Sacrifice of Isaac*, measuring about 2 m^2 and located at the bottom viewing right of the tapestry, shows a male figure; on the right of the scanned area, a section of the border is also included. The results from the SAM analysis shown in Figure 10b provide an estimate of the original colour palette of the tapestry, which has faded due to long exposure to light. Significant changes are observed in the yellow and green areas. Furthermore, the metal threads used primarily on the male figure's clothing, the border on the right and the basket in the background have tarnished (Figure 10a).

The SAM classification endmembers identified in the area of analysis are presented in Figure 10c graphs which show the dyes on silk on the left and the dyes on wool on the right. These graphs show the percentage of area coverage following the spectral matching to the endmember reference library (Appendix A, Table A1).

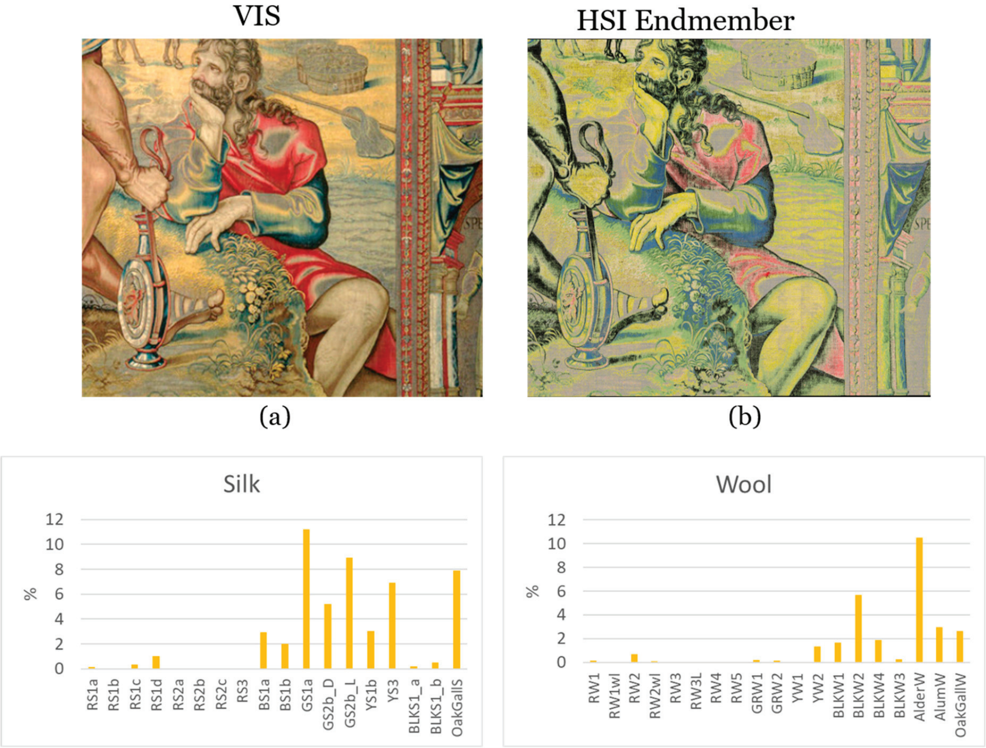


(a) (b)

Name	Percent
🟦 Silk	48.6%
🟨 Metal 1	31.19%
🟥 Wool	20.02%

(c)

Figure 9. The *Oath and Departure of Eliezer* tapestry area analysed. (**a**) The NIR SAM analysis with the identified endmembers mapping (**b**) SAM analysis results (**c**).



(c)

Figure 10. The *Sacrifice of Isaac* tapestry area analysed (**a**). The SAM analysis with the identified endmembers mapping (**b**). The graphs summarize the silk (left) and wool (right) dyes identified after HSI SAM analysis (**c**).

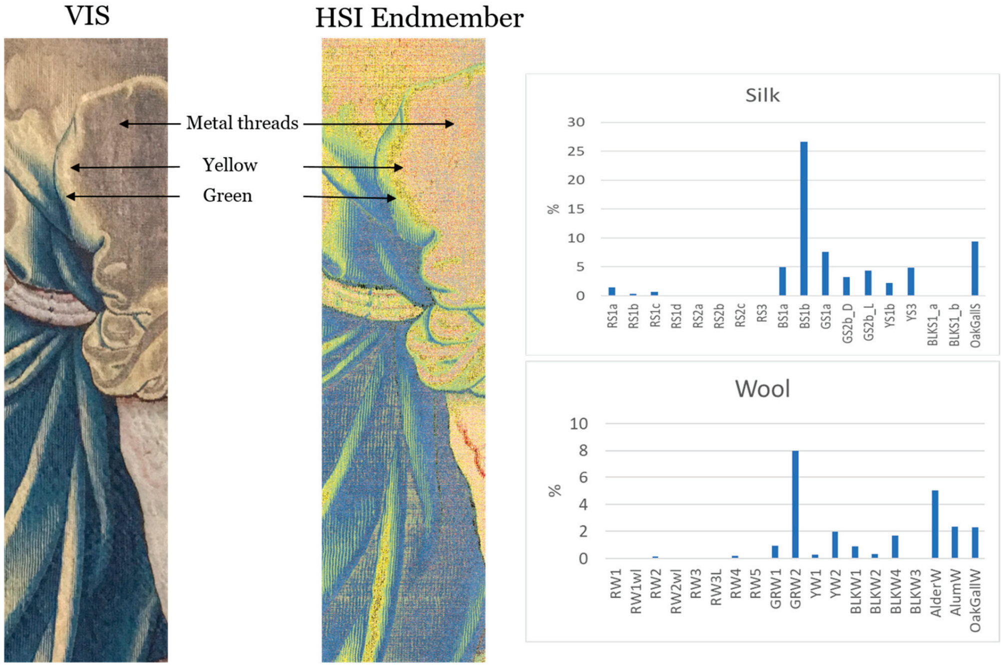
The analysis results indicated that the blue areas were dyed with woad (BS1a), while a darker shade (BS1b) was produced with a longer dyeing time. On the yellow silk areas, greenweed (YS3) was primarily used, while a fewer yarns were dyed with weld (YS1b). However, for the yellow wool yarns, only greenweed (YW2) was used. Green was primarily produced with silk yarns dyed either first with weld and then with woad (GS1a), or threads which were dyed first with woad and then with weld (GS2b) in two different shades, light and dark. For the silk red tones, the use of brazilwood with lye treatment (RS1d and RS1c) was identified, as well as a smaller amount of the brazilwood dye RS1a. Red wool yarns were dyed with madder (RW2 and RW1). Oak gall was identified in silk and wool threads, while Alder and Alum mordanted threads were identified only in wool. Black was identified primarily in wool and was produced with three different recipes (BLKW1, BLKW2 and BLKW4). It is interesting to note that for some of the brown areas on the tapestry, the SAM simulation presents them as black, for example, on the flesh at the two legs of the unseen figure on the left. This might have been due to the use of a black dye with another one to produce the brown colour. However, only the black element was revealed in the analysis.

3.2.3. Eliezer and Rebekah at the Well

The scanned area from the *Eliezer and Rebekah at the Well* tapestry was much smaller than the previous two areas, measuring 0.1 m^2. Nevertheless, the analysis of this area provided the opportunity to study how the tapestry weavers deployed dyes in different tones to deliver the design of the tapestry, which, in this case, is a detail of a woman with a blue dress (Figure 11a). The results from the SAM analysis shown in Figure 11b indicated that the pleats on the dress were originally highlighted with green- and yellow-coloured threads to add volume and texture into the design of the fabric. Furthermore, large areas of the shoulder and the sleeve of the figure were constructed with metal threads. It is interesting to note that for the areas across the metal threads, yellow-coloured threads were used to match their golden colour. The SAM classification mapping image provides an estimate of the original colour palette of the tapestry (Figure 11b) as the present condition of the tapestry, following long exposure to light, has suffered from fading, and the metal threads have tarnished and blackened (Figure 11a). Accelerated ageing studies have confirmed that the yellow dyes (mostly weld) are highly fugitive [42]. Therefore, the yellow highlights on the dress are currently neutral, while the green-coloured areas originally made with yellow and blue dyes are primarily blue, as indicated in Figure 11a,b.

The SAM classification endmembers identified in the area of analysis are presented in the Figure 11c graphs, showing the dyes on silk at the top and the dyes on wool at the bottom. The data show the percentage of area coverage following the spectral matching to the endmember reference library (Appendix A, Table A1).

The blue areas were dyed with woad (BS1a), while a darker shade (BS1b) was produced with a longer dyeing time. The yellow silk areas were dyed with both greenweed (YS3) and weld (S1b), whereas for wool, greenweed (YW2) was primarily used, while weld (YW1) was used less frequently. Green in the silk areas was produced with threads dyed first with weld and then with woad (GS1a); however, threads which were dyed first with woad and then with weld (GS2b) were also identified in two different shades, light and dark. On the green wool areas, only threads dyed first with woad and then weld (GRW2) were identified. Oak gall was identified in silk and wool threads, while Alder and Alum mordanted threads were identified only in wool. Black was identified in wool and was produced with three different recipes (BLKW1, BLKW2 and BLKW4). Finally, small areas of threads dyed with brazilwood were identified. As the area analysed did not have red/pink areas, brazilwood might have been used in the flesh. Alternatively, the areas consisting of metal threads also have a red hue in the SAM mapping, which might be related to the use of brazilwood for the dyeing of the silk cores in combination with young fustic [4,9]. In wool, there was also a small amount of cochineal (RW4) and madder (RW2) identified, which might have been used in the blue colour.



(a) (b) (c)

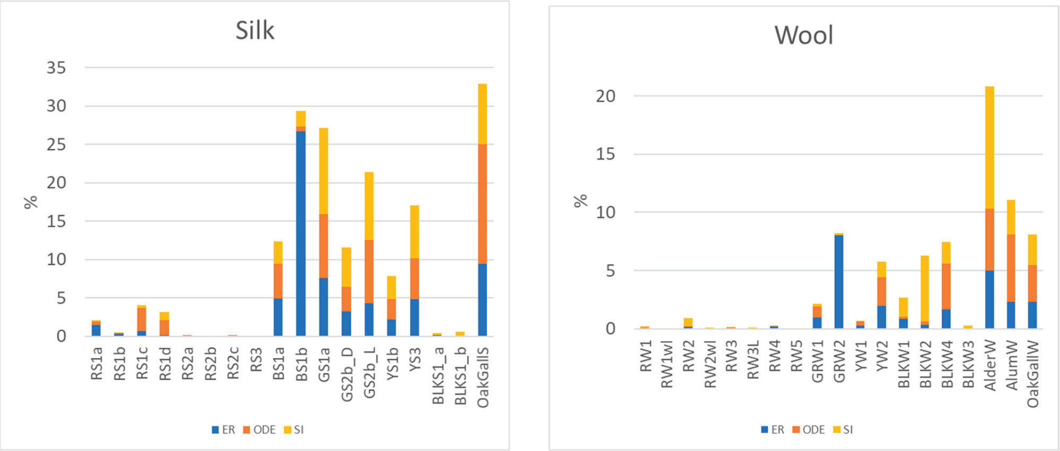
Figure 11. The *Eliezer and Rebekah at the Well* tapestry area analysed (**a**). The SAM simulation with the identified endmembers mapping. The arrows indicate areas of colour fading (**b**). The graphs summarize the silk (top) and wool (bottom) dyes identified after HSI SAM analysis (**c**).

4. Discussion

The SAM classification endmembers identified in the areas analysed on the three *Abraham* tapestries are presented in Figure 12, showing the dyes on silk (a) and the dyes on wool (b). The compilation of the results on the dyes identified are also summarized in Table 5.

The classification of the dyes used in the Abraham tapestries indicated the use of similar materials for their production, confirming that they are part of one set and were made in the same workshop.

The use of brazilwood as the main dye for silk red, pink and dark pink yarns is consistent across all three tapestries analysed, particularly brazilwood with lye treatment (RS1c and d) but also with no lye (RS1a and b). In wool, madder (RW2) was used primarily; however, brazilwood (RW1) and cochineal (RW4) were also traced in small quantities. The fugacious nature of brazilwood has been well-documented for a long time and to characterise its aged form on historic textiles has been challenging. It is only recently that the full characterisation took place [44], while a non-invasive methodology using SERS has also been demonstrated [9]. Furthermore, HSI has been used successfully to identify brazilwood lake pigments [31]. The use of brazilwood in The *Oath and Departure of Eliezer* tapestry was also indicated though the visual examination of the reverse side, which was protected from light exposure and the colour of the yarns had not faded (Figure 9). However, future research should focus on the characterisation of the red dyes with HSI and the impact of degradation to the analytical results.



(a) (b)

Figure 12. The graphs summaries the silk (**a**) and wool (**b**) dyes identified after HSI SAM analysis on the three *Abraham* tapestries: *Eliezer and Rebekah at the Well* (ER), *The Oath and Departure of Eliezer* (ODE) *and Sacrifice of Isaac* (SI).

The blue areas on the Abraham tapestries were dyed with woad (BS1a), which also had a darker shade (BS1b) which was produced with a longer dyeing time.

