DHA36

Dyes in History and Archaeology 36

26 –28 October 2017

Hosted by the RSN at HCP

Abstracts

Welcome

Welcome to all participants in Dyes in History and Archaeology 36, especially those who have not been to Hampton Court Palace before. We have a very varied programme of presentations and posters and I am sure we will have lots to talk about as we discuss new findings, discoveries and opportunities.

We thank Hampton Court Palace Clore Centre for accommodating us for this prestigious international event. You are also particularly welcome to the Royal School of Needlework. Over the next two days we hope to show you a little of the RSN and its work and also the work of the Collection Conservation Centre of Historic Royal Palaces, and for those staying on Saturday we have a fascinating trip to the Dennis Severs house and the Warner textile archive.

We had a bumper crop of abstract proposals this year and so we send a particular thank you to the team who reviewed them all and made the final decisions for inclusion, under the chair of Maarten van Bommel.

I would also like to thank the team members from the RSN who have helped in the preparation of this event, especially Jane Hitchinson and Rowen Hunt.

We are here to explore and celebrate the role of colour in history through dyes and pigments, while you are here also take the opportunity to see the changing colours of autumn in nature, welcome to Hampton Court Palace and DHA36.

Susan Kay-Williams

DHA36 Organising Committee

Programme

Wednesday 25 October

5.00 – 7.30 Welcome reception in the teaching rooms of the Royal School of Needlework at Hampton Court Palace.

Thursday 26 October

9.30 arrivals at the Clore Centre, Hampton Court Palace

9.45 Welcome – Representative of Historic Royal Palaces and Susan Kay-Williams

10:00 – 11:20 session 1 - Chair: Susan Kay-Williams

10:00 – 10:20 Vincent Daniels - *Revealing the Nature of the Madder Vat*

10:20 – 10:40 Monika Ganeczko - *Coloring secrets of vat dyes*

10:40 – 11:00 Anete Karlsone - *The tradition of Natural Dyeing in Latvia*

11:00 – 11:20 Questions

11:20 – 11.40 Coffee/tea

11:40 – 13:00 session 2 - Chair: Dominique Cardon

11:40 – 12:00 Yoshiko Sasaki - *Research on indexing of deterioration state for cultural textiles by fluorescence lifetime measurement*

12:00 – 12:20 Diego Tamburini - *An investigation of the dye palette and fibre degradation in the 8th century Chinese embroidery 'Sakyamuni Preaching on Vulture Peak'*

12:20 – 12:40 Questions

12.40 – 14:00 Lunch

14:00 – 15:20 session 3 - Chair: Anita Quye

14:00 – 14:20 Monica Gulmini - *The dyes of the "Coptic" textiles at the Museo Egizio in Torino (Italy)*

14:20 – 14:40 Regina Hofmann-de Keijzer - *Textile dyeing in Late Antique Egypt – sources, analysis and interpretation*

14:40 – 15:00 Victor Chen - *A Survey of Dyes on Baluchi Carpets from the Boucher Collection of the Indianapolis Museum of Art*

15:00 – 15:20 Questions

15:20 – 15:40 Tea/coffee

15:40 – 17:00 session 4 - Chair: Richard Laursen

15:40 – 16:00 Ana Serrano - *A time capsule at the bottom of the sea: A material study of 17th-century textiles found in the Wadden Sea*

16:00 – 16:20 Mohammad Shahid - *Turkey red: History, Mystery and Chemistry*

16:20—16.40 Questions

Visits to the RSN Studio and Embellishment in Fashion exhibition and/or RSN Collection and Archive and/or HRP Conservation

Friday 27 October

9.00 arrivals at the Clore Centre Hampton Court Palace

9:30 – 10:50 session 5 - Chair: Zvi Koren

09:30 – 09:50 Anita Quye - *The Crutchley Archive of early eighteenth century pattern books and dyeing manuals: colour investigations for historical significance and preservation needs*

09:50 – 10:10 Vanessa Habib - *Examining the Milton printfield manuscripts: Edward Bancroft - a Scottish connection?*

10:10 – 10:30 Isabella Whitworth - *Wood and Bedford / Yorkshire Dyeware and Chemical Company Archives*

10:30 – 10:50 Questions

10:50 – 11.10 Coffee

11:10 – 12:30 session 6 - Chair: Martin van Bommel

11:10 – 11:30 Matthijs de Keijzer - *Cornelis Drebbel's Scarlet*

11:30 – 11:50 Terry Schaeffer - *Treading on Lichen: The use of Cudbear by a Victorian Carpet Manufacturer*

11:50 – 12:10 Maurizio Aceto - *It's only a part of the story: an investigation into the dyes used on the Privilegium maius*

12:10 – 12:30 Questions

12:30 – 13:45 Lunch and second opportunity to visit the Conservation Centre of Historic Royal Palaces

13:45 – 15.05 session 7 - Ilaria Degano

13:45 – 14.05 Maj Ringgaard - *Dye migration in archaeological textiles - an experiment*

14.05– 14:25 Marei Hacke - *Mapping mordants in Paracas textiles*

14:25– 14:45 Maria Melo - *The dark-side of polyphenols in medieval manuscripts: a study on iron gall inks*

14:45– 15.05 Questions

15:05– 15:25 Tea/coffee

15:25 – 16:45 session 8 - Chair: Jo Kirby Atkinson

15:25– 15:45 Marc Holly - *Interaction of paper and early synthetic dyes on textile sample books*

15:45 – 16.05 Francesca Sabatini - *Investigating the degradation pathway of xanthene dyes in textiles*

16.05– 16:25 Ilaria Serafini - *Synthetic dyes of the 1980s: a new multi-analytical approach to the isolation and identification of ACNA wool dyes*

16:25– 16:45 Questions

16:45 Closing remarks Jo Kirby Atkinson

Revealing the Nature of the Madder Vat

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When madder root is placed in water the content of the resulting extract will depend on a variety of factors including temperature and the solubility of the various hydroxyanthraquinone compounds present; at room temperature the solubilities can be surprisingly low. In some cases the presence of alum in the water increases the amount of material that can be dissolved. The solubilities are particularly important for pigment-making. When pigments are made from an aqueous extract the vast majority of soluble colouring material is incorporated into the pigment. The composition of such pigments is thus critically dependent on the composition of the aqueous extract which, at equilibrium, is determined by the solubilities of the constituent hydroxyanthraquinones. There is very little published solubility data for the key components, pseudopurpurin, purpurin, alizarin and ruberythric acid. The solubilities of the aforementioned compounds have now been determined in both water and a 5% alum solution over a range of temperatures from 20-70°C. Both ruberythric acid and pseudopurpurin can decompose in the conditions found in dye/pigment baths (converting to alizarin and purpurin respectively) and this can influence the ratio of compounds in the bath.

It has been suggested that all the purpurin found in in madder and dyed textile samples was originally pseudopurpurin or its glycoside galiosin, thus the properties and stability of pseudopurpurin are of great importance to colouration processes as its decomposition will affect the product. Pseudopurpurin is not commercially available and there was no easy way of preparing it for research purposes however a sufficiently large pure sample made in the 1930s was donated from a historical archive. Not only have the solubility characteristics of pseudopurpurin been studied but also the kinetics of its decomposition .Using these results a convenient new method has been devised for isolating pure samples of pseudopurpurin from madder root.

Alum often interacts with water extracts of madder to give a black precipitate which has been said to possibly be a reaction product of pseudopurpurin and alum. This precipitate has been prepared and characterised. Results will be presented on the likely nature of this product.

Coloring secrets of vat dyes

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Both plants and insects were used as natural source of dyes in ancient textiles. Indigo is one of the oldest dyes, known to mankind, used for dying textiles in blue.. Natural indigo is obtained from plant precursors: indican (mainly found in *Indigofera tinctoria*) and isatan B (*Isatis tinctoria*). The process of obtaining blue dye from both plants, typically is twofold. First, dry leaves are subjected to a fermentation process, and as the result indoxyl is formed. Second, indoxyl under the influence of mixture containing stale urine, lime or ash lye in alkaline conditions transforms to colourless leuco-indigotin.. Obtained in such a process plant originating dye is later used for colorization textile fabrics. The textile fibre, however, do not change its colour as the result of the leuco-indigotin bath but as the result of exposing soaking wet fabrics to air; colourless leuco-indigotin transforms to blue indigotin. Although, indigo synthesis begins from different precursors, the dye composition, prepared from both plants, is very similar. For this reason, accurate identification of indigo's plant source is often difficult and elusive. In the past, high content of indirubin was considered to be characteristic for *Indigofera tinctoria*. However, according to recent results found in literature this assumption might be seen as dubious. The indirubin content in indigo dye prepared either from *Isatis tinctoria* or *Indigofera tinctoria* are indistinguishable. The plants have very similar composition due to distinction between them is problematic and difficult.

The goal of this study is to find a distinctive marker that distinguishes these plants in fabrics.

LC/MS/MS was used for the determination of all chemical compounds in dimethyl sulfoxide extracts prepared from fresh, dried or fermented leaves of *Isatis tinctoria.* From each part of leaves the contemporary wool were dyed according to the historical recipes. Regarding to *Indigofera tinctoria*, only dried leaves were available to analyze . The analysis were compared with the results obtained for the commercially available dyes both from *Isatis tinctoria* and *Indigofera tinctoria*. The analysis of plants' extracts allowed to conclude that indigo prepared using *Isatis tinctoria* and *Indigofera tinctoria* contained similar amounts of indirubin. However, the isatin content was significantly higher for *Indigofera tinctoria* than for *Isatis tinctoria*. Also in extracts from contemporary dyed threads the ratio isatin/indigotin is significantly lower when *Isatis tinctoria* was source of blue colour than *Indigofera tinctoria.* The method has been successfully applied to determine the source of the blue dyes in historical textiles.

Acknowledgements:

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The tradition of Natural Dyeing in Latvia

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Recent years have seen a growing interest among handicrafters in Latvia about dyeing with plant dyes. This has also stimulated scientific research in the field. The tradition of use of dye plants has received little study in Latvia so far from an archaeological or an ethnographic perspective. Previous generations of researchers have collected an extensive body of material, which has so far only been brought together and studied to a limited extent. My own research interest mainly relates to ethnographic sources, although in parallel with this I take an interest in the available information for all time periods.

Researchers began addressing traditionally used dye plants and dyeing methods in present-day Latvia already in the late 19th century. By that time, as elsewhere in Europe, in the Baltic Provinces of the Russian Empire dyeing with natural dyes had become an alternative approach to textile dyeing, priority being given to synthetic aniline dyes. In the late 19th and early 20th century the first Latvian press publications appeared on the traditions of using dye plants. In general, these were records of dyeing methods submitted by individual informants [2, 3, 6, etc.]. Also published at this time were the first limited studies on Latvian dyeing traditions [4, 5]. The written sources from the late 19th century mention only a relatively small number of natural dyes – only 34. Six of these are imported foreign plants (e.g., *Juglans* L., *Solanum tuberosum* L. etc.) or dyewoods and indigo.

The marked deterioration in economic conditions in present-day Latvia brought about by the First World War created the preconditions for the revival of many already disappearing skills, including the use of natural dyes. Following the establishment of the Latvian state in 1918, ethnographic fieldwork was undertaken in the years 1924–1944, in the course of which information was also collected on the use of natural dyes. These records preserve a very extensive body of evidence concerning the natural dyes and dyeing methods used in earlier times. Ethnographic material was also submitted and published in the Latvian press. The ancient Latvian dyeing traditions were of interest not only to Latvians but also to the Baltic Germans [1]. Up to 1944, the written sources mention more than 125 plant species used for dyeing textiles. Information about dyeing with natural dyes was also recorded in the course of ethnographic fieldwork conducted after the Second World War. The tradition continues right up to the present day, although it is disappearing.

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Research on indexing of deterioration state for cultural textiles by fluorescence lifetime measurement

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If the deteriorated state of the cultural textiles can be expressed as a numerical value, it will be very meaningful information for preservation, repair, and exhibition etc of them. In previous studies, we have analyzed the components of Amur cork tree extracted from cultural textiles using HPLC. As a result, it has been shown that the sum of decomposition products of berberine may be a clue to the indicator of degradation [1]. However, since HPLC is destructive analysis, we tried to measure the fluorescence lifetime with the aim of indexing of degradation using nondestructive analysis.

