

DHA31, Antwerp Belgium 2012

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Ina Vanden Berghe, KIK-IRPA
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With the special assistance of Chris Cooksey

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Location

Katoen Natie HeadquARTers,
Van Aerdtsstraat 33,
Antwerp B-2010

18th & 19th October 2012

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DHA31 Antwerp 18-19 October 2012

THURSDAY, October 18th, 2012

8:30 **Registration and coffee ; placement of posters**

9:45 **Welcome**

Session 1. Chair: Maria Melo

10:00 **Yes, it is beautiful - but is it really light - fast? Micro - fade tester as a tool to evaluate the light fastness of natural dyes.**

Judith Bannerman, Margareta Bergstrand* and Jeanette Schäring

10:20 **Using Optical Reflectance Spectra to Analyse Dyed Textile by Principal Component Analysis.**

Jing Han*, Wei Liu, Gang Hu, Xiaomei Zhang

10:40 **Chances and limits of VIS-spectrometry - a non - destructive method of dye - determination applied on ancient textiles.**

Annette Paetz gen. Schieck*and Elke Michler

11:00 **Questions**

11:15 **Coffee**

Session 2. Chair: Vincent Daniels

11:45 **An improved method for the analysis of Tyrian purple samples and the application to historical and archaeological samples.**

Ioannis Karapanagiotis*, Dimitrios Mantzouris and Chris Cooksey

12:05 **An Integrated Microscopic and Chromatographic Analysis of the Molluskan Purple Yarns in the Katoen Natie KTN 1475 Coptic Textile.**

Zvi C Koren* and Chris Verhecken-Lammens*

12:25 **Royal purple in historical, analytical and technical context.**

Jan Wouters* and Chris Verhecken-Lammens*

12:45 **Questions**

13:00 **Lunch, and free visit to the museum collections**

Session 3. Chair: Jan Wouters

14:30 **Identification of anthraquinone markers for distinguishing *Rubia* species in madder-dyed textiles.**

Chika Mouri* and Richard Laursen

14:50 **Characterisation of once-black Queen Victoria's Privy Council dress c.1837.**

Mika Takami* and Ina Vanden Berghe

15:10 **Unravelling the colour palette of 19th century furniture: Reconstruction and analysis of synthetic dyes used as stains.**

Maarten R. van Bommel* and Enrica Fantini

15:30 **Questions**

15:45 **Coffee**

Session 4. Chair: Cheryl Porter

16:15 **Identification of dyes in Persian manuscripts.**

Ambra Idone*, Maurizio Aceto, Monica Gulmini, Angelo Agostino and Gaia Fenoglio

16:35 **Materials in Romanian historical parchment documents: dyes, pigments and inks.**

Irina Petroviciu*, Cristina Carsote, Zizi Ileana Balta, Gheorghe Niculescu, Mihai Lupu, Elena Badea and Doina Creanga

16:55 **Questions**

17:10 **End**

19.00 **Conference Banquet**

FRIDAY , October 19th, 2012

Session 5. Chair: Frieda Sorber

9:00 ***Alkanna tinctoria* (L.) Tausch as Purple Dye in the Recipes of *Papyrus Graecus Holmiensis* and *Papyrus Leidensis X*.**

Christina Kreuzner

9:20 ***κόμμη*; some hypothesis about an enigmatic dyestuff described in certain recipes of Greek alchemical papyri.**

Julia Martínez García

9:40 **A Flemish dye recipes manuscript from the 1620's.**

André Verhecken* and Patricia Pikhaus

10:00 **Questions**

10:15 **Coffee**

Session 6. Chair: Richard Laursen

10:45 **Beyond the eye-sight: the puzzle of a Japanese *manchira***

Maria Perla Colombini, Susanna Conti, Ilaria Degano*, Isetta Tosini and Licia Triolo

11:05 **Provenance analysis of protoberberines in Amur Cork tree in historical textiles: an approach for origin of the textiles in East Asia**

Yoshiko Sasaki* And Ken Sasaki*

11:25 **HPLC-PDA analysis of safflower red and -yellow, cape jasmine and gromwell in mild-acid hydrolyzed samples of Asian historic textiles.**

Jan Wouters* and Ana Claro

11:45 **Questions**

12:00 **Lunch, and free visit to the museum collections**

Session 7. Chair: Anita Quye

14:00 **A discussion on the biological sources identified in kilims and knot carpets belonging to the National Art Museum of Romania**

Irina Petroviciu*, Ileana Cretu, Mircea Dunca, Florin Albu
and Andrei Medvedovici

14:20 **Dyestuff, metal and technical analyses of some historical silk objects from Topkapi Palace Museum.**

Torgan Emine, Karadag Recep and Puchinger Leopold*

14:40 **Thorny Questions About the Athapaskan Porcupine Quill work Collection at National Museums Scotland**

Lore G. Troalen*, Alison N. Hulme, Jim Tate and Chantal Knowles

15:00 **Questions**

15:15 **Coffee**

Session 8. Chair: Ioannis Karapanagiotis

15:45 **Dyes and Textiles from Shipwrecks
Case studies *Vrouw Maria* and *St. Michel* from the Age of Enlightenment**

Riikka Alvik

16:05 **Central coastal textiles from the Chancay culture:
dye sources and technologies**

Thibaut Devière* and Catherine Higgitt

16:25 **Dyes and dye plants of Bronze and Iron Age Europe**

Regina Hofmann-de Keijzer*, Maarten R. van Bommel, Anna Hartl, Andreas Heiss
and Art Ness Proaño Gaibor

16:45 **Questions**

17:00 **Closing remarks**

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Oral Presentations

(In order of presentation)

**Yes, it is beautiful - but is it really light - fast?
Micro - fade tester as a tool to evaluate the light fastness of natural dyes.**

Judith Bannerman¹, Margareta Bergstrand^{1*} and Jeanette Schäring²

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It is well known that natural dyes are very fugitive and sensitive to light, Yet some colours have survived splendidly, as for example the natural dyes in the tapestries of the Swedish/Norwegian textile artist Hannah Ryggen (1894-1970). After many years of experiments she mastered the blue dyeing with her own method of using the indigo urine vat. Today we see a new interest among textile artists who want to use natural dyes, often out of concern for the environment. Jeanette Schäring is currently Artist in Residence at the Steneby School of Arts and Crafts at the University of Gothenburg experimenting with different methods of dyeing. She and other artists are often asked (by conservators, curators and many others) - "yes, it is so beautiful, but is it really light - fast?"