Although difficulties have been reported in the identification of yellow dyes [39], the data from the HSI analysis of the Abraham tapestries suggested that this method might be used to characterise the yellow yarns. The results indicated that the silk areas were dyed with greenweed (YS3) or weld (S1b), whereas for wool, greenweed (YW2) was primarily used. Further analytical work using an established analytical method such as HPLC could be deployed for validation as these results differed from the outcomes of the yellow yarns analysis in the MODHT project, which indicated that for the tapestries included in that study, greenweed was used mostly for silk and weld for wool [40]. Furthermore, for the MODHT historic samples, this trend appeared to be most evident in the combination dyed yarns for the production of green or orange colours and not exclusively on the yellow yarns. Additionally, there was a disparity between the number of wool and silk yarns analysed, which might have also influenced this outcome [4].

The results indicated consistency across the three tapestries for the production of the dyes in the green yarns. In the silk areas, green was produced with threads dyed first with weld and then with woad (GS1a); however, threads which were dyed first with woad and then with weld (GS2b) were also detected in two different shades, light and dark. On the wool green areas only, threads dyed first with weld and then woad (GW1) were detected.

In all of the tapestries, oak gall was classified in silk and wool areas, while Alder bark and Alum mordanted threads were detected only in wool.

Black was limited to wool threads and was dyed primarily with BLKW4, which was produced with a combination of iron sulphate and copper sulphate mordant.

The SAM analysis of the HSI images provided accurate mapping of the dyes, reproducing the design of the tapestry in high resolution. Furthermore, the mapping of the dyes potentially revealed information on the original colours of the tapestries. However, on the *Sacrifice of Isaac*, the brown areas were presented as black after the SAM simulation, an effect which requires further investigation.

Finally, the SAM NIR analysis successfully mapped the different materials used to produce the tapestry and provided an estimate of the percentage area coverage for each of them. This method could be deployed for assessing the quality of historic tapestries and possibly provide a tool to monitor changes in their condition over time.

Table 5. Compilation of SAM analysis endmember matching results for the three *Abraham* tapestries.

Weft Fibre	Name	Code	Dyestuff	Mordant
Silk	Red/Brazilwood	RS1a	Brazil wood	Alum
Silk	Red/Brazilwood	RS1b	Brazil wood	Alum
Silk	Red (pink)/Brazilwood with lye	RS1c	Brazil wood	Alum
Silk	Red (dark pink)/Brazilwood with lye	RS1d	Brazil wood	Alum
Silk	Blue light/woad	BS1a	Woad	-
Silk	Blue dark/woad	BS1b	Woad	-
Silk	Green/woad-weld	GS1a	Woad-weld	Alum
Silk	Green light/Weld-woad	GS2b_L	Weld-woad	Alum
Silk	Green dark/Weld-woad	GS2b_D	Weld-woad	Alum
Silk	Yellow/weld	YS1b	Weld	Alum
Silk	Yellow/Greenweed	YS3	Greenweed	Alum
Silk	Black/$FeSO_4$	BlkS1_a	$FeSO_4$	Oak gall
Silk	Black/$FeSO_4$	BlkS1_b	$FeSO_4$	Oak gall
Silk	Oak gall	Oak gall S	-	Oak gall
Wool	Red/Madder	RW1	Madder	Alum
Wool	Red/Madder	RW2	Madder	Oak gall/Alum
Wool	Red/Cochineal	RW4	Cochineal	Alum
Wool	Green/weld-woad	GRW1	Weld/woad	Alum
Wool	Green/woad-weld	GRW2	Woad/weld	Alum
Wool	Yellow/Weld	YW1	Weld	Alum
Wool	Yellow/Greenweed	YW2	Greenweed	alum
Wool	Black/$FeSO_4$	BLKW1	$FeSO_4$	Oak gall
Wool	Black/$FeSO_4$	BLKW2	$FeSO_4$	Oak gall
Wool	Black/FeSO4	BLKW3	$FeSO_4$	Alder bark
Wool	Black/W4, Cu+$FeSO_4$	BLKW4	$FeSO_4$/$CuSO_4$	Oak gall
Wool	Alder bark tannin	Alder W	-	Alder bark
Wool	Alum mordant	Alum W	-	Alum
Wool	Oak Gall mordant	Oak gall W	-	Oak gall

5. Conclusions

This project explored the deployment of HSI in the characterisation and analysis of historic tapestries. A high-resolution ClydeHSI Art Scanner with both a push-broom visible to very near-infrared (VNIR; 400–1000 nm) and near infrared (NIR 900–1700 nm) hyperspectral cameras was used to analyse three of the 16th century Abraham series tapestries in the Great Hall, Hampton Court Palace. The areas analysed on the tapestries ranged from 0.1 m^2 to approximately 2 m^2 and consisted of wool and silk dyed in a range of colours with metal threads also used in large sections. The tapestries were scanned vertically with an overlap of 15% between consecutive strips to facilitate the stitching at the post-processing phase.

The composite hyperspectral reflectance images were initially processed with an unweighted smoothing average before using principal components analysis (PCA) based on their spectral responses, and the design of the tapestry was reproduced in a high-resolution false colour image. Interrogation of these images revealed information on the use of different dyes in faded areas and identified areas of restoration.

Spectral angle mapping (SAM) algorithm was successfully deployed for processing the data further to study the distribution of the materials across the tapestry areas analysed and identify the dyes used for their manufacture. An external library was produced with spectra acquired from the MODHT tapestry model tapestries, (with known dyes and mordants) and used as endmember reference for the spectral matching and characterisation (Appendix A Table A1).

Future work for this ongoing research project will include the development of the mapping of individual dyes and assessing the impact of degradation on the HSI analysis. Furthermore, the deployment of complementary analytical techniques such as HPLC could provide further evidence on the HSI results with a particular focus on the characterisation of the yellow dyestuffs and the identification of brazilwood. Finally, the deployment of XRF analysis could also confirm the mordants used for the dyeing.

Author Contributions: Conceptualisation, C.V.-M.; methodology, C.V.-M., J.R.G. and J.D.; data curation, C.V.-M. writing—original draft preparation, C.V.-M.; writing—review and editing, C.V.-M., K.H. and J.R.G.; visualisation, C.V.-M. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study can be requested by the corresponding author.

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

Appendix A End Member Library

Table A1. MODHT samples images and associated HSI spectra.

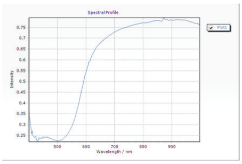
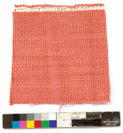
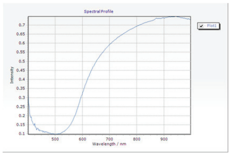
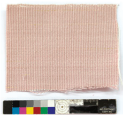
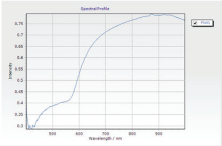
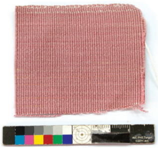
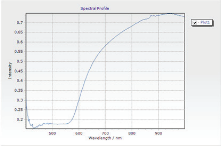
Weft Fiber	Abbreviation	Dyestuff	Mordant	Endmember	Image	HSI
Silk	RS1a	Brazil wood	Alum	⬜		
Silk	RS1b	Brazil wood	Alum	🟥		
Silk	RS1c	Brazil wood	Alum	⬜		
Silk	RS1d	Brazil wood	Alum	🟧		

Table A1. *Cont.*

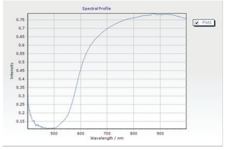
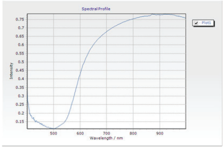
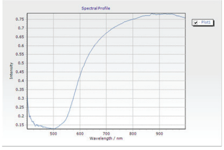
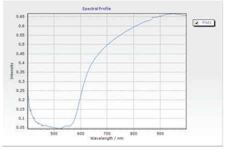
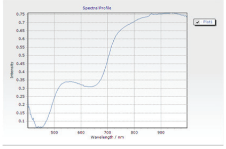
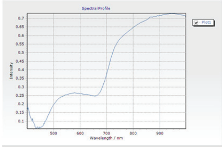
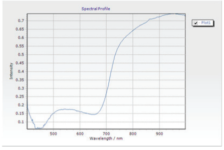
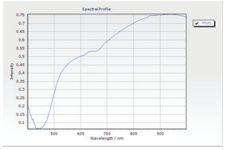
Weft Fiber	Abbreviation	Dyestuff	Mordant	Endmember	Image	HSI
Silk	RS2a	Madder	Alum	🟥		
Silk	RS2b	Madder	Alum	🟥		
Silk	RS2c	Madder	Alum	🟥		
Silk	RS3	Cochineal	Alum	🟥		
Silk	GS1b	Woad/weld	Alum	🟩		
Silk	GS2b_L	Weld/woad	Alum	🟩		
Silk	GS2b_D	Weld/woad	Alum	🟩		
Silk	YS1b	weld	Alum	🟨		

Table A1. *Cont.*

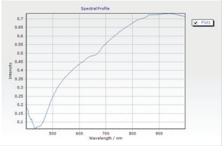
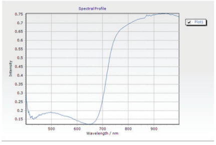
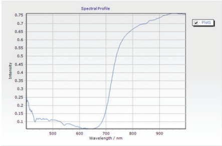
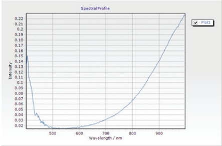
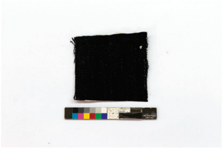
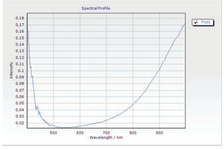
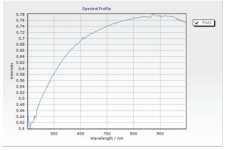
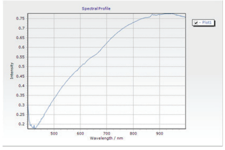
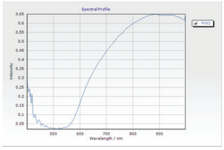
Weft Fiber	Abbreviation	Dyestuff	Mordant	Endmember	Image	HSI
Silk	YS3	Greenweed	Alum	🟨		
Silk	BS1_a	Woad	-	🟦		
Silk	B1_b	Woad	-	🟦		
Silk	Black S1a	$FeSO_4$	Oak g all	⬛		
Silk	Black S1b	$FeSO_4$	Oak gall	⬛		
Silk	CON S	-	-	⬜		
Silk	Oak gall S	-	Oak gall	⬜		
Wool	RW1_wl	Madder	Alum	🟥		

Table A1. *Cont.*

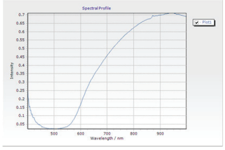
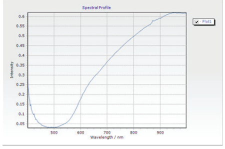
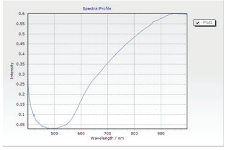
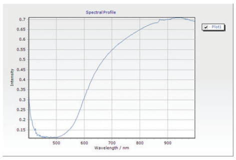
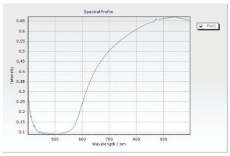
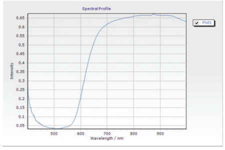
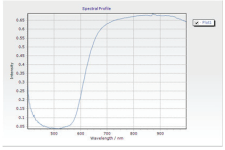
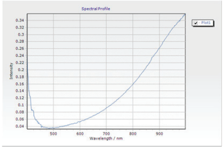
Weft Fiber	Abbreviation	Dyestuff	Mordant	Endmember	Image	HSI
Wool	RW1	Madder	Alum	🟥		
Wool	RW2	Madder	Oak gall/alum	🟥		
Wool	RW2_wl	Madder	Oak gall/alum	🟥		
Wool	RW3	Brazil wood	Alum	🟥		
Wool	RW3L	Brazil wood	Alum	🟥		
Wool	RW4	Cochineal	alum	🟥		
Wool	RW5	Cochineal	alum	🟥		
Wool	BLKW1	$FeSO_4$	Oak gall	⬛		