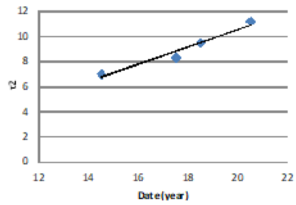

Fig.2 Relation of fluorescence lifetime with manufactured date of cultural textiles

The fluorescence lifetime: t indicates the value unique to a substance under the same circumstance and as a third parameter in addition to the emission / excitation wavelength of the fluorescence spectrum. It can be measured non-destructively and without contact, which is appropriate for the valuable cultural textile [2-4]. Since the t values in the same solvent or matrix are constant, lifetime measurement can be used for the identification of the dye materials. The t values are also sensitive to the change of the circumstance around the dye, and could be used as a parameter to reflect the micro-environment of them.

We have measured the fluorescence lifetime focusing on the protoberberine alkaloids contained in the Amur cork tree used for cultural textiles [5]. Life times in green threads from cultural textiles reveals smaller t values in the older textiles (Fig. 1) which reflect change of micro-environment of silk surrounding the dye.

Investigation of the relationship between the t values and the manufactured date of cultural textiles (Fig. 2) shows that the t values could be an indicator of degradation of silk by non-destructive analysis.

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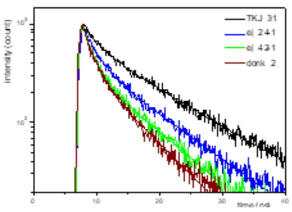

Fig.1 Fluorescence decay of cultural textiles

TKJ_31:modern,

j_24:18C,

ej_42:17C,

donk:14C

An investigation of the dye palette and fibre degradation in the 8th century Chinese embroidery 'Sakyamuni Preaching on Vulture Peak'

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'Sakyamuni Preaching on Vulture Peak', measuring *ca.* 2.5 m height and 1.5 m width, is one of the largest known embroideries from the Tang dynasty period (618-907 AD), probably dating to the 8th century. It was discovered in the sealed Library Cave at the Buddhist cave temple complex of Qian Fo Dong, near Dunhuang, in 1900. The textile was brought back to the British Museum by the archaeologist Sir Marc Aurel Stein, following his second expedition in 1906-8.
When recently assessed for loan, major conservation work was required to enable the fragile embroidery to travel and be displayed safely. This provided opportunities for some further in-depth scientific examination and analytical work of a rare surviving example of early Chinese embroidery.
Scanning electron microscopy (SEM) was used to investigate the state of degradation of the original silk fibres, which appeared very brittle in many areas of the textile. Investigation was also carried out on the linen backing onto which the embroidery was sewn by a restorer in about 1912 as it appeared to no longer provide adequate support to the original materials. Energy dispersive X-ray (EDX) spectrometry was undertaken to give an indication of the mordants used, especially iron, which is known to accelerate fibre degradation [1]. Although the results were difficult to interpret due to elemental contamination, some indications were obtained about the use of Al and Fe mordants on the silk embroidery.
The embroidery also shows a varied a varied and vibrant range of colours, in part due to the textile being protected over several centuries in a sealed cave. Most of the colours were sampled during the conservation treatment and dye analysis was performed using high pressure liquid chromatography coupled with mass spectrometry (HPLC-MS). In some of the areas that are now extremely faded, analyses revealed the use of safflower. A source of indigotin was used for the blues, and the greens were obtained by mixing this with at least two sources of yellow dyes: a berberine- and a luteolin-based dye. Browns were found to be tannin-based. Two sources of reds were also present. A madder-like plant was used to dye the central figure, whereas the other red source is of unknown origin at this stage of the investigation. Finally, a purple stripe was investigated, and analyses highlighted the presence of alkanet, probably from gromwell. However, other components were present, which did not allow a conclusive interpretation of the plant source. Tandem mass spectra experiments have been performed to elucidate the structures of the molecules present in the red and purple dyes, enabling the identification of naphthoquinones, anthraquinones and xanthones with different degrees of hydroxylation. As the literature on ancient dye sources in China is not abundant [2], in the near future the intention is to establish a collection of reference plant materials and undertake comparative investigations of other textiles from Dunhuang, with the aim of shedding light on possible unusual dye sources in ancient China.

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The dyes of the “Coptic” textiles at the Museo Egizio in Torino (Italy)

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The Coptic textile collection of the Museo Egizio encompasses about 250 textiles, dated from the Roman to the Islamic period according to iconography, style and weaving techniques. Many of them are decorative bands (*clavi*), rings/ovals (*orbiculae*) or squares/rectangles (*tabulae*) which were cut out from larger textiles, although the collection also encompasses furnishing textiles (carpets and blankets), some tunics and accessories such as wraps, bags and headdresses.

All the textiles have been considered within a broad project aimed at investigating the production techniques, at documenting the conservation state and (possibly) at reconsidering the attributed age. Within the project the textiles have been analysed by means of a set of analytical techniques in order to reveal the dyes that have been employed to obtain the colours. The textiles were preliminary subjected to a non-invasive screening by portable fiber optics UV-Vis diffuse reflectance spectrophotometry (FORS) and portable fiber optics fluorimetry (FL), which were employed sequentially on a same spot. The analyses lead us to obtain an overall general picture of the dyes by performing a large number of analyses on the same object and by combining the information obtained from each of the two spectroscopic techniques. The non-invasive survey allowed us to focus the sampling on representative textiles and 32 micro-samples were then taken in order to obtain a more in-depth view on the dyes through high performance liquid chromatography coupled with diode-array spectrophotometric and mass spectrometric detection (HPLC-DAD-MS).

The collected data have been compared with previously published results with the aim of highlighting a possible link between the age of the textile and the dyes. Moreover, the combined use of spectroscopic and chromatographic techniques allowed us to compare the results for the non-invasive and the micro-invasive approach, and to go deeper into the dyeing technology by detecting unexpected combinations of dyes.

In particular, the use of a double dyeing with madder and Indian lac dye was revealed in some Roman-Byzantine and Byzantine textiles.

Textile dyeing in Late Antique Egypt – sources, analysis and interpretation

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Dyeing textiles constitutes an essential and highly specialised branch in the complex *chaîne opératoire* of textile production in the ancient world. The aim of the research project *Texts and Textiles in Late Antique Egypt* [1] is to enlarge the knowledge in textile dyeing in the period from c. 300 to 800 CE. The special feature of the project is that texts and textiles from the same period, both housed in the *Papyrussammlung* of the Austrian National Library in Vienna, can be investigated. Besides the dyeing recipes described in the *Papyrus Graecus Holmiensis* and the *Papyrus Leidensis X* (both dated to the late 3rd - 4th cent. CE) written evidence on dyers and dyeing materials is found in several documentary papyrus texts from Egypt. These texts reflect the daily life in the *chora*, i.e. in the land outside Alexandria, however, they provide little information on the skills, knowledge and technology of the ancient dyers. Additional information could be gained by investigating textile finds originating from Egyptian burial grounds.

Based on previous research [2], dye analysis by ultra-high performance liquid chromatography coupled to photodiode array detection (UPLC-PDA) and fibre analysis by optical light microscopy and scanning electron microscope with energy-dispersive X-ray analysis (SEM-EDX) provided results for a better understanding of the dyeing materials and dyeing processes of this period. The only source for blue was indigotin, which was identified together with the red indirubin and the degradation product isatin. As these components can originate from woad (*Isatis tinctoria* L.) as well as from an *Indigofera* species, the question arose which is the most probably source. Red dyes could be assigned to different madder- and cochineal-types, lac dye, sappan wood and dyer's alkanet (*Alkanna tinctoria* (L.) Tausch.). It is remarkable that alkanet, which is often mentioned in the ancient dyeing recipes, was rarely detected in the analysed textiles. Purple to violet shades were usually obtained by double dyeing with an indigotin-source and red dyes or by mixing red and blue fibres in different ratios, only in one sample Tyrian purple was found. The yellow flavonoids luteolin, apigenin and their glycosides are hardly to assign to certain plants.

Is it possible to prove the use of mordants by SEM-EDX-analysis? Did the dyers use alum and – for the shading of colours – iron-containing mordants? Documentary papyrus texts confirm the gathering of alum in the oases of Egypt's Western Desert and provide some insight information in the administrative organisation of the alum monopoly particularly in Roman times [3]. By optical microscopy it could be proven that fleece was dyed and also that some colour shades were created by double dyeing and by mixing of differently dyed fleeces. By the analyses of text and textiles the knowledge on late antique dyeing techniques as well as on the skills of ancient dyers could be increased. This can be applied in various research fields as for instance in experimental archaeology for the reconstruction of garments according to dyeing techniques as close as possible to the historic ones.

1. The research project is supported by the Austrian Science Fund [FWF, P 28282] and co-ordinated by Univ.-Prof. Dr. Bernhard Palme.

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A Survey of Dyes on Baluchi rugs from the Boucher Collection at the Indianapolis Museum of Art

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The Baluchi language group comprises the people thought to have lived in ancient times in areas south of the Caspian Sea in present day Iran. To escape persecution and famine, the Baluchi people have in the past two millennia gradually migrated south and eastward to settle in an area that encompasses a swath of territory spanning present day southern Afghanistan, eastern Iran and western Pakistan, that has come to be known as Baluchistan.

Baluchi weavings mainly consisted of small rugs, travel bags, and other textiles for daily use woven on horizontal floor looms. While the artistic quality of these weavings varies, the so called Baluchi style rugs produced by the Baluchi and other co-locating groups in the vicinity of Khorosan and Sistan provinces in Iran are valued by many rug connoisseurs for their soft wool, brilliant colours, and intricate patterns. Although these rugs have been described by authors such as Edward and Boucher,[1,2] no scientific analysis has been done on them. In 1996, the Indianapolis Museum of Art was the recipient of a group of about seventy Baluchi weavings, which was collected by the late Colonel Jeff W. Boucher.[2] This study describes the results of dye analysis performed on nine rugs and one salt bag dating from 1870-1920.

Between five and ten fiber samples of diverse colour and hue were collected from each object. Each fiber was extracted sequentially by an oxalic acid containing solvent mixture, pyridine-water, and DMSO, and the extracts were analyzed by LC-DAD-ESI-MS. Usable data were obtained from 65 of the 70 samples. Of these, five bright pink samples were dyed with cochineal, wherein each case the presence of carminic acid was detected along with the minor components dcII, dcIV, dcVII, kermesic and flavokermesic acid, as well as anthraquinone compounds assignable to dc2, dc5, dcOfkc, dc7 (or 9), and dc8.[3] Another 26 samples of widely varying shades of orange to dark red were dyed with madder. Half of these also contain a second dye, including 6 with ellagic acid, 6 with variable amounts of conjugated flavonoids of molecular weight 464, 478, and 448, as well as one with a synthetic orange dye of molecular weight 507. All the madder showed significant amount of alizarin and purpurin together with low amounts of lucidin primeveroside, ruberythric acid, and other anthraquinone dyes assignable to munjistin, pseudopurpurin, rubiadin, and nordamnacanthal, indicative of the plant *Rubia tinctoria*.[4] Seventeen samples in various shades of blue were dyed with indigo alone, and one green sample contained indigo together with a glycosylated flavonoid of molecular weight 448. The indigo in these 18 samples was detected along with variable amounts of indirubin and isatin, suggesting a natural product. Other samples dyed with natural colourants included four brownish green fibers found to contain ellagic acid alone. A green sample showed the presence of conjugated flavonoids of molecular weight 464 and 478, and another tan sample contained luteolin and apigenin. The remaining nine samples were found to be dyed with synthetic colourants. Of these, one orange and two pink samples each contained acid orange 7, fuchsin dyes, and rhodamine, respectively, and two purple samples showed methyl violet. The remaining three orange samples contained several currently unidentified synthetic dyes.

In conclusion, our study confirms previous historical descriptions that Baluchi textiles of the late 19th to early 20th century were coloured with mainly natural dyestuffs alongside a handful of synthetic colourants, and shows that a minimal palette of dyes was used to create a wide range of shades of colors. Technical studies of the dyer's materials such as the present one will help to provide an objective basis for continuous understanding the material technology and aesthetic heritage of the Baluchi people.

