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.

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/re-solve?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.

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 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).

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 portrait, 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 spectroscopy (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, $\alpha$-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 focusing 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 Ristinpeltto, 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.

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).

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.

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