Table A1. *Cont.*

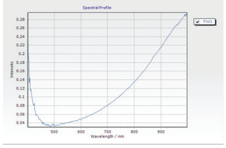
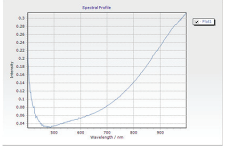
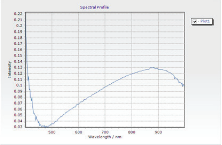
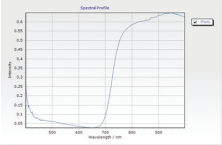
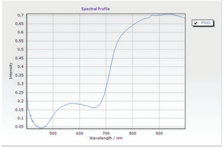
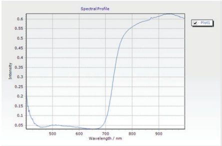
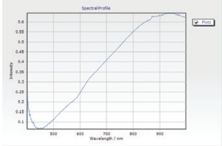
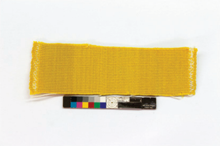
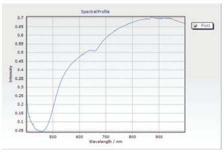
Weft Fiber	Abbreviation	Dyestuff	Mordant	Endmember	Image	HSI
Wool	BLKW2	$FeSO_4$	Oak gall	⬛		
Wool	BLKW3	$FeSO_4$	Alder bark	⬛		
Wool	BLKW4	$FeSO_4/CuSO_4$	Oak gall	⬛		
Wool	BW1	Woad	-	🟦		
Wool	GRW1	Weld/woad	Alum	🟩		
Wool	GRW2	Woad/weld	Alum	🟩		
Wool	Alder W	-	Alder bark	🟧		
Wool	YW1	Weld	Alum	🟨		

Table A1. *Cont.*

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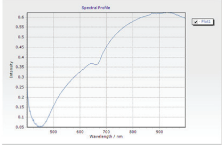
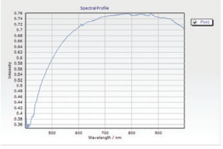
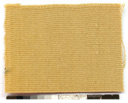
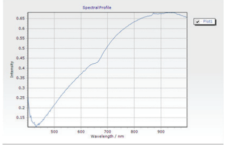
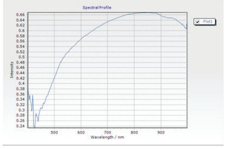
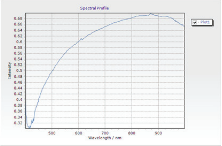
Wool	YW2	Greenweed	alum	🟨		
Wool	Alum W	-	Alum	⬜		
Wool	Oak gall W	-	Oak gall	🟧		
Wool	Wool blank dyed with lye			⬜		
Wool	CON W			⬜		

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Article

Chromatographic Characterization of Archaeological Molluskan Colorants via the Di-Mono Index and Ternary Diagram

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Abstract: One of the main research questions regarding archaeological molluscan purple pigments and dyes is whether it is possible to determine which malacological species produced these colorants. For this determination of the zoological provenance of the pigment, a multicomponent analysis must be performed, which can only be obtained from the HPLC technique—the optimal method for identifying all the detectable colorants in a sample. In order to find any trends in the compositions of the dye components from various species of purple-producing sea snails, a statistical formulation is needed. Though principal component analysis (PCA) is a powerful statistical tool that has been used in the analysis of these components, it is based on an algorithm that combines all the componential values and produces new two-dimensional parameters whereby the individualities of the original dye component values are lost. To maintain the integrity of the dye compositions in the purple pigments, a very simple formulation was first published in 2008 and applied to a limited number of samples. This property is known as DMI (short for Di-Mono Index), and for each sample, it is simply the ratio of the peak area of DBI relative to that of MBI, evaluated at the standard wavelength of 288 nm, which has been used for such peak calculations. Currently, considerably more modern and archaeological pigments have been analyzed via HPLC; thus, in the current study, the DMI has been expanded to characterize these purple pigments. Furthermore, a ternary diagram comprising the blue, violet, and red components that can be found in purple colorants is presented for both modern and archaeological purple pigments from the three Muricidae species known in antiquity to produce purple pigments. This triangular diagram is intuitive, retains the integrity of the original dyes, and is presented here for the first time. Both the DMI and the ternary diagram can discern whether a *Hexaplex trunculus* species or perhaps the *Bolinus brandaris* or *Stramonita haemastoma* species were used to produce the pigment. Further, these two representations can also determine whether the IND-rich or the DBI-rich varieties, or both, of *H. trunculus* were used to produce the purple pigment, either as a paint pigment or as a textile dye.

Keywords: HPLC; indigoids; indirubinoids; dibromoindigo; molluscan purple pigments and dyes; Muricidae; *Hexaplex trunculus*; Di-Mono Index (DMI); ternary diagram

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1. Introduction

1.1. Introducing the Sea Snails

Of all the natural organic and inorganic pigments and dyes—from flora, fauna, and mineralia—used by ancient civilizations [1–3], there is no other prized colorant than "purple" (with all its variegated shades) produced from certain molluscan species. This marine-derived imperial colorant was not only heralded as such in antiquity by Greek and Roman writers, e.g., Homer, Aristotle, Vitruvius, and Pliny the Elder, but even historic, not so-ancient, poets were awed by this molluscan colorant. In the latter case, this wonderment regarding that colorant is uniquely expressed by the famous English poet Robert Browning in his 1855 poem titled "Popularity", who refers to this supreme colorant as the "dye of dyes" [4].

It is well-known that in antiquity, there were three related species of mollusks in the Eastern Mediterranean, from which a purple pigment can be produced, and these sea snails are also found today. This Muricidae family—commonly referred to as Murex sea snails—consists of *Hexaplex trunculus* (also known as *Murex trunculus*), *Bolinus brandaris* (=*Murex b.*), and *Stramonita haemastoma* (=*Purpura h.*). The shells of these mollusks are shown in Figure 1. The chemistry associated with the natural biochemical production of the purple pigment and its components has been published in detail [5–7].

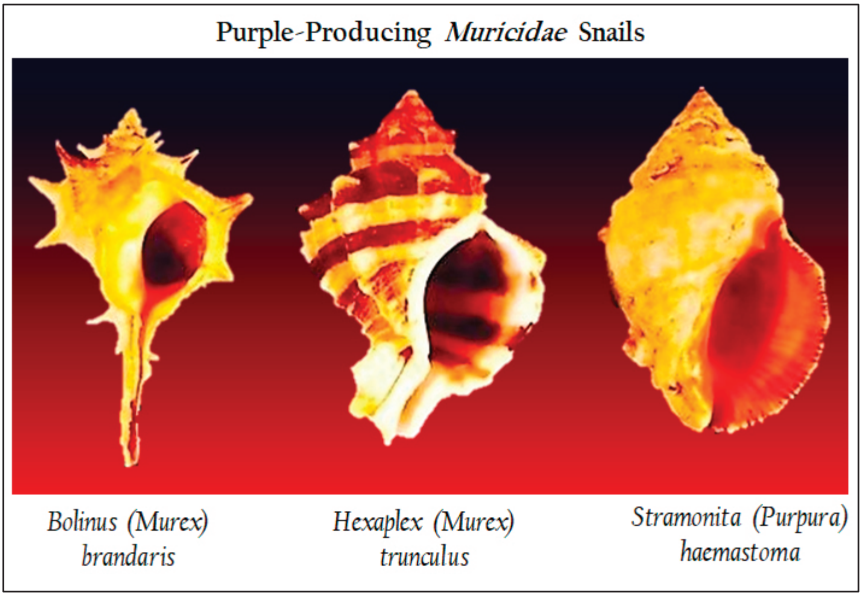

Figure 1. Three of the most common purple-producing Mediterranean molluscan species of the *Muricidae* family.

Much has been written about the historical accounts related to these mollusks, and the most prominent ancient historian and science reporter to have written about them was the 1st century CE Roman naturalist Pliny the Elder (Gaius Plinius Secundus). Writing in his monumental multi-volume work *Naturalis Historia*, he recounted the types of sea snails used for purple pigment production, their biology, the season in which to gather them from the seabed, as well as other relevant information. In his role of reporting on the natural world and its animal inhabitants—and keeping in mind that he was obviously not a chemist or alchemist—he nevertheless accurately recounted the entire process of dyeing with these molluscan pigments. Yet, there are modern authors who have at times misunderstood Pliny's description of the dyeing process. However, if one combines modern chemical principles with his ancient chronicling, it becomes apparent that he correctly described the primary and auxiliary agents—and their processing—that were needed for the reduction and solubilization of the purple pigment [8].

1.2. HPLC Über Alles

As for analyzing the purple pigment and identifying all the detectable colorants in it, the optimal method by far is HPLC (high-performance liquid chromatography). The application of the HPLC method for the analyses of molluscan purple pigments was introduced three decades ago by Jan Wouters and André Verhecken, and they successfully separated four-to-five major components of those pigments [9,10]. With that breakthrough, advancements in HPLC analyses have shown that the purple pigment, especially from the *H. trunculus* species, can consist of about 10 colorants [11]. A typical chromatogram, shown in Figure 2, presents the separation of these components. The dyes constitute the following three chemical groups:

- Indigoids: blue indigo (IND), violet 6-monobromoindigo (MBI), reddish-purple 6,6′-dibromoindigo (DBI):
- Indirubinoids (all reddish-crimson): indirubin (INR), 6-monobromoindirubin (6MBIR), 6′-monobromoindirubin (6′MBIR), 6,6′-dibromoindirubin (DBIR);
- Isatinoids (yellowish): isatin (IS), 6-bromoisatin (6BIS).

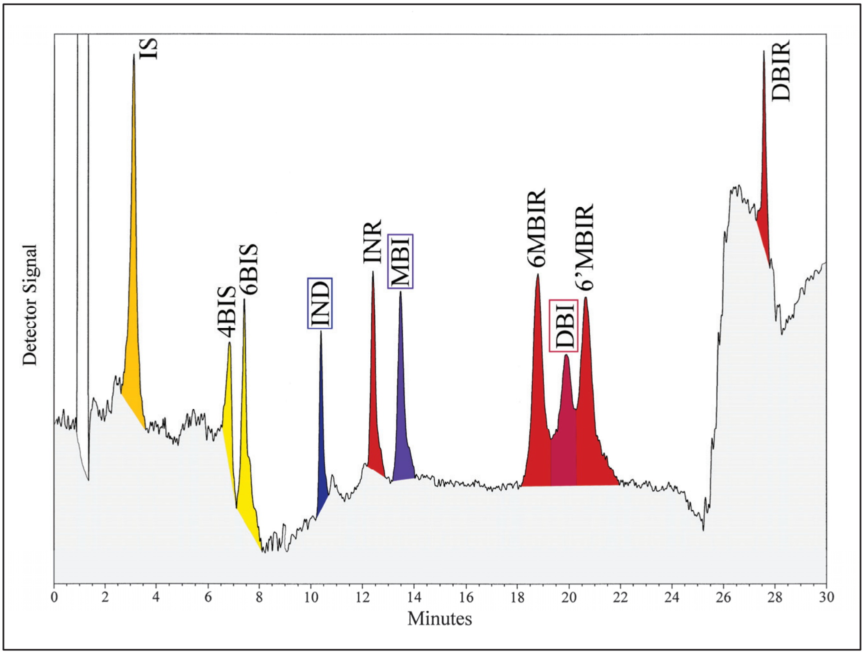

Figure 2. HPLC chromatogram of the various indigoids, indirubinoids, and isatinoids (with their representative colors), which may be present in a molluscan purple pigment. Highlighted (in rectangles) are the three main indigoid components present in pigments extracted from *H. trunculus* species.

- The accompanying UV/Vis spectra of these molluscan colorants, as determined by the PDA (photo-diode array) detector of the HPLC, as well as their molecular structures, are shown in Figure 3. The spectra show that each homologous series of dyes has a common visible wavelength at maximum absorption, λ_{max}, and for the isatinoids, the wavelength is around 415 nm, the indigoids' is about 605 nm, and the indirubinoids' is approximately 540 nm. It is important to note that the λ_{max} values shown in the UV/Vis absorption spectra are specific for the solvent system in which the dye is solubilized. However, dyes dissolved in other solvents will nevertheless typically yield wavelengths that are close to these values.

Undoubtedly, the most efficient methods for analyzing and identifying relatively non-volatile organic components as whole non-dissociated molecules in a multi-component mixture—such as in the case of the purple pigment—is HPLC. Though GC (gas chromatography) has been used in analyzing molluscan pigments [12], the very high oven temperatures needed for gasifying the components may cause their decomposition, and thus the integrity of the whole molecule may be lost in its identification. Even if only a peripheral fragment has broken away from the parent molecule, this may damage the viability of the analysis itself. For example, the brominated indigoids that constitute the purple pigments from *H. trunculus* are indigo with one bromine atom (MBI) and the doubly brominated indigo (DBI). In order to obtain an accurate chromatic fingerprinting of these pigments, it is vital that all the original colorant molecules in the pigment remain intact during the analysis. If an analytic method decomposes either DBI or MBI, then artificial amounts of their decomposition products would be formed. If that occurs, then the debromination of MBI would yield an artificial increase in indigo (IND); similarly, if DBI were to decompose during an analysis, then its quantity would be falsely lower. (The quantity of MBI may not change drastically because it would be both formed from DBI and decomposed to IND.) This type of analysis would harm the ability to determine the various colorants in the original sample.