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A TIME CAPSULE AT THE BOTTOM OF THE SEA
A material study of 17th-century textiles found in the Wadden Sea

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In 2014, a large collection of textile fragments was found in a 17th-century shipwreck (named BZN17) that had sunk in the Wadden Sea, near the island of Texel, The Netherlands. Captured in a time capsule for centuries, this collection represents a unique example of 17th century fashion, comprising over 150 textile fragments, including costumes, parts of costumes and interior textiles. Although buried for centuries, they are in remarkably good condition, which might be related to the archaeological environment and the high quality of the fabrics. Indeed, these are almost entirely made of silk (except one woollen carpet), and embroidered or woven with metal thread. The most striking characteristic of this collection is the well-preserved deep red colour displayed by many of the textiles.
To understand the origin and function of these textiles, as well as their state of conservation for future preservation strategies, it was important to characterize their materials. Hence, a group of 12 objects was selected for evaluation with ultra-high performance liquid chromatography with diode array detector (UHPLC-PDA) and a scanning electron microscope coupled to an energy dispersive x-ray spectrometer (SEM-EDX).
With UHPLC-PDA, coccid insect dyes were identified as the main colorants on the textiles. However, the ratio of their dye compounds seems to have been affected by the maritime archaeological conditions: dcII and flavokermesic acid were not reported in any of the textiles; and an unusually high kermesic acid equivalent was detected, in relation to the major compounds kermesic and carminic acids. Even though American cochineal and kermes could be possibly attributed in some cases, these results substantially hinder the precise identification of the insect sources. Besides these, madder was often found mixed with the insect dyes or in textile parts that are not directly visible on the costumes.
The evaluation of the fibres with SEM-EDX indicated that some fibres show evidence of microorganism attack, and that the majority has preserved their flexibility; although those from fabrics of lower quality (e.g. lining) are more friable. On the metal threads, silver sulphide crystals were observed, and these correspond to the degradation product of silver. Also, gold was detected on few threads, which indicates that they were probably gilded. Due to the corrosion of silver, most gold particles could have been lost in the maritime environment.
While the provenance of these textiles, and the ship that carried them, is still under investigation, the analytical results obtained undoubtedly prove that a very rich finding has been unearthed. Nevertheless, the archaeological conditions certainly had a preponderant influence on their original appearance and this deserves future research.

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Turkey red: History, Mystery and Chemistry

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This research is part of LightFasTR project uniting the materials and processes of making 19th c. Turkey red (TR) with modern dye chemistry and heritage textile conservation science to provide essential light exposure guidance for museums and archives. TR cotton with trademark bright red with bold patterns, which was a major industry in 19th c. Scotland, made it globally popular. TR often described as a complex, repetitive, secret and expensive process, surrounded with mysteries – ambiguity about its origin, ingredients and processes, and technology transfer around globe or even the 'name' itself. In this research we have demonstrated how scientific literature and archival records can be of great use to answer these questions by understanding the historical and geographical context and interpreting TR in written sources and historical collections. A critical analysis TR process will be presented based on 19th c. TR industry dyeing receipts and pattern books in UK archives and museums and published research during the period. Understanding the chemical aspects of TR is essential to understand how materials, maker and methods impact its lightfastness. Historical information combined with modern laboratory experiments on TR will provide new insights into the basic principles of chemistry associated with this beautiful craft.

Acknowledgement

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The Crutchley Archive of early eighteenth century pattern books and dyeing manuals: colour investigations for historical significance and preservation needs

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A set of dyeing records associated with John Crutchley, an eighteenth-century dyer working in Southwark, London, was kept by the Crutchley family for nearly three hundred years until donated to Southwark Local History Library and Archive in 2011. The collection consists of detailed texts and colourful dyed fabrics in fifteen books of patterns (dyed textiles), dyeing receipts (instructions), dyeing calculations and accounting records.

The historical importance of the Crutchley Archive wasn't fully appreciated until assessed in 2014 by Anita Quye [1]. In 2016, an interdisciplinary research project funded by the Worshipful Company of Dyers (WCD) through the Textile Conservation Foundation was initiated to understand in greater depth the significance and preservation needs for this unique record of specialist dyeing with mainly cochineal and madder from around 1722 to 1744 [2].

To date, the research team have photographed the entire collection; reassessed catalogue descriptions; studied selected receipts and instructions; recorded colour names and taken spectrophotometric colour measurements of the dyed broadcloth patterns; carried out microchemical dye analysis of selected patterns; investigated with the donors (Annie Crutchley) and WCD archivist (Ian Mackintosh) the professional and social contexts for John Crutchley and his family; located the likely dye works; and involved conservators to assess the physical condition of the books for preservation and future access.

This paper shows the rich material content of the Crutchley Archive, and presents initial findings from colour measurements and their comparison to similarly-dated broadcloth dyeing records in France [3], and also dye analysis for thirty selected patterns with potential implications for colour preservation [4].

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EXAMINING THE MILTON PRINTFIELD MANUSCRIPTS:

EDWARD BANCROFT - A SCOTTISH CONNECTION?

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Amongst the Day Books and Dye Recipe books in the Milton Printfield manuscript collection at the National Library of Scotland (Mss 17961-17997) are two long copy letters dated 1790 and signed 'Bancroft'. They are principally concerned with his experimental work on a new permanent yellow dye, Quercitron, from the American Oak, *Quercus velutina* and predate his published work 'Experimental Researches concerning the Philosophy of Permanent Colours' of 1794. This paper will look at Bancroft's extensive experimental work on dyestuffs, his Patents and the later success of Quercitron, in competition with the traditional yellow dye, Weld.

Edward Bancroft has not been previously associated with any Scottish printfield. His letters are written on loose sheets of paper, perhaps cut from another notebook . Most of the Milton collection is anonymous, but thought to belong to Patrick Mitchell who was manager and later owner there. However, the Milton field and others in the Vale of Leven in the West of Scotland were internationally known and leaders in the chemistry of dyeing and printing on calico in the later 18th century.

Edward Bancroft's son Edward Nathaniel and his brother Daniel studied at Edinburgh University and he himself obtained an MD from Aberdeen University in 1774. His own studies of botany and natural history brought him into contact with many of the leading figures of the Scottish Enlightenment. He travelled widely in the Americas and Europe. His fictional book of Letters, 'The History of Charles Wentoworth Esq.' (1770) set principally in Guiana, recounts his meeting with a Scot, John Gordon, a man of science who had chosen to settle with the indigenous population there. To some extent this book mirrors Bancroft's own interests in an increasingly globalising world of trade and exploration.

Wood and Bedford / Yorkshire Dyeware and Chemical Company Archives

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A unique archive relating to a Leeds dye manufacturer emerged ten years ago from a Devon attic near the home of the presenter of this paper. In 1850 the dye company started out as Wood and Bedford and most items in the archive range from this period until the first quarter of the twentieth century, covering material relating to three generations of the Bedford family, its research successes and its close connections with the family of Sir William Henry Perkin. The archive therefore covers the time when natural dyes overlapped with, and were gradually replaced by, synthetic dyes, and one focus of the early archive is the family's success in manufacturing and trading in orchil. The archive's owner, Charles Chalcraft, is a descendant of the Bedford family and sought an appropriate home for the archive where it could be made available for public study.

From 2007 the presenter worked on listing and finding a home for the material, and also researched orchil, and the orchil trade, through items found in the archive. For this research she received support from the Worshipful Company of Dyers in London (the Dyers Company) which led to timely connections and meetings with several ex-employees of Yorkshire Chemicals, including Dr Howard Varley, who had latterly worked there as Technical Executive of Colours Division.

Dr Varley was one of the final remaining employees at Yorkshire Chemicals before its eventual collapse in 2005 and had kept in touch with several work colleagues who had preserved documents and photographs relating to the Company. The presenter, meanwhile, visited several Leeds sites of Yorkshire Chemicals that were on the point of demolition, and met the demolition contractors. When a set of photograph albums was discovered walled in to a cupboard, the contractors contacted her and thus the albums were preserved and could be united with all the other material.

Joint meetings between Yorkshire Chemicals ex-employees, Charles Chalcraft, and the presenter took place at Dr Varley's house in Yorkshire, resulting in an approach to the West Yorkshire Archive Service (WYAS), which was informed that the material sought a permanent home. WYAS immediately recognised the significance of this industrial archive, spanning 150 years of the lifetime of one company, and offered to preserve it.

Dr Varley undertook the considerable task of collating and archiving the amalgamated material for efficient access and this work is now complete. This paper will present an outline of the archive with its several routes of acquisition and give a summary of material that will soon be available to researchers.

i. Presentations given at DHA Posnan (2009), DHA Lisbon (2010), and with Professor Zvi Koren at DHA La Rochelle (2013)

ii. Yorkshire Chemicals was the final name of Wood and Bedford, which had been through name changes and amalgamations, but never underwent a takeover

Cornelis Drebbel's Scarlet

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The dye insects kermes, Polish and Armenian cochineal were used for dyeing red in Europe before the American cochineal was imported from Central America in the 16th century. At the beginning of the 17th century cochineal was especially mordanted with alum to yield crimson shades. The Dutch inventor Cornelis Drebbel (1572-1633) born in Alkmaar, Holland, emigrated to England, between 1604 and 1605. In the period 1606-1607 he brought a great improvement from a chemical technological point of view in the dyeing of cloth by the introduction of tin chloride as a mordant in cochineal dyeing. However, there are doubts about the time and place of his invention. He discovered that a solution of tin in aqua regia turned an aqueous solution of cochineal dye scarlet. This intense red dye has various names, such as Drebbel's Scarlet, Dutch Scarlet, Scarlet, Bow dye, Scarlet Bow dye, Hunting Scarlet, Kuffler's red, Kuffelaars and colour Kufflerianus. Around 1622 it seems that the Kuffler brothers, some later Drebbel's sons-in-law, became a companion in Drebbel's dye-work in Stratford-Bow, East London. Between 1630 and 1635, probably after Drebbel's death, Abraham Kuffler (1598-1657) and Johan Sibertus Kuffler (1595-1677), exploited a professional dye-work and developed the use of tin salts with cochineal to dye wool and silk scarlet. They renamed Drebbels innovation in colour Kufflerianus and the recipe was a well-guarded family secret. The Kufflers brought this method to Holland and by the 1650s Drebbel's scarlet process spread across Europe and was conceded to be the finest scarlet dyeing. Some later Drebbel's red was applied for the dyeing of tapestries at the Manufacture nationale des Gobelins in Paris, France.

It is quite remarkable that Drebbel's Scarlet as a dye is hardly analysed in textile objects. One of the earliest proof of Drebbel's red as a dye is in the well dated tapestry to the 150. Anniversary of the Reformation of 1667, owned by the Museum Europäischer Kulturen, Berlin State Museums. This tapestry was presumably produced in Hennstedt in Dithmarschen in Northern Germany. Besides the creator Anna Bump also the date is signed in the tapestry, namely 31.10.1667. Drebbel's red shows a characteristic orange red fluorescence, which could be used as a screening method before element and dye analysis is performed.

Recipes for tin-containing pigments are known from the mid-18th century onwards. Especially in the 19th century the pigments became widely used. Many artists used tin lakes of cochineal, among them Vincent van Gogh (1853-1890). In the years that he lived and worked in France (1886-1890), he purchased different types of cochineal paints. One of these types is the tin-based cochineal lake. He was not the only 19th century artist who made use of this type of paint. Van Gogh's contemporaries Paul Cezanne, Auguste Renoir, Emile Bernard, Edouard Monet, Edgar Degas and Armand Guillaumin all used similar cochineal paints.[1]

The term scarlet was formerly confined almost entirely to the formation of cochineal in the presence of tin chlorides on wool and silk. With the introduction of the synthetic organic dyes this term has been extended to other similar shades. The word scarlet appears in the synthetic dyes Biebrich Scarlet, Crocein scarlet, Cotton scarlet, as well as other azo-varieties obtainable from the Ponceaus (β-naphthol disulfonic acids). At the end of the 19th century and the beginning of the 20th century the Drebbel process was gradually replaced by synthetic dyes. In Britain scarlet broadcloth for the army officers' uniforms was dyed with cochineal and tin chloride up to 1952, when it was finally replaced by a synthetic dye.

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Treading on Lichen: The use of Cudbear by a Victorian Carpet Manufacturer

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In 1842 William Henry Worth, a partner in the carpet manufacturing firm of Butcher, Worth and Holmes in Kidderminster, began to assemble a book of dyed woollen yarns with recipes. In its final state the book contains 182 dyed yarn samples accompanied by about 139 recipes for a large range of colours. Nearly one-third of these recipes list cudbear as an ingredient. This purple dye, prepared from lichens and famously made in Scotland in the late 18th and early 19th centuries, continued to be manufactured in Britain at the time Worth created his record book. Perhaps it is not surprising that Worth used it extensively, as partner James Holmes was a Scottish dyer, who learned his trade there.

In addition to employing cudbear as the only dye in four recipes for purples, Worth also used this dye as an ingredient in some recipes for bluing crimsons, in many drab recipes, and in recipes for brown, salmon and grey. The arrangement of the recipes in the book and the often graded variations in amounts of ingredients suggest that Worth was creating a methodical record of shade variations that could be created with a limited number of dyes, mostly of modest cost. Where cudbear is included to change the shade of a dyeing, a relatively small amount of this more expensive dye is usually used. In contrast, cudbear provides up to 40% of the total dye weight in a few of the drab recipes for deeply coloured yarns.

For this study, reference materials such as archil-dyed yarns from the Helmut Schweppe collection, cudbear prepared from British lichens by Dr. Robert Hill in the mid twentieth century and commercial orcein have been used.[1] Several analytical techniques, mainly spectroscopic methods, have been used to confirm the presence of cudbear and the other dyes in the yarn samples accompanying the recipes. Among these, fluorescence spectroscopy is particularly suited to detection of cudbear because the orcein constituents of this dye are very fluorescent.[2] Creating excitation-emission 3D contour plots of fluorescence is a sensitive means for detection of minor dye components in the yarns.[3] This technique can confirm the presence of cudbear in the yarns when it is not a major recipe component. If sample size permitted, the identities of the dyes were confirmed with high performance liquid chromatography – diode array detection.

Fiber optic reflectance spectroscopy (FORS) has also been used to characterize the appearance of the yarns. This procedure has provided objective documentation of how the added cudbear altered the shade of particular colours. For example, spectra of paired yarn samples of bodied and blued crimsons, with and without cudbear in otherwise similar recipes, show how Worth subtly changed the extent of blueing by adding the lichen dye. Comparisons of FORS spectra of drab yarns can also elucidate the roles of other dye ingredients that Worth used in combination with cudbear to achieve his color variations.

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We thank the Getty Conservation Institute and Dr. David Hill for the Schweppe and cudbear samples, respectively.

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It's only a part of the story: an investigation into the dyes used on the *Privilegium maius*

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The *Privilegium maius* is one of the most famous and most spectacular forgeries in medieval Europe. In 1156 Austria became a duchy. For this solemn act emperor Friedrich I Barbarossa issued a charter with a golden bull for the ruling family in Austria, the Babenbergs. But two centuries later duke Rudolf IV, a member of the Habsburg family, commissioned a forgery of this charter and of four others. He wanted to elevate the rank and the prestige of his family and to show that they at least equalled the electors of the Holy Roman emperor. These five charters are kept now in the Haus-, Hof- und Staatsarchiv Department of the Österreichisches Staatsarchiv in Vienna. Since almost 200 years it is known that the documents are false: due to their inner and outer characteristics, historians have been able to see through the albeit excellent forgeries.

To shed light on the controversial story of the *Privilegium maius* charters, these documents have been recently subjected to a diagnostic study that involved the different parts they are made of. These are the parchment support and the text they were written with, the beeswax seals linked to the document and the coloured threads that link the seals to the document.

The present contribution concerns the dyes used to impart the colour to the threads: are they compatible with the presumed age of the charters? If not, when were they applied? Though showing only a part of the whole story of the charters, dyes analysis could contribute in assessing the complex history of their manufacturing. Firstly, non-invasive *in situ* measurements were carried out by means of FORS and spectrofluorimetry analysis, to have a preliminary identification of the dyes. With concern to red hues, this allowed classifying the threads into three groups: 1) dyed with orchil, 2) dyed with an anthraquinonic alizarin-like dye and 3) dyed with a modern colourant. Samples from the threads were then taken to perform micro-destructive measurements by means of Surface Enhanced Raman Spectroscopy (SERS) and HPLC-MS analysis. This allowed confirming the presence of orchil in the first group, while the members of the second group resulted to be dyed with artificial alizarin instead of madder, according to the presence of synthetic by-products. The third group resulted to be coloured with PR14, a modern azo pigment. It is apparent that most of the threads have been reworked in recent times. Work is in progress in order to characterise all the dyes, including green and yellow ones, and to try to locate the different stages of the intervention on the colouring of the threads.

Dye migration in archaeological textiles - an experiment

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An experiment mimicking Archaeological textiles from wet sites was conducted to document and analyse the changes that occur during burial in soil in wet conditions, investigate how different factors like mordants, dyestuffs and natural pigmentation affect the rates of deterioration (Ringgaard & Sharff 2010). One of the aims was to explore if dye or mordant stay in the textile or will leak into the surrounding soil and if the dye components can migrate or bleed from one textile to another; this poster / paper will focus on this subject.
Wool and silk fabrics were dyed with a range of different natural dyestuffs and mordants. Some of the dyed samples had small swatches of natural white fabric sewn on top to investigate if dyes are able to migrate from one textile to another. Identical sets of textiles were buried in slightly acidic peat to imitate textiles from bog-finds. Identical boxes with soil and textiles were kept in a greenhouse with subtropical climate at constant temperature and high humidity. Textiles were excavated after 8 and 16 months and 2 and 6 years of burial.
Methods used for the determination of the degree of deterioration include colour changes documented by measures with a spectrophotometer; quantitative and qualitative element analysis using SEM-EDX and IPC-MS; and the testing of dyestuff remains with HPLC.

Results: The experiments showed a range of the dyes were identified in samples not dyed with this dyestuff. This was primary the red dyes madder and cochenille. These dyes were able to migrate from one textile to another, not only to samples directly in contact with the dyed fabric, but also to some textiles in near surroundings. Also Indigo migrated to yellow textiles dyed with weld only – an interpretation of the dye analysis from these textiles would have been that they originally were dyed green. Also Ellagic acid was traced in textiles not dyed with this component – it is not certain if this acid has migrated from dyed textiles or originates from the surrounding peat.
As archaeological textile finds often lost their original colours and appear in different brownish shades bleeding dye is not visible. Therefore these results must be taken into account in the future when taking samples and interpreting dye analyses.

Figure 1. - *Significant amounts of alizarin and purpurin had migrated from the madder-dyed textile lower left and were found in the cochineal dyed textile centre u. An interpretation of the dye-analysis would have been the textile was dyed clear red with a combination of the two dyes. If the sample for analysis had not been taken in this corner, the results would have been different*

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Mapping mordants in Paracas textiles

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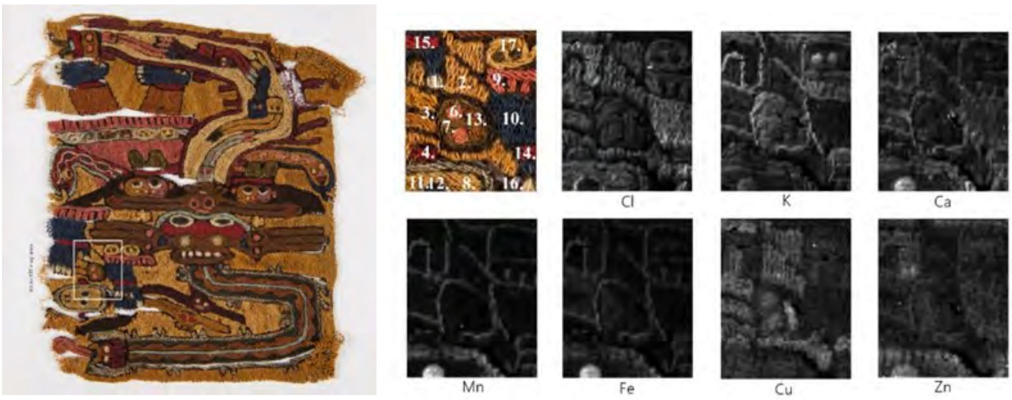
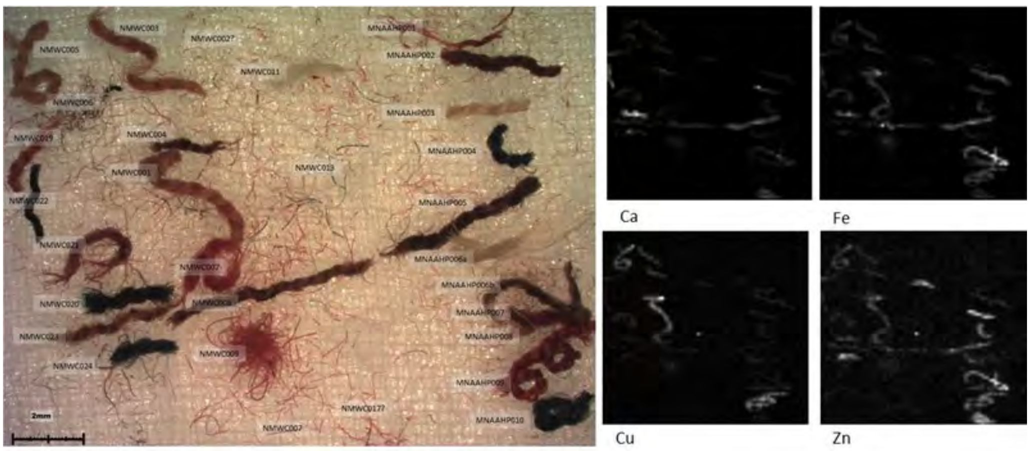
A selection of Peruvian Paracas textiles was investigated using micro-XRF mapping and SEM-EDS. Mordants and other auxilliaries in dyed textiles are notoriously difficult to analyse and very little such work has been carried out on textiles from the ancient Andean cultures. Elements detected by XRF or EDS are often present all over the textiles and difficulties with quantification of results from point analyses typically prohibit a clear assignment of these elements to either contamination or inherent components of the textiles. It is only when mapping the distribution of inorganic components across the textiles that their relative quantitative levels can be correlated to colours. Some trends and even more disparities were observed from the XRF-mapping results of five textiles and twenty two thread samples; for example chlorine was sometimes strongest in the blue areas, while iron, magnesium, potassium, calcium and strontium were often associated with browns and blacks. Copper was a common mordant for red and pink but also some yellows, greens, browns and black. Nickel was found only in one pink and one black area. Zinc was mostly detected in light coloured areas of grey, white and beige, some of which had previously been deemed undyed, implying the possibility that now-faded fugitive dyes had once been present or that batch mordanting was used even for threads that were then left undyed. Aluminium, as the historically most important mordant, was detected by SEM-EDS and shown to be present at higher levels in camelid fibres when compared to cotton fibres. The evaluation of results from SEM-EDS versus XRF will be discussed. In addition, a comparison of the physical condition of thread samples to their XRF results was attempted and will be discussed.





The dark-side of polyphenols in medieval manuscripts: a study on iron gall inks

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Iron gall inks were used to write the medieval codex, substituting, in part, carbon black inks that were more prone to detachment [1]. The origins of this writing ink-making process get lost in the depths of the most ancient records of the history of human civilizations [2]; the formation of intense blue black complexes was obtained by adding iron salts to specific plant extracts such as of *Quercus infectoria*. The catechol with 2 OH or galloyl with 3 OH groups present in phenolic compounds provide binding sites for metal ions to chelate, Fig. 1. In this presentation, we will discuss the chemical structures of these complex polyphenol systems used to write the medieval book and the analytical challenges posed to an accurate description of a medieval ink. We will analyse references by HPLC-DAD-MS, Raman microscopy and microFourier Transform Infrared Spectroscopy. References will include both iron complexes with tannic acid, gallic acid, mono and digalloylglucose as well historically accurate reconstructions of medieval inks.

Our preliminary studies show that free gallic or tannic acid are minor components in the gall extracts. This means that research strategies focused on the study of gallic acid or tannic acid as standards for galls, which are found largely as polygalloyl esters of glucose, may not lead to molecular structures representative of the colorants of iron gall inks, Fig. 1 [3]. Based on historical accurate reconstructions of medieval inks we will also discuss the causes of its colour. These results are part of the project "Polyphenols in Art: chemistry and biology hand in hand with conservation of cultural heritage".