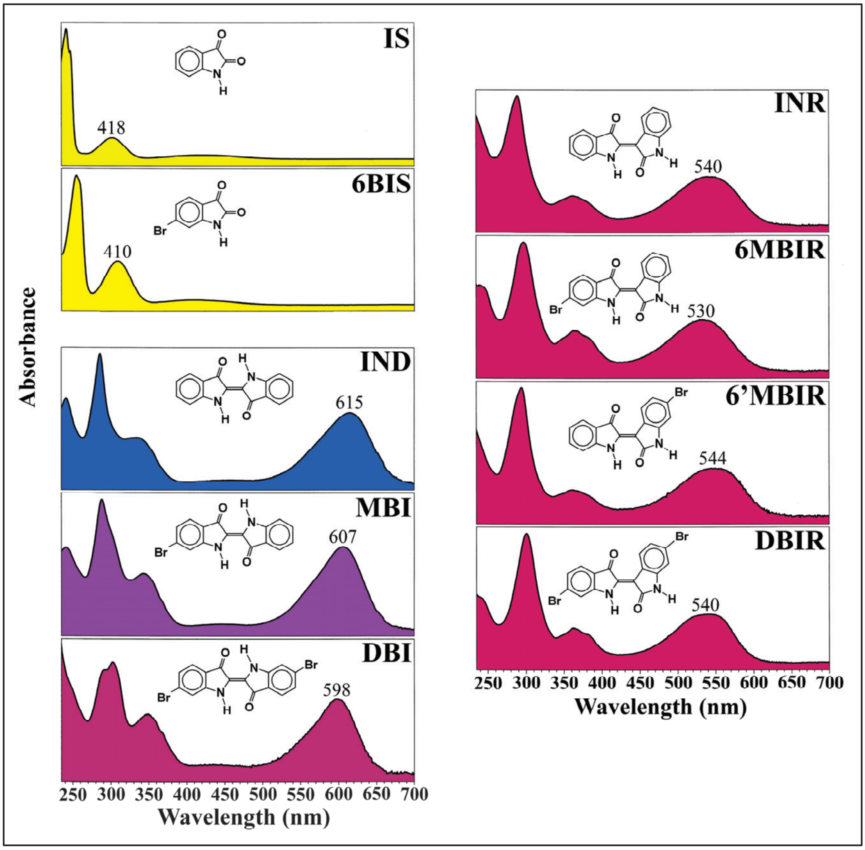

Figure 3. UV/Vis spectra and molecular structures of the isatinoids, indigoids, and indirubinoids, showing the visible wavelengths at maximum absorption in the methanol/water/H_3PO_4 eluent system.

It is important to emphasize the superb detection powers of HPLC to easily "see the invisible" even on the nanogram—or lower—level. Though the HPLC technique is a "destructive" method, it can be described as actually being a "nano-destructive" scheme. As an example of the latter, a successful analysis of a single one- or two-centimeter fiber removed from a yarn of an archaeological textile has been performed via HPLC [13]. This single fiber was effectively invisible to the "naked eye", but can only be clearly seen via a microscope. With that analysis, a clear separation of four dye components on a single fiber was carried out, with relatively strong HPLC peak signals in the chromatogram.

Analytic methods based on spectrometric techniques have also been used to study dyes, in general, and the purple pigment. These methods include Raman, mass spectrometry (MS) without first chromatographically separating the dyes, FTIR, and UV/Vis spectrometry (in the old pioneering days of analysis). However, all of these analytical tools are spectrometric, and the outcome of such an analysis would produce one graph—a spectrum—that is a combination of the spectra of all the components in that pigment. While these techniques may identify the main colorant—or two—in a mixture, spectrometry is limited in that it produces an "overlap of information". Chromatography yields a "separation of information", which provides the identification of all the detectable colorants in a pigment or dyeing. This "separation" yields a "chromatic fingerprint" and is essential in trying to identify the biological provenance of the dyestuff, whether from flora or fauna, and from what specific species [14].

1.3. Statistical Characterizations of Molluscan Purple

The separating powers of multicomponent HPLC analyses may allow us to determine which malacological species produced the various archaeological pigments and dyes. Towards this end, we need a statistical characterization of the pigments that have been properly analyzed via HPLC. One statistical algorithm for such a characterization is principal component analysis (PCA), and it has been used in the analysis of these components [15,16]. However, this tool has the feeling of a "black box" that incorporates the quantities of the various components, condenses and digests them mathematically, and churns them out in a way that the individuality of the components is lost.

There is a very simple statistical formulation for characterizing molluscan pigments, and it incorporates only two dyes. It was first published in 2008 [17] for a very limited number of samples and has now been expanded to include the results of more recent analyses of archaeological purples. This parameter is known as the Di-Mono Index and is presented in this study to identify the various species of purple-producing mollusks.

Another representation of a statistical characterization of the purple pigments, which maintains the individuality of as many dyes as possible, is the ternary (or triangular) diagram. This graphical depiction best characterizes the dyes so as to allow maximum distinctions among all the species. This intuitive representation would allow for the identification of the zoological provenance of these pigments. This ternary diagram for the molluscan pigments is presented here for the first time.

2. Materials and Methods

2.1. HPLC: Sample Preparation and Analysis

The sample preparation and the chromatographic elution system used has been previously published [17] and is summarized here. Extraction of the pigment or dye was performed in a glass vial (and not in a plastic one, as the pigment can adhere to the plastic when heated to a high temperature). The duration of the extraction was 5 min via 200–400 µL DMSO at 100–150 °C, depending on the size of the sample, and in subdued light to prevent the artificial photo-debromination of the components. In order to perform a fully quantitative extraction, no residual color must remain on the sample; thus, additional fresh quantities of DMSO may have been needed for the extraction, and all the extracted solutions were combined.

The resulting hot extracted mixture was immediately filtered in a 0.2- or 0.45-µ microspin polypropylene centrifuge tube with nylon filter for 3 min, and immediately injected into the HPLC. In these analyses, the reverse-phase Waters HPLC system consisted of a 3.0 × 150 mm C_{18} symmetry column as the stationary phase, and the ternary eluent system consisted of methanol, water, and 5% H_3PO_4 as the mobile phase.

2.2. Materials Analyzed

The samples analyzed, and their results, consisted of modern and archaeological purple pigments and textile dyes, performed for this study and by other researchers, and are described in Tables 1–3 below in the Results and Discussion section. For the current study, a number of Roman Period archaeological textiles found in the Judean Desert, Israel, have been analyzed and reported in Table 3.

3. Comparison Problems

3.1. Problems in Comparing Results from Different Researchers

In order to build as full a picture as possible regarding the characterization of archaeological molluscan colorants, the analytical results of all laboratories need to be combined. However, there are inherent problems in comparing and integrating results from different researchers. Firstly, for reasons described above, only HPLC results will be considered, as this is the only method through which the multi-components in the sample can be determined. Comparing analytical results from different researchers who used different extraction methods and conditions is risky, and it is important to recognize the potential problems that may be encountered, which are detailed below.

3.1.1. Extraction in Minimal Light

Extraction of the dye or pigment should be performed under subdued lighting conditions so that there is just enough light to see the experimental setup. Performing an extraction in a well-lit laboratory room will, at least partially, photo-debrominate the dissolved colorants; thus, the results of dye analyses will be artificially skewed to less DBI and more IND, as mentioned above regarding the limitations of GC analyses. (The quantity of MBI may change only slightly as it is both formed from the debromination of DBI and decomposed when irradiated.) Analysts have not, in general, designated whether their sample extractions were performed in subdued light and this can be a problem when using their results.

3.1.2. Maximizing Extraction via the Optimal Solvent, Temperature, and Time

Different analysts have used different solvents for extracting the pigments [18]. Firstly, in any system, the solubility of a solute will vary when attempting to dissolve it in different solvents. The components in the purple pigment are no exception. The various solubilities of the purple's components have been studied and published [15]. A further factor in the ability of a solvent to dissolve a sample is the temperature of the mixture and the duration of the extraction process. Thus, these three factors (choice of solvent, temperature, and time) may produce different results for the composition of the colorant when analyzing the same sample, if at least one of these three factors is different among the researchers.

Examples of the effective solvents that have been used for the extraction–dissolution of the indigoids and related compounds in the pigment, and the corresponding temperatures and times, include the following:

- Pyridine: 100 °C [9,10];
- DMF: 150 °C, 3 min [19]; 80 °C, 60 min [20]
- DMSO: 100–150 °C, 5 min [17]; 80 °C, 15–30 min [15]

Though the indigoids have good solubilities in all of these hot solvents, the most effective solvent in dissolving the most stubborn of the indigoids—DBI—is DMSO at high temperatures of 100–150 °C, depending on the quantity of the sample. Even when the extraction is performed in subdued light, as mentioned above, no debromination occurs even at 150 °C as analyzed using HPLC.

It is important to mention that the acidic-methanolic system for extracting mordant dyes is poor in extracting purple's components. What is a good extracting solvent system for mordant dyes is not necessarily effective for vat dyes. In the typical aluminum–dye complex that is formed in naturally dyed textiles, the acid is needed in order to break the metal–dye bond, and the organic solvent (methanol) is then needed for dissolving the dye that was set free. However, the solubilities of the indigoids in that acid–methanol system are very low, where the solubilities decrease from IND to MBI to DBI. Thus, when using that methanol–acid system, the artificial compositions will show relatively high values for IND, lower than actual for MBI, and much lower for DBI. Additionally, if any indirubin and related brominated derivatives are present, and though their solubilities in methanol are relatively low but higher than the indigoids, then the reported indirubinoid content would also be artificially skewed higher. Thus, the results obtained from the acid–methanol extracting system were not incorporated in the current study.

3.1.3. Immediate Filtration and Injection into the HPLC

As soon as the indigoids are extracted into the solvent, the hot mixture should be immediately filtered and injected into the HPLC, so as to preserve the indigoids in the solution. The automation that is found in modern HPLC/UPLC instruments, with the sample tray able to contain tens of sample vials to be tested, should not be employed for analyzing indigoids. Experiments conducted in this laboratory have shown that if, e.g., DBI is dissolved in hot DMSO and left for extended periods of time, then that dye begins to precipitate out of the solution; thus, an analysis of the solution will not produce the correct compositions. Additionally, even in the dark, the indigoids will eventually decompose, at least in part, to yellowish isatinoids. This precipitation phenomenon is probably due to the occurrence of an association between the solute particles as they can form intermolecular hydrogen bonds among themselves and thus produce larger, heavier, molecules—aggregates or agglomerates. These associated complexes and the low room temperature can cause the indigoids to precipitate out of the solution.

3.1.4. HPLC Elution Methods

Different stationary and mobile phases, as well as elution methods, have been utilized to chromatographically separate the indigoids in the purple pigment. The nature of the eluents used affects the solubilities of the components in the column's stationary phase. Thus, as the absorption of light of the HPLC detector is measured for each eluting component, different eluents may produce different absorbances as the solutions are different. Even if two researchers use the same mobile phase solvents, but their time-dependent gradient elution methods are different, the compositions of the mobile phases may be different. Thus, using different stationary and mobile phases and different changes of the volumes of the eluents with time may yield different results for the compositions of the purple colorant among the various researchers.

3.1.5. HPLC Detection Wavelength

When comparing the results of the HPLC analyses on a set of dyes, the same wavelength of detection of the dye component must be used throughout since different wavelengths will yield different absorptions of light in the UV or visible regions. The wavelength chosen is the one at which all of the investigated dyes have significant light absorptions; thus, these absorptions may be used for comparison purposes. The current standard of absorbance measurements for indigoids is 288 nm, which was first used by Wouters and Verhecken [9,10] and has been adopted by others. If the measured ability of each component to absorb light at a given wavelength is known—and this is known as absorptivity (a) or extinction coefficient (ε)—then the actual mass of each dye component can be ascertained. However, not all of the researchers of this purple pigment have used the same wavelength in their measurements; thus, initially, these values cannot be used for comparing one set of measurements at one wavelength with another set of results at a different wavelength. However, this apparent problem may be overcome by knowing the ratio of absorbances at the different wavelengths and then re-calculating the absorbance at the desired wavelength.

When measuring the absorbance of each indigoid, it may be best not to first measure its absorbance at the UV wavelength of choice (288 nm), but rather at the visible wavelength at which the dye in question has its maximum absorbance, λ_{max}. Afterwards, knowing the ratio of absorbances at the standard UV wavelength and the visible wavelength, a calculation of the absorbance at 288 nm can be performed. This type of re-calculation was previously performed [17] and was also conducted in the current study. The reasoning for measuring at the visible wavelength first is that an archaeological sample has impurities from the ground in which it was excavated, and some of these non-colorants may absorb UV light at or approximately the standard UV wavelength. Thus, directly measuring the peak area at the time of the eluting dye at the standard UV wavelength, may partially mask its actual peak, thereby reducing its peak purity and possibly incorporating into it the absorbance of not only the dye, but also of the impurities, which would produce a false measurement.

4. Results and Discussion

4.1. Modern and Archaeological Purples

Considering all of the limitations and concerns about combining the analytical HPLC results from various analysts, as discussed above, it is, nevertheless, expected that all the analytical results would not deviate far from their true values in order to obtain an overall pattern for the dye components. The results of different researchers were also incorporated into the PCA studies mentioned above.