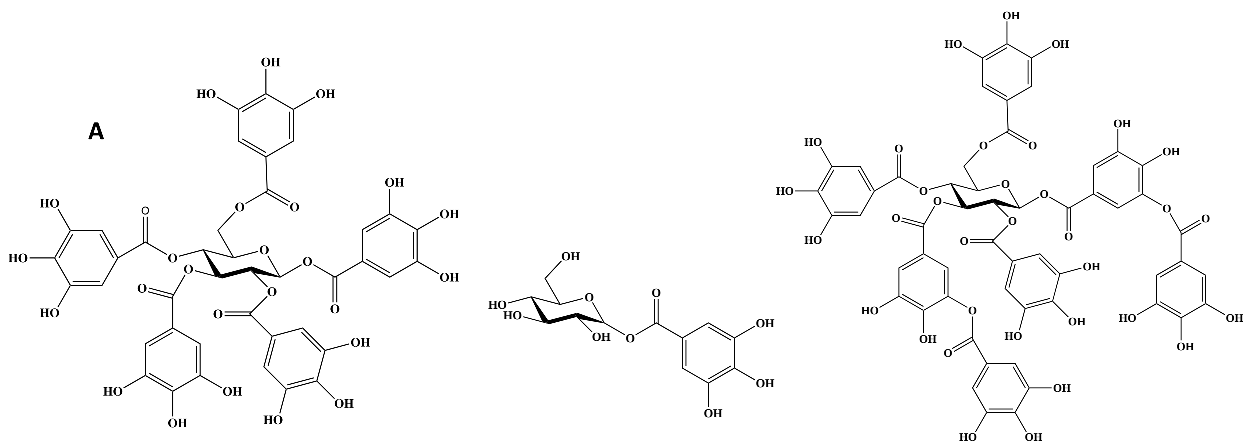

Figure 1. Polygalloylesters of glucose: A-Pentagalloylglucose; B- Monogalloylglucose; C-Heptagalloylglucose

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Interaction of paper and early synthetic dyes on textile sample books

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In the sample book “BASF Indigo Rein” a colouration of the paper when in contact with the textile samples can be observed.[1] The study of this phenomena was topic of my Masterthesis at the Cologne Institute of Conservation Sciences, TH Köln. [2]

It deals with the interaction of paper and early synthetic dyes on textile sample books of the BASF, MLB -Hoechst and other dyestuff companies from the mid 19th to early 20th Century. These books document the wide range of early synthetic dyes, their making, supply and use. The dyes where present on all kind of natural and early man-made textile fibres.

In order to develop adequate conservation strategies, it was necessary to gain a deeper knowledge on the materials and the observed alteration. No relevant published research on this topic exists. This work will provide the first step to find suitable conservation strategies for this group of sample books.

The phenomena where observed in several examples dated from 1898 to 1914, as well as in in cases of older and younger books. No examples where found in in the case of sample books related to natural dyes. Typical reaction pattern – partial ageing of the paper and migration of the dye - will be presented in detail.

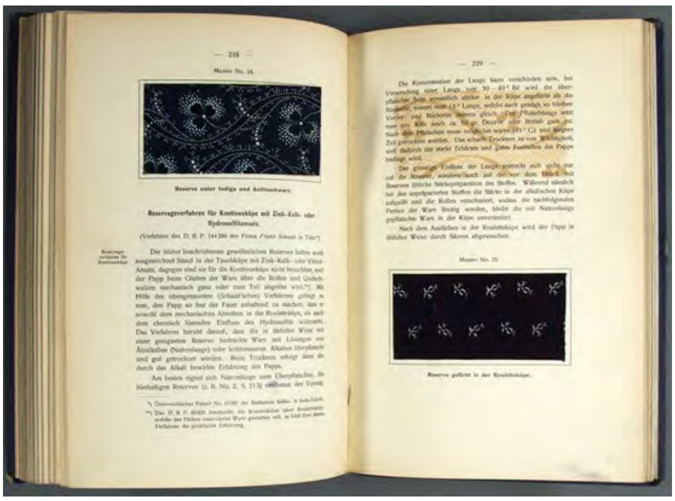
In the Book “BASF – Indigo Rein” up to 56 % of the samples shown a visible Interaction with the paper. In other Books from Piquet, Bayer and MLB – Hoechst it varies from 6 to 55 %.

Aniline black and Alizarin red were always shown a visible interaction with paper and they will be the focus of this presentation. Aniline black dyes cause a brown discoloration and possible local alteration of the paper. Alizarin red dyes shown a migration of the dye from the textile sample into the paper. The phenomena is observed in both dyed and printed textiles. It is suggested that the storage conditions of the books have a significant influence on the phenomena.

A dual strategy was developed to better understand the phenomena. On the one hand minimally invasive analysis of the materials and the discoloration was carried out. The changes in the paper and textiles where studied with FTIR-ATR, XRF and SEM-EDX. The FTIR results were interpreted in light of existing research on cellulose ageing [3]. No obvious change in cellulose chemistry could be observed. XRF of intact and discoloured paper excluded the presence of any metals which could be the source of the discoloration.

On the other hand ageing tests were carried out on suitable reconstruction. Aniline black-samples on cotton where reproduced with different washing parameters. They underwent accelerated ageing in combination with paper. After 6 weeks at changing temperature and RH, a reaction was visible under UV light in some samples. The results will be here presented and discussed.

Figure 1. Local ageing reaction of the paper on the contact site of the sample book “Indigo Rein” of the BASF. [2] Dyes: Anilin black with Indigo and White Reserve.



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Investigating the degradation pathway of xanthene dyes in textiles

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Xanthene dyes and pigments are aromatic compounds derived from the molecule of 9H-Xanthene and characterized by intense fluorescence and photosensitivity. Rhodamine B and Eosin Y are two molecules belonging to this class. The former was firstly synthesized by Cérésole in 1887 [1] and widely exploited ever since to dye in violet. In fact the addition of substituents gives rise to a complete class of red and violet pigments [2]. The latter was synthesized by Caro in 1873 [3], and was usually precipitated with lead and aluminum salts and employed for brilliant pink-scarlet coloration.

This work aims to investigate the degradation pathways of Rhodamine B and Eosin Y due to the aging and fading within textile matrix. An ultra sensitive analytical method based on HPLC-DAD-FD-MS techniques and making use of a novel C18 solid silica core column (Poroshell 120 EC-C18) was developed and optimized. The analysis of artificially aged wool yarns mock-ups, provided by IPERION network [4], allowed us to study the mechanism and the kinetic of degradation on the base of the different products and their relative amount detected in samples subjected to different irradiation times.

Tandem mass and UV-Vis spectra allowed us to demonstrate that Rhodamine B incurs in subsequent functional groups losses and in a blue shift of the maximum absorbance of the degradation products. Interestingly, the ageing pathway has been confirmed by the analysis of a restored Florentine velvet cope dated to XV century and belonging to the Musée des Tissus de Lyon (France).

For what concerns eosin, the oxidation mechanism, already hypothesized for painting matrices and presented at DHA 35, has been evaluated also in textiles. Moreover, the redox behavior of eosin, including both oxidation and reduction, has also been investigated by electrochemical methods at the Heyrovský Institute of Physical Chemistry in Prague. Cyclic voltammetric analyses at glassy carbon electrode were performed in order to understand the mechanism of oxidation and reduction of eosin at variable pH. Exhaustive electrolysis on carbon paste electrode allowed us to isolate possible end-products and to analyze them by HPLC-DAD-FD-MS. These insights are fundamental to completely evaluate the various parameters affecting eosin ageing behavior in artworks.

The presented multi analytical approach combining spectrophotometric and spectrometric techniques with electrochemical ones has revealed to be a powerful strategy in order to shed light on the challenging photo-fading processes of xanthene dyes within highly complex and textile matrices.

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Synthetic dyes of the 1980s: a new multi-analytical approach to the isolation and identification of ACNA wool dyes

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In the last years, the scientific research has moved its attention also on the identification of synthetic dyes; in fact, it is now undoubted that not only ancient dyes and historical textiles should be restored and be object of conservation program, but also contemporary materials and their dyes have to be considered part of our history. Their conservation is fundamental (1). It is obvious that in contemporary art the materials used have been the most varied and, moreover, for what concerns the dyes employed, subjected to the great variability due to the development of new synthetic products. Thus, it has led to an enormous number of possible colourants, which could have been used.

For this reason, the opportunity of studying the dyes synthetized by one of the most important Italian industries (the ACNA, Azienda Coloranti Nazionali e Affini, active from 1929 to 1999 in Cengio –SV- and other Italian sites) can represent an important way to obtain or, better, to collect a database to which refer to when it would approach to contemporary dyed materials (2). Starting from the assumption that not all these dyes can be studied in a single work, this paper would propose and test a multi-analytical approach applied on dyed wool produced by ACNA in order to achieve the goal of the certain identification of these dyes. Together with this aim, the acquisition of data through no invasive techniques, such as the Surface Enhanced Raman Spectroscopy, is linked to the opportunity of collecting data, useful when it has to approach to art materials, available as very small-scale samples. In this work, five samples were studied, coming from ACNA tests and prepared in the 1980's.

First of all, SERS on fiber analysis has been performed, in order to obtain a spectroscopy fingerprint of each dye employed. After that, in order to recover the dye, the innovative ammonia extraction method has been applied (3). This extraction protocol, initially thought and developed only for natural dyes, is for the first time applied on synthetic dyes, in order to evaluate also its applicability to the different class of dyes present.

Once applied the extraction protocol and obtained the residue of each dyed yarn, the samples have been subjected to the multi-analytical approach for their identification. Chromatographic separations have been performed in order to purify the products that compose the dye. After that, the fraction containing the isolated compounds have been subjected to a series of spectroscopic analyses. Mono- and bi-dimensional NMR experiments (^{1}H, ^{13}C, COSY, TOCSY, HSQC, HMBC) have been performed and the data obtained have been later got together whit those coming from FTIR experiments. Finally, the identification of these compounds has been achieved comparing the MS spectra with the information present in Colour Index, which has allowed identifying thoroughly the dyes employed.

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Determination of the distinguishing characteristics of Italian and Ottoman velvets

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This study was performed on velvets believed to have originated from the 16th and 17th centuries in Topkapi Palace Museum. It was unknown whether these velvets were produced by Ottoman Culture or Italian Culture [Figure 1]. In order to support this study, velvet production studies were performed and compared to known Ottoman and Italian velvets. The dye, string, metal threads, and techniques belonging to Ottomans and Italians were used independently for each study. All results obtained were compared to the original findings of Ottoman and Italian literature.

The results of this study indicate that these velvets indeed originate from the 16th and 17th centuries in Topkapi Palace Museum. It is however unclear if they originated from Ottoman or Italian production.

Figure 1. Topkapi Palace Museum (inventory number 13/1918).

DYE ANALYSIS OF WOOL FABRICS BY USING HPLC-DAD

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This study was carried out in an ongoing research within the scope of textile conservation process on woven wool fabrics (which are called as Gürün wrap) obtained from the Ethnography Museum in Ankara. The Ankara Ethnography Museum was opened in 1927 with the attempt of Mustafa Kemal Atatürk. Turkish folk clothes and belongings from the Seljuk period until the present day compiled from various regions of Anatolia are exhibited in the Ankara Ethnography Museum.

The poster presentation aims to establish, dye analysis of two historical wool fabrics. In order to detect the dye sources of the fabrics, HPLC-DAD method was used for yarn samples. The dye extractions were carried out with 37% HCl/MeOH/H_2O (2:1:1 v/v/v) mixture. Dye compounds, which were identified for yarn samples according to the HPLC analysis, are as follows:

Fabric 1; Carminic acid, flavokermesic acid, laccaic acid-D, indigotin and synthetics,

Fabric 2; Flavokermesic acid, laccaic acid-D, indigotin and synthetics.

Both natural and synthetic dyes were used for these two fabrics. According to these results it can be concluded that the fabrics belong to late 19th or early 20th century.

Fig. 1: General appearance of fabric 1

Fig. 2: General appearance of fabric 2

Mass spectrometric analysis of arylcarbonium blue, violet and green dyes: unlocking structural differences though data mining

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The synthesis and production of triarylcarbonium dyes, such as methyl and crystal violets, diamond green, magentas, etc. started in the late nineteenth century and is still ongoing. As highlighted by studies dealing with the composition of dyed patterns in historical dyeing manuals for the early synthetic dyes [1] or with the assessment of the photo-fading of inks prepared with such dyes [2], they consist of very complex mixture of homologous species, often differing only in the presence or position of the same substituent on the aromatic rings. The separation and PDA detection of the single species composing the dyes is of paramount importance for the comprehension of the synthesis and production strategies – still, the confirmation of the nature of the individual components can only be achieved if tandem mass spectrometric techniques are applied and can solve structural issues [3].

This poster presents the results obtained by the analysis of historical samples (available thanks to the Dye-vesity project [4]) and dyed replicas, also subjected to artificial ageing (available through the IPERION network [5]). The strategies used to differentiate the compounds under study and to exploit them to differentiate homologous series will be presented, along with a proposal for a general database of mass spectrometric data of this class of dyes.

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Developing a protocol using FORS for the selection and study of historical textiles in the Victoria and Albert Museum

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The Victoria and Albert Museum holds one of the largest and most varied textile collections in the world, ranging in provenance from China to the Americas and in date from Antiquity to the 21st century. Selecting textiles for study, even within the framework of a well-defined project, can thus be challenging. This is particularly true if the identification of the natural dyes that compose the pieces is pivotal to the study, as presently the most powerful techniques for the characterisation of natural dyestuffs (such as HPLC [1] or SERS [2]) are reliant on sampling these precious objects. A means of non-destructively optimizing this process is desirable, both as a survey to aid in the selection of potential candidates for further study and to limit unnecessary damage as a result of redundant sampling on valuable pieces.

Fibre optic reflectance spectroscopy (FORS) in the visible region of the electromagnetic spectrum has been shown to be a useful, non-invasive technique for acquiring preliminary information on the natural colourants present in historic textiles [3]. The approach is portable and sufficiently safe to be carried out *in situ*, directly on the textile fibres. In addition, it provides information in real time, allowing conservators, curators and scientists to make rapid and informed decisions during the course of a survey.

This work, carried out in collaboration with the British Museum, describes how this methodology has, for the first time, been developed into a protocol for the selection of textiles from the V&A's textile collections. Two studies are here presented, aiming to investigate the possible technology transfer from Turkey to Italy and Spain in the production of ~~embroidere~~d velvets from the late 14th to 16th centuries and to identify the provenance of Late Antique and Medieval textiles from the 7th to 12th centuries. In the latter case, the classification of the textiles, as "Byzantine", "Sicilian" and "Spanish", has to date only been assigned on stylistic and iconographic grounds. Many other factors, such as fibre characterisation, textile weave, and, in the case of the velvets, the nature of the metallic threads used as patterning wefts, are of course fundamental to these investigations. However, in both cases, the identification of dyes is of great significance to either determine or disregard a possible place of production.

As a result of the adopted selection protocol based on FORS analysis, some areas of interest were chosen from a reduced number of pieces for sampling and further investigation by HPLC-MS. By default, the FORS measurements simultaneously provided preliminary data on the textiles that were not selected.

An overview of the final results comparing the invasive and non-invasive analyses is presented and the potential and limits of the protocol, as applied to the group of textiles investigated, is discussed.

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Analysis of natural dyes in historic textiles using Flowprobe™-ESI-HRMS

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In the last decade, techniques based on direct mass spectrometry such as MALDI-MS (matrix-assisted laser desorption/ionization mass spectrometry) [1] or TOF-SIMS (time-of-flight secondary ion mass spectrometry) [2, 3] became popular for the characterization of organic dyestuffs in historic textile samples. These techniques enable dyestuff analysis directly from the fiber. However, MALDI-MS and TOF-SIMS experiments are performed under vacuum conditions and require a suitable sample fixation and preparation prior the measurements. In addition, aspects such as the microscale topography of the sample as well as the sample mounting can influence mass accuracy, mass resolution or ion yield [1, 4, 5].

In contrast, many ambient MS techniques allow a rapid and direct sampling of uneven and rough surfaces under ambient conditions without or with minimal sample preparation. Since the introduction of the DESI (desorption electrospray ionization) technique in 2004, this research field has developed very rapidly, with various applications in life sciences. However, in the field of archaeometry ambient ionization techniques are rarely used.

In this study we present minimal-destructive analyses of anthraquinone- and indigoid-type dyestuffs under atmospheric pressure through real-time *in situ* microextractions of fibers by flowprobe™-ESI-HRMS (electrospray ionization high-resolution MS) [6]. This setup combines a commercial LMJ-SSP (liquid microjunction surface sampling probe) device and an Orbitrap mass analyzer equipped with an ESI source and allows the detection of natural dyes in tiny fragments of historic textiles without any extra and time-consuming sample preparation or a sophisticated sample fixation. Moreover, this technique is useful for the analysis of various types of textiles regardless of the fiber material, the 3-D shape of the sample (e.g. unspun fibers, single yarns or plied yarns) and the state of preservation. Moreover, the complete analysis takes less than 5 minutes.

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Developing Black color by Natural Dyeing for Contemporary Fashion

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The aim of this study is to develop an effective dyeing method for black color, using natural Indigo, Madder, Amur cork tree, Alder fruit, Logwood and Gallnut on the silk, wool and cotton fabrics. All natural dyestuff were water-extracted, concentrated and powdered. The color difference (ΔE) from the chemical black dyed on the same fabric was compared.

The profound black color on the silk fabric could be obtained by the subtractive mixture of the three primary colors of red, yellow, and blue in the order of Indigo(blue) - Amur cork tree(yellow) - Madder or Lac (red). The color difference (ΔE) from the chemical black was the lowest in the Indigo - Amur cork tree - Lac - Iron method.

The black dyeing of the wool fabric was carried to obtain excellent black color by subtractive mixing of the three primary colors. Especially black color could be obtained in the order of Indigo(blue) - Madder or Lac (red). In the subtractive mixing method, black dyeing was possible without Iron mordant at the end. The color difference (ΔE) from chemical black in the wool fabric was the least in the Indigo - Lac - Iron method.

Black dyeing on cotton fabrics was more effective, when the Logwood, Logwood + Alder fruit and Alder fruit dyeing were repeated twice. The dye samples were darker black color and increased in K/S value. In the cotton fabrics, black color was not obtained by subtractive mixing of the three primary colors. After the blue(Indigo) dyeing, either yellow(Amur cork tree) or red(Madder or Lac) color was not dyed on the fabric in each dyeing step. The color difference (ΔE) from the chemical dyed black was lowest in Logwood - Iron method.

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Use of Natural Colorants Mixture for Hair dyeing

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Abstract

Natural colorants are attracting globally because they are lower toxic and more eco-friendly than synthetic dyes. However, they have many limitations on color range and fastness properties to washing and light [1,2]. To overcome this problem related to application onto hair dyeing, we applied wool to get optimum condition. Wool is sometimes used as the substitute of human hair because they are very similar in morphological and chemical structure. We tried to get wider color spectrum by using mixed colorants. And it could be applied to hair dyeing.

We selected sappan wood, amur cork tree, gardenia fruit blue, logwood were selected to obtain red, yellow, blue, and brown shades. Various natural dyes and the mixtures were dyed at some conditions. Compared with dye uptakes of wool and hair dyeing, the optimum condition of wool dyeing was adopted. Human hair dyeing onto bleached sample was applied as follows; coated with the mixed paste, wrapped in aluminium foil, and then kept in an oven at 40□ for 30min. Dyed hair samples were analyzed by UV-Vis spectroscopy, colorfastness to light and washing. As a result, reasonably good dye ability was shown on wool and hair. Compared with sappan wood and logwood, K/S values of wool were a little lower than human hair when gardenia fruit blue and amur cork tree were used. The use of colorant mixtures enables human hair to get wider range of color spectrum than that of single ones. In Munsell hue diagram, better linearity in hue was obtained by controlling dyeing conditions including concentration and additives.

Keywords: Natural hair dyeing, Color property, Munsell system, CIE system, Colorfastness

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Benzopyran Natural Colorants for Black Hair dyeing via Metal Chelation

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Abstract

As the substitute of synthetic black hair coloring materials, we focused on benzopyran natural colorants as known as a pleochroism dyes which forms coordination complexes with metal ion. The reaction between the ligand and the exchanged metal forms a metal-chelate complex immobilized on the surface of the fiber [1]. It causes a bathochromic shift of the color of dyes and other compounds whose chelating groups interact with the π-electron system of aromatic rings. As a result, different colors are obtained depending on the metal and the ligand [2].

We selected sappan wood (brazilin) and logwood (hematoxyilin) to represent benzopyran based colorants. Bleached hair sample was coated with the mixed paste, wrapped in aluminium foil, kept in an oven at 40□ for 30min. Dyeing properties and color fastness were comparable with the type of mordants ($FeSO_4$, tannin) and dyeing condition such as time(5~60min) and temperature (20~100□). The colorants of the sappan wood and logwood by water extraction showed maximum absorption wavelengths at 445 and 450nm. They were shifted to 520 and 545nm with the addition of ferrous sulfate. Black color obtained in this study was less than 7% in surface reflectance. Light colorfastness of the dyed hair was relatively good; the rating 4 was maintained up to 100 hrs. And the rating to washing was maintained 5 up to 30 cycles.

Keywords: natural hair dyeing, sappan wood, logwood, benzopyran, color measurement

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HPLC-DAD-MS analysis of 19th century artistic paints belonged to a famous Polish painter, Jan Matejko.

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The protection of cultural heritage requires familiarization with the technologies related to the artist's workshop and thus become intimately acquainted with the materials used to create a given artefact. The identification of materials used plays an important role in the scientific investigation of works of art. The characteristic features of specific art works can be defined based on those materials. Moreover, a precise determination of material composition leads to the information about the technology used in the creation of artistic objects and their history. Natural organic dyestuffs are components of many objects of cultural heritage.

The identified organic dyestuffs present in the paints are one of the helpful parameters used to characterize the painter's workshop. This poster presents results of identification of organic colouring substances, which are components of paint palettes belonged to a famous 19th century Polish painter, Jan Matejko. Liquid chromatography-mass spectrometry with atmospheric pressure negative electrospray ionization LC-ESI(-)-MS was successfully applied for identification of the main components in these artistic paints. LC–MS was also employed to analyse selected reference dyestuff samples. Based on the identified colouring substances, it is possible to establish which dyer raw materials had been used for the production of the paints. The isolation of dyestuffs from such matrices is a difficult task without changing their original structure. The use of mild extraction procedure plays important role in proper identification of the dyes. An improved mild extraction method with hydrofluoric acid enabled the intact dye fingerprint in paint samples.

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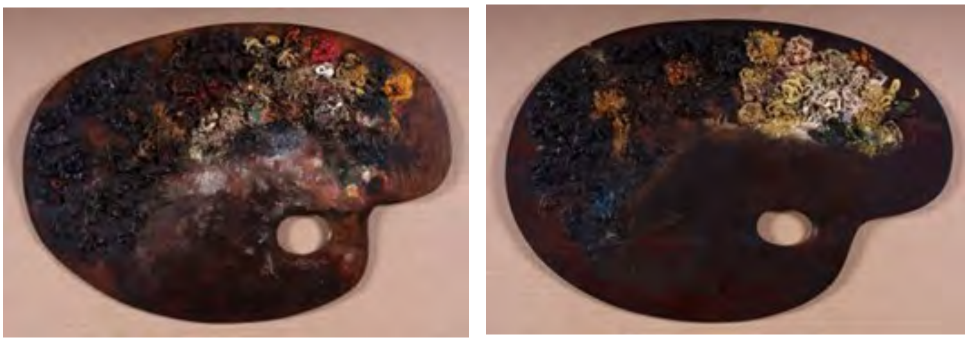

Figure 1. Paint palettes belonged to a famous 19th century Polish painter, Jan Matejko

Dye analysis of medieval Nubian textiles (Sudan, 13th c.)

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The poster will present the first results of dye identification in medieval textiles from Sudan, applying HPLC-MS method, with a focus on an innovative method to identify more precisely the indigo provenance. The presentation will show also how the dye analysis, in association with technical analysis, can provide interesting information about long-distance trade.

Figure 1. Fragment textile from Meinarti, 13th c. (Sudan National Museum, inv. SNM 18130)

In search of "lost yellows": identification and occurrence of ancient polyphenol yellows in Portuguese plants

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Yellow dye plant sources were systematically studied in the past ten years and advances in our knowledge are linked to the development of new extraction methods of dyes from artworks as well as to the advances in mass spectrometry techniques. Research coordinated by R. Laursen on the characterization of yellow dyes in ancient textiles can be described as a landmark [1,2]. These recent works [1-4], delivering full molecular fingerprints, provided further support for the hypothesis that yellow dyes are more regional than reds or indigo blues.

This state of the art offers the framework for the quest of “lost yellows” in medieval illuminations, a term coined by Mark Clarke [5]. Clark argues that colours we presently perceived as "colourless" could have been originally bright yellows obtained from a plant source, possibly regional. To assess this hypothesis, medieval yellow paints were produced, using extracts from a representative selection of plants found in Portugal, collected in botanical field expeditions [flora-on database] and their stability to light assessed. First data obtained, including yellow chromophores profiled by HRMS (High Resolution Mass Spectrometry), will be presented in this poster. To confirm the use of these yellows we have relied on “Natural Dyes. Sources, Tradition, Technology and Science” by D. Cardon [6].