The following tables show the integrated peak area values as percentages for the five main indigoid and indirubinoid components that can be found in modern and archaeological pigments produced from the purple-producing sea snails. These data are all based on an effective extraction system and the HPLC methodology discussed above. A form of these tables was initially determined by Karapanagiotis et al. [15,16,21] and has now been expanded in the current work to include more samples and information.

The following sample descriptions appear in the tables below: the geographical region where the pigment or dye was produced; a description of the manner in which the colorant was obtained; the solvent used for sample preparation as well as the temperature and heating duration; the HPLC-produced integrated peak areas (as %) of the five main components evaluated at 288 nm; and the original literature reference that discusses these samples in detail. For completeness purposes, each colorant's DMI value, which is discussed below, is also shown in the tables.

Table 1 outlines the information regarding purple pigments produced from modern *H. trunculus* sea snails from different researchers, and each sample was given a "T" number in the tables that were previously established, as mentioned above [15,16,21]. Similarly, Table 2 shows the relevant data regarding modern *B. brandaris* and *S. haemastoma* pigments, and these samples are given "B" and "H" numbers, respectively.

Table 3 lists the various archaeological materials—pigments and textile dyes—that have been analyzed. These historic items span parts of the globe from the Aegean Sea to the Mediterranean and the Middle East to Siberia and England, and are dated from the 17th century BCE up to about only a century ago.

Table 1. Relative dye components (calculated at 288 nm as % peak areas via the HPLC-PDA detector) of modern *Hexaplex trunculus* colorants.

Sample	Region	Description	Solvent Temp., Time *	Dye Components					DMI **	Reference
				IND	INR	MBI	DBI	DBIR		
T1	Carthage, Tunisia	Shells crushed and exposed to air and sunlight	DMSO 80, 15	62.90	1.20	32.10	3.70	0.10	0.12	[15]
T2	Croatia	Snails removed from water, exuding pigment when expiring	DMSO 80, 15	49.80	4.40	37.60	7.10	1.10	0.19	[15]
T3	Tunisia	Tunisia "red"; gland excised in the dark	DMSO 80, 15	35.10	0.40	49.70	14.40	0.40	0.29	[15]
T4	Tunisia	Tunisia "blue": T3 pigment in boiling water	DMSO 80, 15	54.00	1.50	39.40	4.90	0.20	0.12	[15]
T5	Tarragona, Spain	Stained, non-vatted, cotton	Pyridine 100, ?	56.00	0.00	37.00	7.00	0.00	0.19	[9,10]
T6	Tarragona, Spain	Vat-dyed wool	Pyridine 100, ?	53.00	14.00	33.00	0.00	0.00	0.00	[9,10]
T7	Akhziv, Israel	Pigment extracted from glands at the seashore	DMF 100, 5	4.05	0.00	17.79	60.00	18.16	3.37	[17,22]
T8	Saronikos, Greece	Glands exposed to 6 h sunlight, extracting 1 h with DMF, and dried	DMF 80, 15	35.20	8.10	30.50	15.80	10.40	0.52	[15,20]
T9	Akhziv, Israel	Same as T7	DMSO 100, 5	0.35	0.00	7.41	68.39	23.85	9.23	[17]
T10	Spain	Pigment	DMSO 100, 5	40.72	3.34	41.33	4.25	10.36	0.10	[17]
T11	France	Pigment on talc substrate	DMSO room, 10	10.30	2.90	44.40	36.80	5.60	0.83	[23]
T12	Hermione, Greece	Pigment	DMF ?, ?	27.80	7.50	37.40	23.20	4.10	0.62	[15]
T13	Thessaloniki, Greece	Excised glands exposed to direct sunlight for 3 h	DMSO 80, 30	7.3	2.2	30.4	22.9	37.2	0.75	[21]

* A question mark appears if the temperature and /or duration of heating were not reported in the publication. ** A blue color for the DMI value is indicative of an IND-rich *H. trunculus* pigment, and a red color represents a DBI-rich *H. trunculus* pigment; see text for the detailed discussions.

Table 2. Relative dye components (calculated at 288 nm as % peak areas via the HPLC-PDA detector) of modern *Bolinus brandaris* and *Stramonita haemastoma* colorants.

Sample	Region	Description	Solvent Temp., Time	Dye Components					DMI	Reference
				IND	INR	MBI	DBI	DBIR		
				Bolinus brandaris						
B1	Tarragona, Spain	Sample was stained cotton (not vat)	Pyridine 100, ?	0.00	0.00	0.00	85.00	15.00	∞	[9,10]
B2	Tarragona, Spain	Sample was dyed wool (vat)	Pyridine 100, ?	0.00	0.00	6.00	81.00	13.00	13.5	[9,10]
B3	Saronikos, Greece	Glands exposed to 6 h sunlight, extracting 1 h with DMF, and dried	DMF 80, 15	0.001	0.00	1.60	97.20	1.20	60.8	[15,20]
B4	Fiumicino, Italy	Pigment	DMSO 100, 5	0.00	0.00	1.36	94.88	3.76	69.8	[17]
B5	Thera, Greece	Glands exposed to direct sunlight for 3 h	DMSO 80, 30	2.00	0.50	1.80	79.30	16.40	44.1	[21,24]
				Stramonita haemastoma						
H1	Tarragona, Spain	Stained, not vatted, cotton	Pyridine 100, ?	0.00	0.00	3.00	91.00	6.00	30.3	[9,10]
H2	Tarragona, Spain	Dyed, vatted, wool	Pyridine 100, ?	0.00	0.00	3.00	91.00	6.00	30.3	[9,10]
H3	Palmahim, Israel	Pigment extracted at seashore	DMSO 100, 5	0.00	0.00	0.86	85.48	13.66	99.4	[17]

Table 3. Relative dye components (calculated at 288 nm as % peak areas via the HPLC-PDA detector) of archaeological colorants. All extractions performed in DMSO.

Sample	Region	Description	Period	Dye Components					DMI	Reference
				IND	INR	MBI	DBI	DBIR		
Ak1 *	Akrotiri	Lump of purple pigment	17th c. BCE	1.10	0.00	20.10	71.80	7.00	3.57	[15]
Ak2 *	Akrotiri	Purple pigment from wall painting		1.70	0.00	18.80	77.60	1.90	4.13	[15]
Ak3 *	Akrotiri	Purple pigment in New Pillar Pit		3.20	0.00	27.10	65.90	3.80	2.43	[15]
Tr *	Trianda	Purple pigment		2.50	0.00	24.40	66.20	6.90	2.71	[15]
Ra *	Raos	Purple pigment from wall painting		1.60	0.00	15.50	77.30	5.60	4.99	[15]
E1 *	Greece	Epitaphios textile, Benaki Museum	Byzantine14th c. CE	48.60	0.00	25.90	25.00	0.50	0.97	[15]
E2 *	Greece			48.00	0.40	25.40	25.60	0.60	1.01	[15]
DsP *	Daskyleion, Turkey	Painted decoration on burial couch	5th c. BCE	21.3	0.1	31.4	8.8	38.4	0.28	[21]
DsT *		Textile from the burial site		14.0	0.1	42.0	12.8	31.1	0.30	[21]
Ro *	Thessaloniki	Purple fabric from sarcophagus	3rd c. CE	2.50	0.00	32.70	58.30	6.50	1.78	[16]
Da **	Iran	Pigment from painted stone jar	5th c. BCE	0.19	0.00	14.84	82.61	2.36	5.57	[17]
K1 ***	Egypt	Polychrome textile in Katoen Natie, Antwerp	5th c. CE	50.50	0.00	35.10	13.70	0.70	0.39	[13]
K2 ***	Egypt			28.98	0.00	42.48	26.88	1.66	0.63	[13]
K3 ***	Egypt			2.36	0.00	53.48	43.02	1.14	0.80	[13]
J1 **	Judean Desert, Israel	Various purple textiles from Ancient Israel	1st c. BCE	11.23	0.08	36.05	50.62	2.02	1.40	Herein
J2 **			1st c. BCE—1st c. CE	33.07	0.07	48.15	17.89	0.82	0.37	Herein
J3 **				22.01	0.34	28.19	49.47	0.00	1.76	Herein
J4 **				19.35	0.25	45.53	34.87	0.00	0.77	Herein
J5 **				11.76	0.00	40.28	47.97	0.00	1.19	Herein
J6 **				34.19	0.00	30.68	33.84	1.29	1.10	Herein
J7 **				3.87	2.54	46.61	46.99	0.00	1.01	Herein
J8 **			2nd c. CE	89.00	0.00	10.00	1.00	0.00	0.10	Herein
J9 **				90.40	0.00	9.10	0.50	0.00	0.05	Herein
J10 **				56.16	0.00	35.56	8.28	0.00	0.23	Herein
P0 **	Siberia	Pazyryk polychromic saddle cloth	4th c. BCE	6.7	0.00	44.6	48.6	0.00	1.09	Herein
P1 **	Siberia			26.1	0.00	56.4	17.5	0.00	0.31	Herein
P2 **	Siberia			30.9	0.00	51.49	17.6	0.00	0.34	Herein
P3 **	Siberia			15.9	0.00	44.9	39.2	0.00	0.87	Herein
L **	Leeds, UK	Purple-dyed cotton of C.S. Bedford	≥1910 CE	12.00	0.00	1.00	87.00	0.00	87.00	[25]

* DMSO extraction at 80 °C for 15 min. ** DMSO extraction at 100 °C, 5 min. *** DMSO extraction at 150 °C, 5 min.

4.2. Di-Mono Index

In order to classify all the malacological pigments, and based on that categorization, be able to determine the zoological provenance of the purple pigment, a simple predictive index was developed. This indicator is known as the Di-Mono Index (DMI), and for each sample, it is the ratio of the peak area of DBI relative to that of MBI, measured at the standard 288 nm wavelength:

$$\mathrm{DMI} = \mathrm{A(DBI)/A(MBI)} \ @ \ 288 \ \mathrm{nm}$$

The reason that IND, which is found in *H. trunculus* pigments, was not chosen for this property is because one cannot rule out the fact that the indigo may not have solely originated from a molluscan source but that a plant-based indigo was added. It is especially important to emphasize that there have been dyeings that were found to be double-dyed with a molluscan source and either madder, a red-scale insect, and, perhaps, even plant indigo.

In the three tables, the DMI values are also presented. From the values of Table 1, it could be discerned that there is a difference among *H. trunculus* snails, and that some pigments have very low DMI values and others have higher numbers. On the other hand, Table 2 shows that the non-*H. trunculus* snails have very high values.

Figure 4 shows the DMI values for modern pigments produced from *H. trunculus* obtained from different geographical regions (listed in Table 1). It is apparent that for *H. trunculus* snails, the IND-rich (i.e., DBI-poor) bluish or violet pigments have a DMI of up to about 0.6, whereas the DBI-rich reddish pigments have DMI values from about 0.8 to 9.

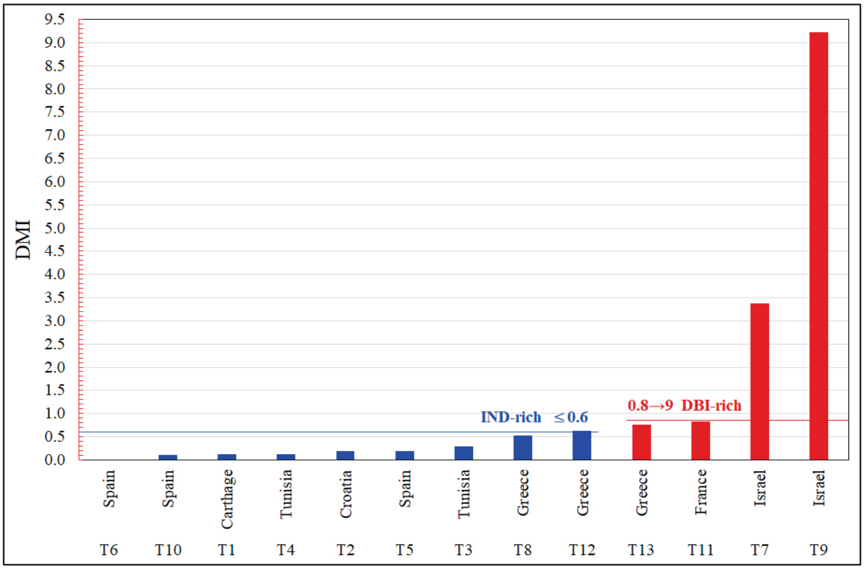

Figure 4. DMI values for modern *H. trunculus* from different geographical regions.

The DMI values for purple pigments from the non-*trunculus* Mediterranean snails—*B. brandaris* and *S. haemastoma*—are shown in Figure 5.