Stability to light can be accurately measured through quantum yields of reaction. These values will enable us to discuss the assumption that natural yellow dyes are more or less light sensitive than anthraquinone reds, indigo blues and brazilwood lake pigments. All chromophores that we have systematically found in medieval illuminations are in good conservation condition [7]. If these yellows will display similar photodegradation quantum yields, then we will need to revise our previous assumption on “lost yellows”.

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“Persian yellows”: A survey of Iranian literature

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Persian carpets have experienced growth and development in quality and aesthetic features along with the progressions in culture and civilization within the past centuries. The color is an important element that articulates the unique patterns of Persian carpets and ascertains its identity. Therefore, it is most important to consider the period and the region of a historical artifact like carpets while investigating the origins of the dyes and dyeing method. In this poster, we have focused on the literature of yellow dyes to explore their application in Persian carpets.

Because there are few Persian books in which, the authors have mentioned the names of the dye-plants, the main sources for our research are the oral sources from the dyeing experts that are still operating in the rare dyeing workshops in Iran. We have also surveyed existing references about the history and techniques of carpet dyeing in Iran such as [1][2].

According to our systematic research, natural sources of yellow dyes can be categorized into three groups: *1)* Plants mentioned in non-Persian references as yellow dye sources in Iran; such as, a study by Böhmer *et al.* declared larkspur (*Delphinium sembarbatum*) as the most frequent plant [3] and Mouri *et al.* have also revealed the probable use of tamarisk (*Tamarix* sp.) in a historical textile [4]. Our investigations did not find evidence of their applications in today’s Persian dyeing techniques; *2)* Dyes that are widely mentioned as the main sources of yellow color in non-Persian references and have been used in Persian dyeing workshops for a long time. Cardon describes the application of weld, in and outside Europe, which is also an important source of dyeing in Iran [5]; *3)* Yellow dyes are widely used in Persian dyeing workshops which are also mentioned in Persian references, but for which there is no evidence of their application in other regions and in non-Persian references. White mulberry (*Morus alba*) or grape (*Vitis vinifera*) leaves are examples of this group of Persian dyes.

The experimental design to assess the stability of these yellow dyes will be also presented. In the end, this study will contribute for a better understanding of dyeing methods for yellow colorants in the history carpet weaving in Iran.

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Identification of organic dyes in the assemblage of women's garments from the early17th century discovered at the Benedictine Church of Sopron

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In 2010, during the reconstruction of the Benedictine Church in Sopron (Hungary), a wooden coffin was discovered under the stairs of the crypt of Family Viczay. The location of the grave and the richness of the women's attire with metal threads found in it suggest that the person buried here was a member of a prominent family. The specialty of the artwork is that it is not possible to find clothes of this age and style, only those of the highest layer of the aristocracy that were found in Hungarian collections. Only pictorial representations and estate inventories have proven their existence. The inventory of 27 items consists of several larger units:

- the overgown worn by the buried lady
- the bodice of the overgown
- cape which was placed folded on the deceased in the coffin
- golden plated silver belt
- remains of embroidery, the base fabric of which was broken down and presumably used to decorate the deceased's shroud
- several pieces of garment fragments found under the corpse but not matching in style of their original clothing (fur)

In-situ removing and disassembly of the find [1], material analysis [2], analysis of manufacturing techniques [3], state/condition assesment and conservation [4], involving several museums and research institutes, has been achieved through extensive collaboration. There were two reconstructions on the garments in different colours (traditional reconstruction in black, digital artwork "archeological brown"). Despite the examinations carried out, however, the original colour of the subject remained questionable. In 2016, it was possible to further investigate the object, aiming to prepare the colour of the suit on the basis of the results of dye analysis.

The uniformly brown fabrics were dirty, incomplete, mouldy, torn, extremely fragile and deformed. Samples of the colouring tests have been taken from 17 sites so far, which were first tested with SEM-EDX for the determination of the fibres in question and the inorganic components. Based on our results, on the wool and silk fabric, copper sulphate or potassium aluminium sulphate were used as mordants. After the extraction of the samples available, HPLC-MS/MS was used to identify the organic dyes, which resulted in the determination of plant dyes. A small amount of the sample (0.1 mg) and the degree of degradation of some parts didn't make our work easier, in such cases, the solution had to be concentrated.

During our work, we managed to identify alizarin, purpurine, xanthopurpurine and munjestin among the various pieces. In comparison to the results of the material tests carried out, we made an attempt to prepare the colour reconstruction of an unique find in Hungary, with the results of the measurements of the reference sample compiled in parallel with the examination of the artwork and cultural history descriptions.

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Preparation of Biocatalyst for Indigo Reduction and Its Application

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The aim of study is to prepare biocatalyst, dried bacterial cultures, originally isolated from naturally fermented indigo vat. Ultimate objective is to develop the eco-friendly indigo reduction process to solve the problem of environmental pollution of indigo chemical reducing process. Bacterial communuty of the naturally fermented vat was deduced by metagenomic approach [1]. Four bacterial strains were isolated based on the community analysis and their indigo reducing ability was investigated. Four bacterial strains - *Dietzia* sp. KDB1 (KC433534), *Nesterenkonia* sp. KDB2 (KC433535), *Nesterenkonia* sp. KDB3 (KC433536), and *Nesterenkonia* sp. KDB4 (KC433537) - were classified to be facultative alkaliphilic organisms and reduced indigo at around pH 10-11. These bacteria strains should be cultured every time when being used for indigo reduction dyeing, which is inefficient practically. It is necessary to explore ways to make bacterial cultures being used more conveniently and efficiently for storage and transport as well as for dyeing. So, we prepared dried bacterial cultures by freeze-drying (lyophilization) method. To reduce cell damage of bacteria during lyophilization, cryoprotectants such as starch, sucrose, dextrin, trehalose, etc were used [2]. The survival rates of dried bacterial cultures were measured according to storage time and type of cryoprotectant [3]. The indigo reducing ability of the dried bacterial cultures was measured and compared to find optimum cryoprotectant for practical use. It was confirmed that using cryoprotectant, bacterial cultures could be preserved in dried powder state up to 150 days with high survival rate. Therefore, it is considered that alternative eco-friendly biotechnological process can be developed using bacteria isolated from traditionally fermented indigo vat.

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A Dyestuff Database for the Analysis of Natural Dyes in Textiles

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During the past dozen or so years we have analyzed, using HPLC with tandem diode array and mass detection (HPLC-DAD-MSD), several thousand samples of plant and animal dyestuffs and dyed textile samples, both textiles dyed with known dyestuffs and textile specimens containing unknown dyes from archaeological sites, museums and private collections. Our particular interest has been identification of the probable sources of colorants in ancient textiles (>1000 years old) that were produced before international trade routes were well established and/or for which there are few written records.

Primarily included in this compilation are dye sources that produce the primary colors, blue, red and yellow, from which most secondary colors and various hues can be obtained. Excluded are browns and blacks, for which useful analytical methods do not yet exist. There is only one blue dye—indigo—and although there are many species of plant that produce indigo, there are no methods so far that can identify plant source of indigo. There are a number of red dyes, the light-stable ones being anthraquinones, from species of madder and certain scale insects. By far, the color having the largest number of sources is yellow, which is also found in green- and orange-dyed fibers. Sources of yellow include the flavonoids, protoberberines and some others. Of these, the most numerous are the flavonoids, which are present in all photosynthesizing plants, and of which over 8000 have been characterized chemically. Most flavonoids are glycosides, and key to identifying the source of flavonoids are mild extraction methods that keep the glycosides intact. Also, because most flavonoids have similar UV-Vis spectra, molecular mass detection is essential, although even mass spectrometry cannot completely characterize every flavonoid. Since dyers, at least in ancient times, tended to use whatever was available locally, yellow dyes are especially useful in identifying where a particular textile (or yarn) was dyed, since most yellow dyestuffs have distinctive patterns, or “fingerprints,” of components.

For yellow, although flavones from plants such as weld and sawwort were widely used in Europe, flavonols, specifically flavonol 3-O-glycosides, were often used elsewhere; for example, from pagoda tree buds in China, yellow larkspur in Central Asia and jashir in Iran. Protoberberines seem to have been used more widely in Japan and China than in the West. Flavone dyes derived from grasses and poplar leaves appear to have been used in Japan and the Tarim Basin, in Xinjiang, China, respectively. Plants containing chalcones seem to have been used more frequently in South America.

The most common red dyes are derived from species of madder and their relatives, specifically, *Rubia tinctorum* from Europe through Central Asia and the Middle East, *R. cordifolia* in southern Asia, *R. akane* in Japan, and species of *Relbunium* in South America. These can generally be distinguished by HPLC analysis. Anthraquinones from insects were also used.

Included in this database are HPLC profiles of plant and dyed textile extracts and UV-visible spectra of representative components, along with tabulated retention times, electronic spectral and molecular mass data, and putative identification of components. In addition to these data, separate sections discussing the chemistry of the dyeing process and dye analysis methods are included. It is our intention to make this information available to all on-line, at no cost. In the meantime a preliminary version of the database and other information can be obtained by writing to <laursen@bu.edu>.

Cloister gardens. Dyes used in embroidered hangings from the Church of the Benedictine Nuns of the Blessed Sacrament in Lviv

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The National Museum in Warsaw has an interesting set of nine hangings from the church of the Benedictine Nuns of the Blessed Sacrament in Lviv. The textiles are embroidered in wools and silks in *petit point* and satin stitch on the linen canvas. Each hanging is decorated with floral motifs and a likeness of a man in Polish cloth or a finely coiffed woman. It is believed that the wall hangings were embroidered by nuns in 1720s for their newly founded church. Dye analysis carried out on the silk and wool samples revealed an extraordinary richness of dyes [1]. This result encourages us to consider whether the hangings were really embroidered in the local workshop in Lviv. The textiles were studied in preparation for an exhibition devoted to the problem of color in art which will be held at The National Museum in Warsaw in 2018.

Some more dye analysis on 19th-20th century Romanian ethnographical textiles

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Identification of natural dyes in Romanian 19th-20th century ethnographical textiles was first made in 1997, within a joint research between local institutions and the Royal Institute for Cultural Heritage in Brussels (KIK/IRPA) [1]. The results, obtained by HPLC-DAD, demonstrated that local biological sources, imported natural dyes and synthetic dyes co-existed in the mentioned period. This assessment is in perfect agreement with literature [2].

In the present work, dye analysis on selected textiles from the same period, preserved in the ASTRA National Museum Complex, Sibiu are presented. The objects - blouses, cauls, belts, towels - are part of the Romanian traditional costume and are among the first to be acquired for the museum collections, around 1905 [3]. Oral and written sources mention such objects as homemade, with nearby materials. Apart from the esthetic value, the colorful handmade embroidery made by natural dyed silk and wool reveal a persons' statute while the use of cotton would indicate dating after 1900 [4]. The 19th century cauls and belts are worked in a unique technique of Sprang [5]. Fiber and dye identification indicate changes in the materials and technique. With a single exception, natural dyes were detected in these objects (cauls and belts).

Dye analysis were performed by LC-DAD-MS, according to a procedure described in detail in an earlier publication [6]. The main local dye sources identified are madder, dyer's broom, weld, young fustic, *Rhamnus* berries, emodin based dyes while the imported ones include *Caesalpinia* sp. and carminic acid containing insects. Early synthetic dyes, such as amido black, indigocarmin and Prussian blue were also detected.

The results obtained enrich the existing knowledge on the studied objects, underpin the conservation strategy and the display options and provide a better valorization of the Romanian traditional costume as witness of the rural society at the end of the 19th – beginning of the 20th century.

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Dye analysis of textile patterns for aniline colours in nineteenth century British dyeing manuals by UHPLC-PDA and LC-ESI MS

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Dyeing manuals published in the mid- to late nineteenth century helped industrial dyers produce consistent and desired colours on commercial textiles. These books gave valuable practical information about the new synthetic dyes, and authors often included dyed textile 'patterns' to show their colours. Multiple copies of historical dyeing manuals are now found in libraries and archives worldwide. If the patterns really were made with the dyes named in the text, these books and their material content would be reliable references for the synthetic dyes used in commercial textile production at the time. Such direct material evidence would greatly benefit current research to understand and identify these dyes and their colours in heritage dress and textiles collections.

This paper presents initial results from the 'Dye-versity' project, the first known systematic analytical study of dyed patterns in historical dyeing manuals for the early synthetic dyes [1]. Patterns linked to three groups of aniline (arylcarbonium) dye – magentas, violets and blues – in British dyeing manuals dating from 1862 to 1893 were analysed, first by ultra-high performance liquid chromatography with photodiode array detection (UHPLC-PDA) at the University of Glasgow following extraction with DMSO and oxalic acid [2], and then selected extracts by high performance liquid chromatography with electrospray ionisation tandem mass spectrometry (LC-ESI-Q-ToF) at the University of Pisa.

The UHPLC-PDA results revealed a characteristic component profile for each aniline dye group, and distinctive peak clusters that distinguished sub-groups like soluble and spirit aniline blues. Component clusters in the magenta, violet and blue dyes, and also dyes with red (R) and blues (B) designations in their names, had increasing component retention times and longer wavelength absorbance maxima. Such chromatographic behaviour and visible spectral properties can be explained by similar components with structural differences in extended side-chains and increasing conjugation through alkyl and aryl functional groups. This aligns with the industrial synthetic chemistry methods described in the texts of the historical dyeing manuals and similarly-dated publications for the commercial manufacture of the arylcarbonium dyes said to be in the patterns. When selected extracted pattern samples were further analysed by LC-ESI-Q-ToF, similar structural interpretations could be made [3], although further investigation is needed to confirm them.

In conclusion, initial analytical results for named aniline dyes said to be on textile patterns inside published nineteenth century dyeing manuals appear to be consistent with their expected chemistry and historical manufacture.

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Two Millennia of Controversy Characterising the Biblical Purples *Tekhelet* and *Argaman*

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The Hebrew Bible contains numerous references to the use of three precious dyed wools: *tekhelet*, *argaman* and *tola'at shani* [1]. *Tekhelet* and *argaman* are purples dyed with marine molluscs, the former a violet blue ('hyacinth purple') and the latter the reddish 'Tyrian purple'. *Tola'at shani* is kermes crimson.

The Talmud (Tractate *Menahot* folio 40) describes a bitter dispute in the Roman era over the fake dyeing with plant *qala ilan*, instead of molluscan *tekhelet*, for the ritual tassels *tzitzit* prescribed in Numbers (15:38), as a result of which that imperative was largely discontinued unless chemically authenticated to be of the molluscan source (*ibid*. folio 42b). But eventually, in the 7th century, this Jewish observance was completely discontinued, engendering a rabbinical debate as to whether the *tzizit* may be worn without any *tekhelet* cords attached.

Are there separate species of shell-fish that specifically produce only *tekhelet* or *argaman*, or are these two dyeings obtained from the same species? Following the acrimonious dispute over this issue between Bizio and Lacaze-Duthiers respectively in the 19th century, although the latter view has been adopted in some archaeological circles, the biochemistry of the relevant dyestuffs has substantiated the findings of Bizio, namely that *tekhelet* is the unique product of banded dye-murex (*Hexaplex trunculus)* [2].

Notwithstanding the recognition of this source for *tekhelet*, competing materials are still chosen by some for its supposed historical derivation, e.g. Prussian blue, or *Janthina* [3]. Furthermore, in the current commercial dyeing of *tzitzit* cords with banded dye-murex, the purple dyeing is inappropriately debrominated chemically to leave merely indigotin as the blue end-product!

Why do banded dye-murex dyeings with different catches vary in colour? Also, why do some individual banded dye-murex specimens in the same catch yield blues, and others purples [4]? The various hypotheses that have been examined for explaining these phenomena have not yielded as yet a satisfactory rationalisation.

Relevant too to the tint of the banded dye-murex dyeings, the distinguishing dyestuff present is mono-bromo-indigotin (MBI), which has been shown to undergo a thermochromic transition from purple to blue. While Ziderman *et al*. [5] have found that the transition also occurs in pure synthetic MBI, Ramig *et al*. [6] incongruously did not observe any change in colour on heating their MBI preparation.

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The Use of Organic Dyes in Indian and Himalayan Paintings on Paper and Cloth

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This presentation will trace the evolution of the use of organic dyes in Indian paintings, including miniature paintings in opaque watercolour on paper, Kalighat paintings, patua scroll paintings and Himalayan thangka's.

The most commonly used dyes in miniature paintings were red lac, blue indigo and Indian yellow. However, in the case of patua scrolls, a number of more obscure dye stuffs, derived from plants found growing wild in the states of Bengal and Bihar were used from the late 18th century until the arrival of prepared artists materials. These imported, prepared colours were either made from mineral pigments or were of synthetic origins. They were imported into Bengal by the East India Company from the mid nineteenth century onwards

The dye extracted from the lac beetle has been used as a colouring agent in Indian miniature painting from the Sultanate period onwards. It is extracted from the crushed bodies and the resinous secretion of the larva of the lac insect (coccus lacca) which feed on the leaves of the acacia tree. The red dye is extracted by crushing stick lac and extracting with hot dilute sodium carbonate solution, before precipitating the colouring matter with alum, or another suitable mordant. Lac is applied with a brush as a pale red colouring for under drawing in miniature paintings as well as being used in Himalayan Thangka's – Buddhist, devotional paintings on cotton cloth supports. Evidence suggests that lac has also been used for dying textiles since very early times throughout the Himalayan region.

Indian yellow is extracted from the urine of cows fed on an exclusive diet of mango leaves, which was used as a pigment by artists in India from Mughal times. It has great symbolic significance for any subjects which depict Krishna, or his consorts, as the bright yellow pigment/dye was considered especially auspicious. Indian yellow has a particular luminescence which made it very useful as both a colour in its own right and as a colour used as a ground or base colour below important areas of the painting to make them stand out. Indian yellow was only produced in very small quantities in the eastern state of Bihar. The production of Indian yellow was outlawed by the British in 1907, as the restricted diet caused the cow to suffer pain and occasionally death. It remained however a popular colour for painters of high quality miniatures due to its luminosity and brilliance.

Indigo is a dye which has been used as a colour in manuscript painting from the 11th century onwards. It has been found as a colouring material on Buddhist manuscripts on palm leaf and it is also found on Jain manuscripts on paper from the 14th century. It is unclear when Indigo dye was first made into a pigment for use by artists, although it has been used as a textile for dying cloth from very early times. The transparency of the dye leant itself to use as colour for both outlining and underdrawing in thangka paintings.. The fine particle size and high tinting strength of indigo made it ideal for mixing with orpiment to give a green suitable for depicting foliage. From Mughal times, indigo was also mixed with Indian yellow to make a green which was both luminescent and was less susceptible to fading and degradation from atmospheric pollution than green made from orpiment.

Fifty Shades of Purple

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After a quarter century of performing dye analyses on archaeological and historical colorants from various geographical regions, primarily from the Ancient Near East and especially from Ancient Israel, an incredibly colorful picture emerges of how the dyer and weaver succeeded in creating variegated shades of purple. From molluskan sources alone, various shades of reddish and bluish purples are possible. In re-constructing the colors of woolen “purple” dyeings produced in antiquity, by utilizing the same materials, methods, and tools available to the ancient dyer, one finds that the latter violet colors were produced from indigo-rich *Hexaplex trunculus* sea snails, while the redder purples were obtained from a dibromoindigo-rich *H. trunculus* species as well as from all other mollusks. Today, we can produce even more shades by, e.g., artificially photo-debrominating the reduced dye solution prior to the actual dyeing, a technique that could not, and would not, have been used in ancient times.

Combinations of different dyes can also literally shade the final color to produce a cornucopia of blues, violets, and purples. While the typical millennia-old combination of the classical red-madder and blue-indigo dyeing is already well-known to have been used to produce the common people’s purple, other surprising chemical and physical combinations have also been observed. Some of these involve over-dyeing or double-dyeing the same fleece with two different dyestuff sources, while others involve the plying of differently colored yarns. Why certain combinations were performed to produce the final color is still confounding and is seemingly nearly beyond reason. Other combinations are even anathema to the very heart of using a molluskan source in the first place.

These ancient dyers and weavers were indeed successful in producing a plethora of purples – at least 50 shades of purple. These colorful mysteries will be discussed in my presentation.

CHARACTERIZATION OF AN OTTOMAN SEVAYI FABRIC BY USING HPLC-DAD AND FESEM- EDX

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In this study, the analysis of dyestuff and metal thread samples of an Ottoman Sevayi fabric were examined by using HPLC-DAD and FESEM- EDX. Sevayi fabrics began to be produced in the 18th century. It is a typical Ottoman silk fabric which also includes metal threads. Sevayi fabrics were used in the making of woman's dress. The pattern of the fabric is formed by using little branched and leafy flowers embellished in an order, in spreading form or within a geometric schema. Branched and leafy flowers were woven with metal threads [1].

In order to characterize the dyes used for fabric RP-HPLC-DAD method was used. The dye extractions were carried out with 37% HCl/MeOH/H_2O (2:1:1 v/v/v) mixture. Dye compounds of the samples which were identified according to the HPLC analysis are as follows: picric acid and fuchsin. FESEM-EDX micrographs showed that metal strips had almost 279 μm width. Results indicated the presence of silver and copper as the components of the gilt metal. Furthermore, sulphur and chlorine determined as contaminants.

Fig. 1: General appearance of the Sevayi Fabric

Fig. 2: Detailed appearance of the pattern of the Sevayi Fabric

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Identification of Dyes in Archaeological Textiles Discovered on the Silk Road

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Dye analysis of these archaeological textiles was carried out by using high performance liquid chromatography coupled with mass spectrometer (HPLC-MS). The objects were discovered in four archaeological sites on the Silk Road. Madder, indigo and populus were likely used to dye woolen yarns from Zagunluk site dating back to 500 BC. Kermes, interestingly, one of coccid species which is native to South Europe [1] was found in a pink shroud of a mummy child (figure 1) from the site. In addition to the local plants such as madder (*Rubia tinctorum*) and populus, the analysis identified *Rubia cordifolia* and *Phellodendron* spp. in Niya and Yingpan burial sites [2] (25 - 420 AD). Most of dyestuffs which were grown in Central and East China were found in the Tang dynasty textiles (618 - 907 AD) that were used for Buddhist ceremony in the Mogao Grottoes. In summary, the HPLC-MS results suggest that the woolen textiles were most likely dyed with local plants grown in Xinjiang, whereas the silk textiles were probably dyed with the materials out of Xinjiang. Moreover, it should be noted that either a few foreign dyes or the textiles in European dyes have been imported to Xinjiang before the first century AD.

Figure 1. Mummy Child with Pink Cloth Excavated from Zagunluk Burial Site.

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An English medieval embroidered folded almanac: identification of the dyes

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The folded almanac MS.8932, written in Latin and produced in England around 1400, is a remarkable artefact. Astronomy and astrology played a significant role in medieval life, and calendars, based on Metonic cycles, enabled the sun and moon's movements to be predicted. Almanacs containing these calendars became increasingly popular with a wide range of users, including the clergy who used them to forecast the dates of religious festivals, and medical practitioners who related celestial activity to health.

MS.8932, previously in a private collection, was purchased by the Wellcome Library in London in 2013. It is a small book (H160 x W38 x D21 mm) consisting of eight vellum leaves sitting within an embroidered binding. The leaves are joined at their extended tabs and folded three times to fit within the covers. Few examples of this type of medieval folded manuscript have survived. It was probably worn hanging from a belt. On the opening page, John Somer identifies himself as the author and his text contains a calendar with additional information, including the Zodiac Man, a diagram depicting the association of the signs of the zodiac with specific parts of the human body. The brief but practical nature of the text suggests its use as a working manual. On the other hand, MS.8932's exquisite embroidered binding is unique and indicates a prestigious artefact. Each cover is made of three layers: woollen fabric, vellum and linen embroidered with silk, all stitched together around the edge. Braids sewn down the middle may once have extended out beyond the binding, to fasten the almanac and create an attaching handle. The study of medieval embroidery has been limited by its poor survival rate. MS.8932 therefore presents an unrivalled opportunity to learn more about bindings, embroidery and production methods dating from the medieval period.

The identification of the dyes in the embroidery was achieved by means of micro-invasive techniques such as Surface Enhanced Raman Spectroscopy (SERS) and HPLC-MS. Despite the small size of the micro samples (less than 2 mm of very thin threads), it was possible to identify orchil for pink hues, indigo/madder double dyeing with aloe (possibly used as mordant and/or as antibacterial agent) for purple hues, and indigo/weld double dyeing for green hues. This information will enable comparisons to be made, helping to situate the artefact and understand its significance.

The RSN Studio Wall of Wool

Logwood. Cochineal, lac, woad, madder, saffron, indigo, safflower