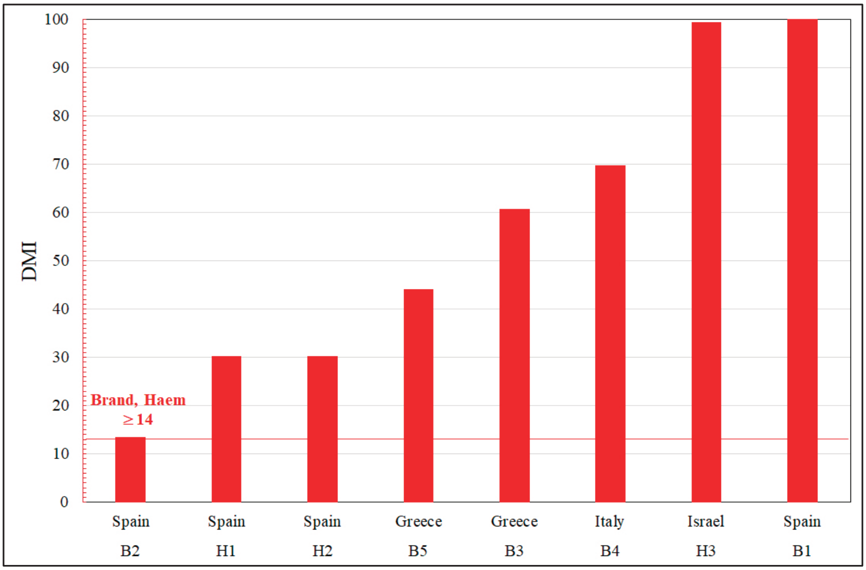

Figure 5. DMI values for modern *B. brandaris* (B) and *S. haemastoma* (H) from different geographical regions.

The DMI values shown in Figure 5 are very high, significantly higher than even the DBI-rich *H. trunculus* snails. However, as the *B. brandaris* and *S. haemastoma* share these very high DMI values, it is not possible to differentiate between the pigments from these two species. These elevated values can be simply explained by the special nature of the MBI component, whose properties have been studied [26]. The very high DMI values for non-*trunculus* snail pigments are due to their very low and even negligible quantities of MBI in their pigments, whereas, in general, all *trunculus*-based pigments—whether reddish- or bluish-purple—have significant amounts of MBI [27]. From Figure 5 and Table 2, it is observed that when using the optimal extracting solvent (DMSO) for these analyses, the pigments from non-*trunculus* snails have DMI values greater than 40, which is nearly five times the highest value for the DBI-rich *trunculus* pigment with the highest DMI value.

Except for one special case of a historic century-old dyeing from Leeds (UK), which was dyed with non-*trunculus* snails off the African coast [25], all the archaeological samples reported in Table 3 have DMI values of less than 6. This is indicative of *H. trunculus* pigments as depicted in Figure 4. Thus, based on the DMI property alone, it could be inferred that the archaeological samples were produced from *H. trunculus* snails that are either IND-rich (with DMI < 0.6) or DBI-rich (DMI between 0.8–9). It is, of course, possible that both types of *H. trunculus* were mixed, or even that some non-*trunculus* snails were used as red-color additives. However, most probably, the *H. trunculus* was always used.

4.3. Ternary Diagram

The ternary diagram (also known as a triangular diagram) incorporating the results of the HPLC analyses on modern and archaeological samples is depicted in Figure 6.

The ternary diagram is an aesthetic visual method of presenting multicomponent data in a graphical manner. Ternary or triangular diagrams were first used in the mid-18th century [28] and have become a standard method of data display today for samples that contain at least three components or condensed into three. Numerous examples are found of the use of ternary diagrams in many areas of science related to archaeological or modern samples in, e.g., metallurgy and geology [29–31], physical chemistry and material science [32–34], and botany and zoology [35–37].

Though it is represented in two-dimensional space, the ternary diagram maintains the identities of all the main original dyes and their colors, blue (IND), violet (MBI), and reds.

In the triangular chart, each apex represents 100% of the corresponding dye, and the opposite base designates 0%. In the diagram, IND and MBI are denoted as such, and the third coordinate, labelled "reds", includes the sum of all the main dye components that yield reddish colors, specifically, DBI, DBIR, and INR. Thus, the apex at the top represents 100% IND, the apex at the bottom left designates 100% MBI, and the apex at the bottom right represents 100% "reds". All the various colors from the five main components that could be present in molluscan purple pigments are represented in this diagram, which maintains the individual original identities of the dyes.

The ternary diagram shows that the IND-rich *H. trunculus* pigments are clustered in the middle-to-upper left of the chart within a semi-oval (also known mathematically as a semi-stadium). This positioning is as expected for these indigo-rich and DBI-poor pigments. The chart also indicates that the DMI values for this semi-oval group is ≤ 0.6, as discussed in the tables above. The other variety, the DBI-rich *H. trunculus* species, are grouped at the bottom right within a shoe-shape arrangement, with DMI values ranging from 0.8–9. The other Muricidae sea snails, *B. brandaris* and *S. haemastoma*, are compressed to occupy a miniscule area at the extreme bottom right, as expected, for these pigments that are even more red than the DBI-rich *H. trunculus* species. Their DMI values, as also previously noted, are ≥ 14, and the optimal DMSO extractions > 40.

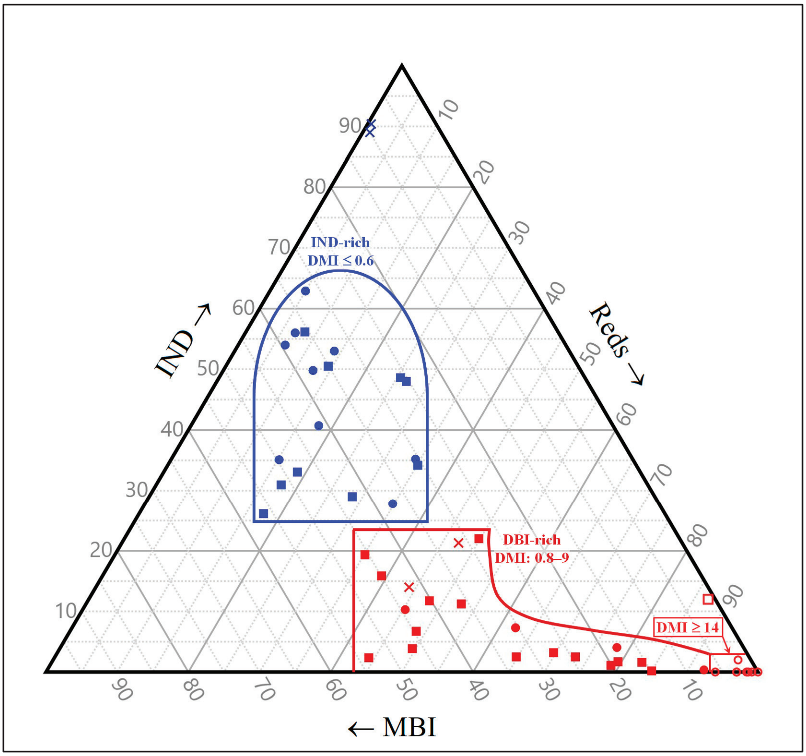

Figure 6. Ternary diagram showing the relative dye compositions (as % peak areas in the HPLC chromatogram at 288 nm) of pigments produced from modern and archaeological Muricidae sea snail species. The "reds" axis and apex represent the sum of all the main reddish components (DBI, DBIR, INR). The open red circles at the extreme bottom right represent modern *B. brandaris* and *S. haemastoma* purples; the closed circles represent modern *H. trunculus* pigments (blue for IND-rich and red for DBI-rich pigments). The squares and Xs represent various archaeological samples.

The ternary diagram shown in Figure 6 also includes the various archaeological purple pigments and dyes. With very few exceptions, all the archaeological colorants appear within the semi-oval or shoe-shaped areas, and no archaeological pigment is present in the small shape to the right of the tip of the "shoe", which is inhabited by the *B. brandaris* and *S. haemastoma* pigments. This indicates that all archaeological molluscan purples were probably produced from *H. trunculus* species, either the IND-rich or DBI-rich varieties. The red-only non-*H. trunculus* snails may have been added to the DBI-rich *H. trunculus* pigments to produce even redder dyeings. It is important to mention that the archaeological pigments represented by the points present at the borders between the semi-oval and the shoe shape could have been produced from a combination of the two varieties of *H. trunculus* snails.

It is important to note how the two statistical formulations presented in this paper complement each other to determine the zoological provenance of a molluscan pigment. For example, at the tip of the "shoe" in the ternary diagram lies pigment T9 (a DBI-rich *trunculus*), which borders B2 (*brandaris*); thus, it seems that they are nearly clustered together. However, their DMI values are significantly different: the *trunculus* pigment's DMI value is about 9 and the *brandaris* is 14.

5. Conclusions

The presence of any brominated dye in a colorant automatically indicates that the source of this pigment or dye is malacological, since only sea snails can produce that kind of colorant. HPLC analyses of various modern and archaeological molluscan pigments have shown that *H. trunculus* snails are unique, different from all other purple-producing snails from all of the world’s waters. The pigments from all purple-producing sea snails contain DBI—this is the common dye of all molluscan purple pigments. However, all non-*H. trunculus* mollusks produce mainly DBI; thus, their purple pigments are always reddish. The singularity of *H. trunculus* is that its pigments contain all three indigoids (as well as indirubinoids): DBI (as all do), MBI, and IND. This major point about the exclusivity of *H. trunculus* snails is that they alone contain a significant amount of MBI, which is what distinctly separates them from all other species, and is observed in their DMI values.

Further, it was found that within the *H. trunculus* species, there are two varieties—maybe even subspecies—where one type produces reddish-purple pigments and another produces bluish-purple (violet) pigments. The *H. trunculus* snails producing reddish-purple pigments are DBI-rich, more than IND; however, these pigments are not as reddish as the pigments from non-*H. trunculus* snails, which mostly have DBI in their pigment. The other variety of *H. trunculus* produces bluish-purple or violet pigments because of the overwhelming amount of IND in the pigment, and they are IND-rich. Both types of pigments are termed the generic “purple”, which is not a pure color but a mixture of red and blue. A schematic summary of the differences among the sea snails is depicted in Figure 7. While the *H. trunculus* has probably always been used in Mediterranean pigments, the other snails were also employed, not alone but as color additives, if desired, to produce even redder dyeings than those obtained from the DBI-rich *H. trunculus*.

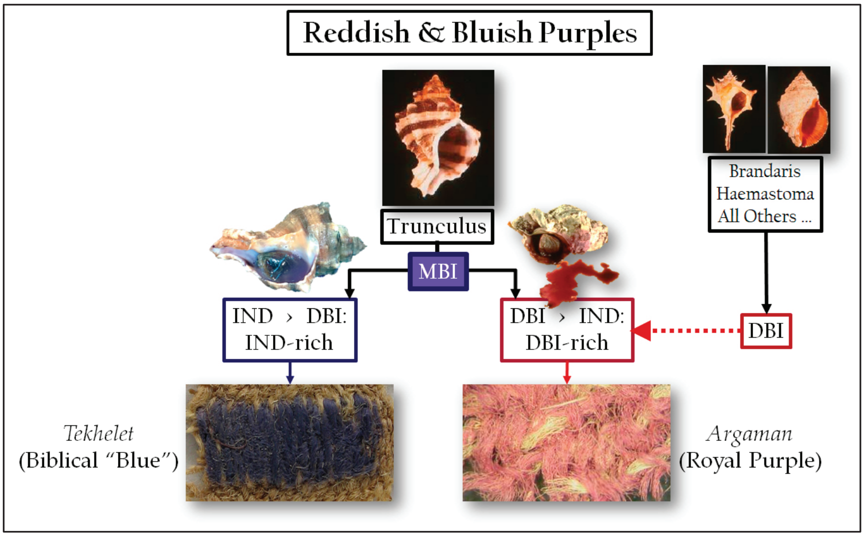

Figure 7. Relative compositions of reddish-purple and bluish-purple pigments produced from *H. trunculus*, and reddish-purple pigments from all other mollusks. In addition, a Roman Period Royal Purple textile (the biblical *Argaman* color) from King Herod (1st c. BCE) and 1st c. BCE—1st c. CE violet, bluish-purple yarns (dyed to the biblical *Tekhelet* color) are also shown, both excavated at Masada in the Judean Desert, Israel.

The uniqueness of the current research is that to date, the characterization of the three color components (reddish, violet, and bluish) of molluscan purple pigments by means of a ternary diagram has not been applied. This is one of the major innovative themes of the study. This type of classification should therefore become an accepted standard for characterizing the various color components of such molluscan colorants in order to enable quantitative comparisons among them by using a more visual—and aesthetic—statistical formulation for these samples. The current study has shown that by combining the DMI values with the ternary diagram, the malacological identities of molluscan purple pigments can be determined.

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Article

Thermochromicity in Wool Dyed with 6-Bromoindigo Depends on the Presence and Identity of a Solvent

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Abstract: The thermochromic effect of wool dyed with 6-bromoindigo was found to depend on both heat and a solvent. The dyed fabric must be immersed in a solvent while heating for a color change from purple to blue to occur. Ethanol was the most effective solvent in causing the color change. Water was effective as well. 1-Butanol caused a slight color change, while toluene was completely ineffective. These results are interpreted as interaction of the solvent with both the wool surface and adsorbed dye molecular aggregates, causing changes in the size of large red aggregates to smaller blue ones. The mildest conditions for the color change, immersion in water at 60 °C, are so easily obtained that it is possible that ancient dyers knew of this as a finishing process for their dyeing, or knew to avoid post-dyeing heat treatment.

Keywords: 6-bromoindigo; thermochromic; dyeing; wool; Tyrian purple

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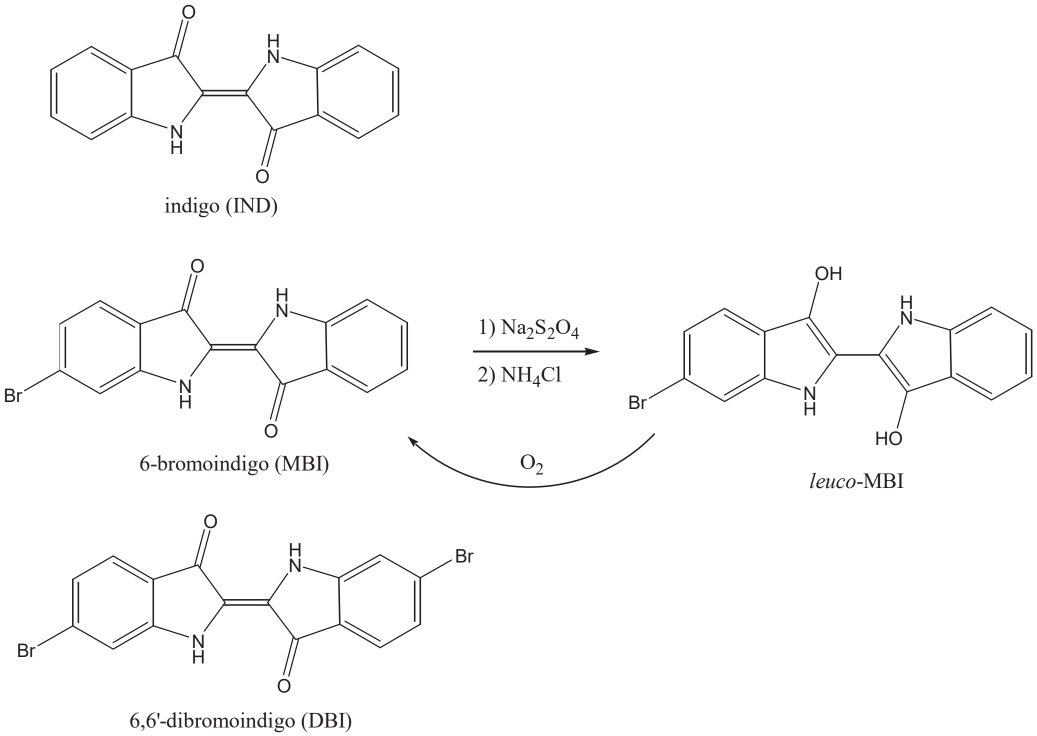
1. Introduction

Shellfish purple (also known as Tyrian purple) is a pigment that is produced from the hypobranchial glands of a variety of shellfish when exposed to sunlight. The precursor in the gland is tyriverdin, which is yellow; as it is converted to the dark-purple 6,6′-dibromoindigo (DBI), the gland fluid undergoes a striking variety of color changes [1]. The color changes were first observed in detail by Mr. William Cole in 1685, when he studied the hypobranchial gland fluid from the dog whelk *Nucella lapillus* when spread onto linen or silk. The initial yellow color changes to light green, then deep green, sea-green, Watchet blue, purplish red and finally deep purple red, "beyond which the sun can do no more" [2]. The similar color changes which take place using the Mediterranean species *Hexaplex trunculus* (*Murex trunculus*) or *Bolinus brandaris* (*Murex brandaris*) were illustrated by A. and G. de Negri in 1876 and reproduced by Cooksey and Sinclair [3]. In contrast to this riot of colors, dilute solutions in dimethyl sulfoxide of the major components of shellfish purple, indigo (IND), 6-bromoindigo (MBI) and DBI (Scheme 1), are all blue [4]. Reflectance spectra of wool dyed with IND, MBI and DBI show a wide diversity. Indigo shows a maximum absorption at 650 nm and 6,6′-dibromoindigo at 527 nm. 6-Bromoindigo in low concentration is similar to indigo, but at higher concentration, moves towards the maximum of 6,6′-dibromoindigo [5]. The study of 6,6′-dibromoindigo was extended to cover the dyeing of six fabrics [3]. The shades of purple obtained are shown in Table 1. The result was illustrated in Plate 14.4 of reference [3].



Scheme 1. Structures of IND, MBI and DBI. Additionally, reduction of the colored oxidized form of MBI by sodium dithionite followed by neutralization by ammonium chloride, giving its reduced colorless *leuco* form, and oxidation of the *leuco* form by aerial oxygen back to the colored oxidized form.

Table 1. Shades of purple obtained from dyeing of fabrics with DBI [3].

Fabric	Color
Cellulose acetate	Strong purple
Cotton	Light purple
Nylon	Moderate violet
Polyester	Pale purple
Acrylic	Light purplish blue
Wool	Moderate reddish purple

More extensive studies were later undertaken using 13 fabrics [6,7]. It was first reported by Ziderman in 2003 that wool dyed with MBI, originally blue–violet in color, turns blue upon heating at 60 °C in water [8]. These conditions are so simple to obtain that ancient dyers may have used this as a post-dyeing treatment, or they may have avoided such treatment, since it would change a rare and costly purple garment into a more commonplace blue one. There are many potential causes for this thermochromic effect, one of which is a chemical change in MBI: MBI could be thermally decomposing through the loss of a bromine atom, resulting in the production of IND. IND is known to dye wool blue. Although the reduced colorless form—the so-called *leuco* form (Scheme 1)—of MBI is known to lose its bromine atom upon exposure to light [9–11], the oxidized colored form which ends up on the fabric is not known to photochemically or thermally decompose. However, it remained to test for thermal decomposition by extracting the dye from heated MBI-dyed fabric, and analyze the MBI for presence of IND. Another possible cause for the thermochromic effect is a physical change in MBI. The color of a substance can depend on its crystal structure, and heat can cause a change to this crystal morphology. A complicating factor is that dye molecules may interact with a fabric via several modes of interaction, such as hydrogen bonding, dipole–dipole interactions and van der Waals forces. This makes it difficult to model and, thus, predict the final color of a dyeing. For example, MBI is a blue–violet color in bulk form, but may dye fabrics a wide variety of shades of blue and purple [7].Therefore, it is possible that heat could affect bulk MBI differently than MBI adsorbed onto a fabric.

1.1. Effect of Heat on Both Wool-Adsorbed and Crystalline MBI

The theory that MBI adsorbed onto wool loses its bromine atom to become IND, and thus causes the wool to turn blue, was put to rest by an extraction experiment. Wool dyed with MBI was heated in boiling water, and the resulting blue fabric was extracted with a hot solvent to remove the dye from the wool. Analysis with high-performance liquid chromatography (HPLC) showed negligible conversion of MBI to IND [12]. Thus, the color change is not due to a chemical change in the dye molecule.

It has been reported that crystalline MBI undergoes a change in both physical form and color upon heating to the vaporization point, and after deposition of the vapor [8]. We reproduced those experiments, and found that MBI does not change color upon heating to its sublimation point, around 200 °C. Additionally, the vapor-deposition experiment was repeated. The crystals of MBI obtained did appear to the eye to be of a different crystalline form, but X-ray crystallographic analysis showed them to be identical with crystals obtained by recrystallization from a solvent [12,13]. In addition, a crystal obtained from recrystallization [13] did not change in color or in crystallographic properties upon heating to 77 °C [12], a temperature at which MBI-dyed wool rapidly turns blue in water. Thus, it was concluded that MBI, unadsorbed onto wool, does not undergo a heat-induced physical change that would affect its color.

Further experiments and analyses were based on the idea that a physical change to the fabric-adsorbed MBI was occurring. Additionally, IND and DBI were included in the experiments, because they are so closely related in structure to MBI.

1.2. Divergent Behavior of MBI and DBI

Not only did we successfully reproduce the thermochromic effect seen before for MBI-dyed wool, but we also found that many other MBI-dyed fabrics show this same bluing effect upon heating in water [7]. When the thermochromic studies were extended to IND- and DBI-dyed fabrics, our expectation was that they might show this same thermochromic effect, due to similarities in chemical structure between the three indigoids. However, it was found that a wide variety of IND-dyed fabrics showed little, if any, color change upon heating in water, while DBI-dyed fabrics turned distinctly more *red* in hue [7]. Figure 1 shows four wool fabric pieces, each dyed with MBI or DBI, plus the effect of heating the fabrics in water.

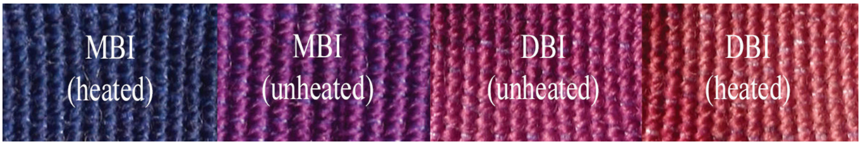


Figure 1. (Left to right) MBI-dyed wool heated in water, MBI-dyed wool with no heat application, DBI-dyed wool with no heat application, DBI-dyed wool heated in water [7].

1.3. Reflectance Spectroscopic Analysis

The color changes were studied qualitatively using reflectance spectroscopy. As has been seen before [5], we found that the reflectance spectra of MBI-dyed wool and DBI-dyed wool are remarkably similar in their spectral features; each has a reflectance minimum around 530 nm (which equates with perceived red color), and a shoulder on this main minimum around 620 nm (which equates with perceived blue color) (Figure 2) [7]. This means that both types of dyed wool appear to be a mix of blue and red, or similar shades of purple. After boiling in water for 10 min, the reflectance spectra change markedly: MBI-dyed wool shows a loss of the "red" 530 nm minimum, and production of one main "blue" minimum at 620 nm. To the eye, the fabric is now true blue. Conversely, the DBI-dyed wool loses its "blue" shoulder at 620 nm, and is left with only a "red" minimum at 520 nm. To the eye, the fabric is now very red. On the other hand, the spectrum of IND-dyed wool does not change much after heating in water.

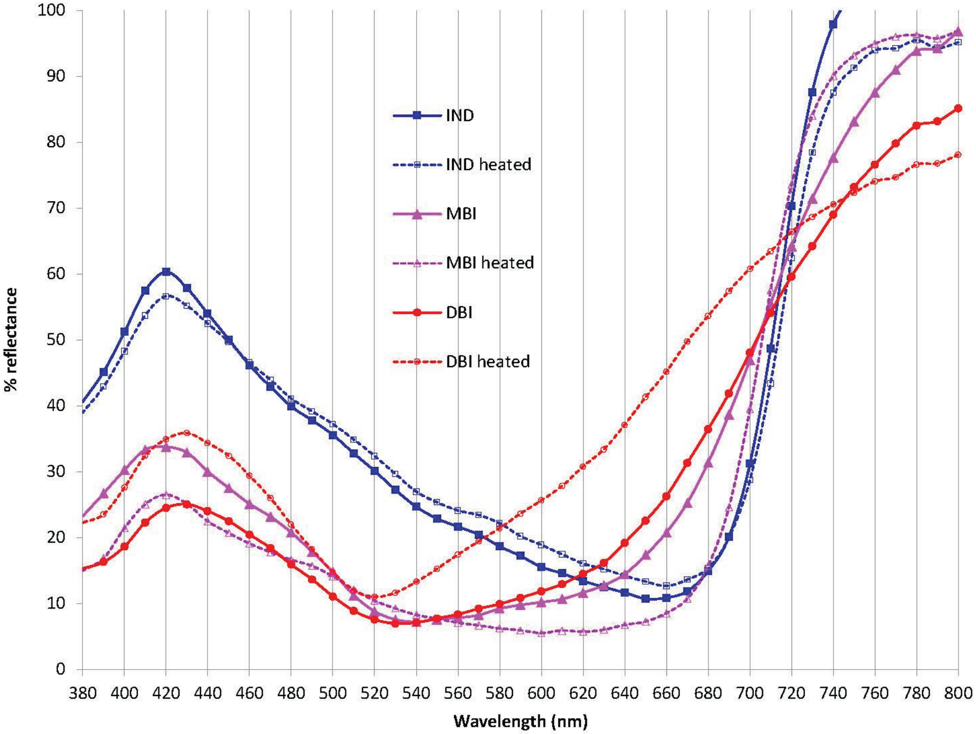


Figure 2. Reflectance spectra of wool dyed with IND, MBI or DBI, showing the effect of heating in water.

1.4. Colorimetric Analysis

The color changes were analyzed a quantitative basis using colorimetric analysis [14]. The shade of MBI- and DBI-dyed wool is determined by the red and blue hue components. For MBI-dyed wool, the blue and red components are of approximately equal magnitude, while for DBI-dyed wool of a similar dye loading, the red component is significantly greater than the blue. The consequence is that MBI-dyed wool can be considered truly purple in color, while DBI-dyed wool is a more reddish purple. Colorimetric analysis of the dyed fabrics after heating in water shows rearrangement of blue and red hue components: for MBI-dyed wool, the magnitude of the red component decreases markedly, and the blue component drops very little, while for DBI-dyed wool, the red hue component rises and the blue component drops [12].

1.5. Generality of the Thermochromic Effect

Another important finding was that the thermochromic effect is not dependent on the type of fabric. Two other natural fabrics (silk and cotton) plus ten synthetic fabrics, when dyed with MBI or DBI, also showed the same type of thermochromicity [7]. Noteworthy is the fact that IND-dyed fabrics showed very little, if any, thermochromic effects. This mirrors the behavior of IND-dyed wool mentioned earlier. Again, it was seen that strong thermochromic effects on a wide variety of fabrics are only seen with the two brominated indigoids.

1.6. Analysis of Dyed Carbon Nanotubes Using Transmission Electron Microscopy

Taken together, the reflectance spectra and colorimetric analyses suggest that both MBI and DBI, after dispersion on fabrics in their *leuco* forms and aerial oxidation, exist predominantly in two physically distinct types of dye aggregates, one that gives rise to a red color, and the other, a blue color. It was envisioned that they might be viewed using transmission electron microscopy (TEM). However, the dimensions of a fabric fiber are so much greater than that of a possible submicroscopic dye aggregate, it was impossible to analyze a dyed fabric directly. Recourse was made to use carbon nanotubes as a fabric surrogate. Carbon nanotubes are tiny strand-like pieces of tubular graphite, about five nanometers in diameter by about three micrometers in length. Since it had been established above that the thermochromic effect is not substrate-specific, it was hoped that the *leuco* form of MBI could be deposited on carbon nanotubes in the same way as on fabrics, and that whatever happened on the dyed fabrics in hot water would also happen on the dyed nanotubes in hot water. The black nanotubes were vat-dyed with MBI in the usual manner, giving nanotubes which were still black, but which showed a metallic luster [7]. The dyed nanotubes showed dark spots clinging to the surface of the nanotubes, and the spots contained bromine atoms, as determined using energy dispersive X-ray analysis (Figure 3). Therefore, the spots were considered to be dye aggregates, containing dozens or hundreds of individual dye molecules. The aggregates were measured to give a size distribution plot that showed them to be mostly 12 nanometers in diameter, plus a lesser amount with a diameter of 27 nanometers. These dyed nanotubes were heated in water, causing disappearance of the larger aggregates, and appearance of a new set of aggregates only seven nanometers in diameter. Thus far, these results were consonant with the reflectance spectra and colorimetric analyses, which suggested the presence of two dye aggregates, a red type and a blue type. After the TEM analysis, it appeared that the red aggregates were the larger type, while the blue aggregates were the smaller type. If that were the case, then nanotubes dyed with DBI should give the opposite behavior, where smaller aggregates should be converted to larger ones upon heating in water. This turned out to be just the case: DBI-dyed nanotubes before heating showed aggregates of mostly seven nanometers in diameter, while after heating, they became mostly 17 nanometers and larger [12]. The reflectance, colorimetric and TEM analyses summarized above all strongly suggest that size redistribution of dye aggregates is the cause of the thermochromic effects detailed here.

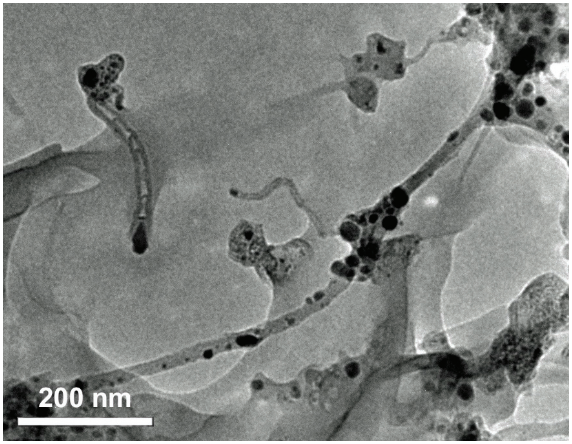


Figure 3. MBI-dyed carbon nanotubes [7].

2. Materials and Methods

2.1. Solvents

Water was distilled. Ethanol (≥99.5%), 1-butanol (≥99.4%) and toluene (≥99.5%) were obtained from Sigma-Aldrich.

2.2. Treatment of the Dyed Fabric with a Solvent

MBI-dyed wool was cut into squares of approximately 1 in. X 1in., and immersed completely in one of the solvents above, which had been pre-heated to 80 °C, for 20 min. The fabric was removed from the solvent, allowed to dry completely, and analyzed using colorimetry.

2.3. Colorimetric Analysis

In the CIELAB color space [14], a color is characterized by three attributes: the lightness, L^*, the hue, which is given by two values, a^* and b^*, and the saturation, which is indicated by the absolute values of a^* and b^*. The L^* value varies from 0 (black) to 100 (white), while the a^* value is positive for redness and negative for greenness, and the b^* value is positive for yellowness and negative for blueness. High absolute values of a^* and b^* signify a highly saturated or vivid color, while low absolute values of these mean a color towards gray. The ΔE^*_{ab} value [14] is a measure of the difference between two colors, and is the Euclidean distance between two points in the three-dimensional color space. The formula for ΔE^*_{ab} is the square root of the sum of the squares of the changes in L^*, a^* and b^* values. CIELAB data were collected with a Konica Minolta Color Reader CR-10 tristimulus colorimeter, with a 10 mm/8 mm aperture/viewing area, 8° illumination angle with CIE standard illuminant D_{65} and CIE 10° viewing angle with diffuse viewing. All samples were backed with an opaque white background. At least six different areas of the front and back of the fabric were analyzed, to give an average reading that had a very small standard deviation.

3. Results and Discussion

We now continue our study to answer several questions about the thermochromic effect: Does the dyed fabric change color over time at room temperature in the absence of water? Does the color-changed fabric revert to its original color over time? Is water a necessary component of the thermochromic effect, or would it happen with just heat? If water is necessary, is it the only solvent that causes a color change? If other solvents are effective at causing the color change, is there a dependence on a fundamental property of the solvent, such as molecular polarity?

Enough time has passed since the production of the dyed fabrics and their heated counterparts to answer the first two questions posed above. Dyed fabrics stored for at least five years under ambient conditions did not change from their original colors, as judged by colorimetric analysis. The same is true for the dyed fabrics which had been heated in water. Thus, heat is a requirement for the color change, or perhaps the combination of water with heat is the requirement.

We proceeded by using wool dyed with MBI under standard conditions [12]. Three different samples of MBI-dyed wool were employed, each dyed under identical conditions. Figure 4 shows a typical sample. The L^* values ranged from 28.1 to 29.1, a^* values from 24.4 to 26.9 and b^* values from −24.2 to −25.6, with standard deviations of 0.5, 1.4 and 0.7, respectively. Small pieces of this dyed fabric were immersed in four solvents, according to the conditions shown in Table 2. The piece was removed from the solvent and allowed to dry at room temperature, and analyzed using colorimetry. The ΔE^*_{ab} value refers to difference in color before and after heating. All solvents except water dissolved some of the dye from the fabric, as evidenced by a blue or violet color change to the solvent during heating.

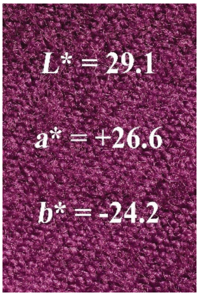


Figure 4. Wool dyed with MBI according to a standardized procedure [12].

Table 2. Effect of four solvents and heat on the color of MBI-dyed wool.

Entry	Solvent	T (°C)	Time (Min)	ΔL^*	Δa^*	Δb^*	ΔE^*_{ab}
1	H_2O	80	20	0.5	−9.8	2.2	10
2	ethanol	80	20	5.2	−19.5	1.5	20
3	1-butanol	80	20	−3.7	−4.9	3.4	7
4	toluene	80	20	0	−0.8	−0.3	0.9
5	toluene	110	100	1.1	−2.3	1.9	3.2
6	(none)	100	20	0.1	−0.3	0.3	0.4
7	(none)	100	60	0.2	−0.7	0.5	0.9
8	H_2O	r.t.	(60 days)	12.4	−4.4	4.5	14

For water (entry 1), 20 min at 80 °C was required for the fabric to exhibit its maximum color change; after 10 min, the ΔE^*_{ab} value was only 5.5, while further heating after 20 min did not change ΔE^*_{ab}. After 20 min at 80 °C, the lightness component L^* had not changed appreciably. However, the hue components a^* and b^* both lessened in magnitude; since the red-green a^* showed greater diminishment, the bluing of the fabric is due to loss of redness rather than gain of blueness (Figure 5). Three other solvents, ethanol, 1-butanol and toluene (entries 2, 3 and 4, respectively), were tested under the same conditions as water. Ethanol had an even greater effect on a^* than water: the a^* value decreased to 7.4 from its original value of 26.9, a drop of 72%. This decrease was the main determinant of the large ΔE^*_{ab} seen. 1-Butanol was less effective in causing a color change: all three color components decreased to a small extent, giving a small ΔE^*_{ab} value and a barely perceptible bluing of the color. The non-polar solvent toluene was completely ineffective at causing a color change after 20 min at 80 °C: the changes in the color components were within the standard deviations of the three values (see above), so, taking this into account, the ΔE^*_{ab} value is actually zero. Further heating in boiling toluene for 100 min (entry 5) was required for a barely perceptible color change.

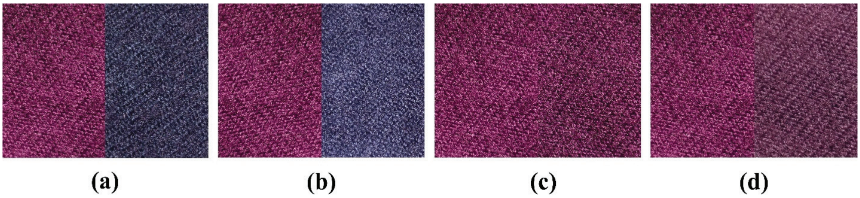


Figure 5. MBI-dyed wool from Table 2 before (left) and after (right) heating in water, ethanol and 1-butanol. (**a**) water, 80 °C; (**b**) ethanol, 80 °C; (**c**) 1-butanol, 80 °C; (**d**) water, r.t.

Table 2 also shows that heat alone is ineffective at causing a color change. Heating the dyed fabric at 100 °C for 20 min (entry 6) or 60 min (entry 7) caused no color change, as the changes in the three color components were within the standard deviation limits.

Treatment with water at room temperature for an extended period of time (entry 8) does cause an appreciable color change, but apparently the change is of a different nature than all the others: the change in the L^* value is the main determinant of ΔE^*_{ab}, and indicates significant lightening of the dyed fabric. Over such a long time period, it is possible that a chemical change to either the dye or fabric had occurred, causing the observed color change.

To summarize, both a solvent and heat are required for a color change, which appears to be irreversible. Water is the most polar of the four solvents, as measured by its dipole moment. However, ethanol was the most effective at causing the color change. Toluene is the least polar, and was ineffective at causing a color change. The more polar solvents would be expected to interact strongly with the polar surface of wool, and also with MBI through hydrogen-bond donation and acceptance. On the other hand, weakly polar solvents such as toluene would be expected to interact with MBI mainly through dispersion forces, but not strongly with the wool the MBI is adsorbed to. The solvent- and heat-induced change in the size of wool-adsorbed dye aggregates appears to involve the interaction of a polar solvent with both the wool and MBI.

4. Conclusions

The data presented here indicate that the size change of wool-adsorbed dye aggregates depends on the interaction of the solvent with both the fabric surface and the aggregates adsorbed to that surface. The sizes and shapes of molecular aggregates deposited when the reduced *leuco* form comes in contact with wool during the vatting process are expected to be different than the sizes and shapes of the oxidized dye aggregates. This is because the *leuco* form of MBI is so different in chemical structure from its oxidized colored form (Scheme 1). Thus, the colored dye aggregates resulting from exposure of the *leuco* form to oxygen in the air may be in a metastable state. The interaction of a solvent with both the dye aggregates and the fabric they are adsorbed to, at an elevated temperature, appears to be essential for the change in size of the adsorbed dye aggregates to their final, more stable sizes. The detailed mechanism of the size change, and why it occurs at all, will be the subject of further investigation.

It is possible that dyers in ancient times knew of these color changes caused by the application of both heat and water. The recipe for purple dyeing was lost and the subject of speculation for over 500 years, until the secret was discovered relatively recently [15,16]. In a study of a Coptic textile dating from the second or third century AD, which is a fragment of a purple medallion and is now in the *Österreichisches Museum für angewandte Kunst* in Vienna, it was found that the major dye, 79%, was 6-bromoindigo [17,18]. Since the color is purple rather than blue, it seems likely that the dyeing was performed without heating of the fabric in water after the final aerial oxidation step.

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Data Availability Statement: The data presented in this study are available in this article.

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