Could the light-fastness also depend on the method used? Fermentation dyeing methods (such as the urine vat) without the use of inorganic mordants, have been used for a long time up until the 20th century, (although historically the different methods of vegetable dyeing in Sweden have not been fully investigated). Knowledge of the use of dyeing methods could help explain the difference in light-fastness observed in many ethnographical and art textiles in our museums.

This paper will report on a study of naturally dyed textiles - mainly woad (*Isatis tinctoria*), indigo (*Indigofera tinctoria*) and including local dyes, on wool and silk from J. Schärings experiments, - in order to investigate the impact of different methods of dyeing. Micro-fade testing is used for the study on light ageing and light fastness. Testing of the fibre tenacity is also done.

A micro - fade tester is a tool that allows the user to carry out accelerated light -aging tests. The procedure is rapid and almost non-destructive - it is normally done directly on an artefact and does not require sample removal. The device sends a very intense beam of light to a test area that is 0,3 mm in diameter and monitors the intensity and spectrum of the reflected light. The reflected light data is collected every 30 seconds over a 10-minute period, yielding continuous measurements of the fading of fugitive colours. The reflectance spectrum is recorded and the fading rate is then compared to ISO Blue Wool Standard cards.

The micro-fade tester could become a tool for museum conservators, curators and others to identify fugitive dyes and pigments on historical objects.

Using Optical Reflectance Spectra to Analyse Dyed Textiles by Principal Component Analysis

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Non-destructive analysis of dyes on textiles can provide strong support for both research and conservation. Optical reflectance spectroscopy can achieve in-situ non-destructive analysis of dyes on textiles by obtaining optical reflectance spectra. The samples used for research include textiles with different dye species, textiles with different fibre species and structure, textiles dyed by different techniques, artificial ageing samples and archaeological samples. Direct observation of optical reflectance spectra could distinguish characteristics of different dyes. The characteristics of multi-coloured samples and mordanted samples were also obvious. But fibre species affected the spectra greatly and disturbed the identification of dyes. The changes of dyes during ageing were also quite obscure. To obtain further information in the spectra, the method of Principal Component Analysis was used to process and analyse the data. It was shown that principal component analysis could distinguish dye species by the position in the graph of the principal components. Fibre species, textile structure and dyeing techniques had little effect on the identification of dyes, ensuring relatively correct identification of dyes. When aged samples were divided by colour groups, the ratio of correct identification remained high. The positions of archaeological samples were in the area of the samples that had been severely aged. Moreover, main wavelength ranges of the dyes and changes during ageing were found by the key wavelength range reflected by the principal components.

Chances and limits of VIS-spectrometry – a non-destructive method of dye-determination applied on ancient textiles

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Archaeologists and textile conservators consider archaeologically preserved textiles as a precious category of finds. Since ancient textiles of this kind are rare, highly fragmented, and fragile, destruction of the material should be avoided.

Quite often, the preservation conditions cause a total change in colour, preventing a determination by eye-sight. Interpreting textiles can only be maintained by taking all information into account, and dyestuffs make a great portion of it.

Colours transmit important information about the cultural background of an object, about availability of materials in Antiquity, of trade-routes, as well as of social meanings.

Conventional procedures of dye-analyses, such as the chemical method of HPLC, always afford sampling and cause the destruction of a portion of the object. When taking the conservation of an object as the binding principle, the necessity for non-destructive methods of determining dyestuffs is evident, and when searching for possibilities, the VIS-spectrometry method comes into focus. Measuring the colour spectrum of visible light being reflected from the object, it is characteristic and even allows the determination of dyes and the mixture of components.

Originally invented for print media, Prof. Dr. Robert Fuchs of the CICS Cologne adapted the method for cultural goods and successfully employed it to determine pigments of paintings and book illustrations.

Investigations on textiles, though, have only just recently been carried out, in fact initiated by a test-series on late Roman textiles from Egypt (4th to 8th Century AD) of the collection of the German Textile Museum at Krefeld (DTM), Germany. A second series was then performed on a similar group of textiles of the collection of the Reiss-Engelhorn-Museums (REM) at Mannheim. They have been measured with VIS-spectrometry on the one hand, and on the other hand, a selected number of them have also been sampled for HPLC in order to cross-check the results of the VIS-spectrometry. Chemical analyses were carried out by KIK-IRPA, Brussels.

As result it can be stated that dyestuffs producing black, yellow, or those that contain yellow as a component, such as green, cannot be determined by VIS-spectrometry. They still require the chemical analysis. For most of the other colours, though, the VIS-spectrometry turned out to be reliable, even when dealing with mixed dyes. The advantages can clearly be named: quick, cheap and non-destructive.

Since this method is fairly unknown to archaeologists and textile researchers, this paper will introduce the method to a wider audience.

An improved method for the analysis of Tyrian purple samples and the application to historical and archaeological samples

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DMSO [1], DMF [2] and pyridine [3] have been used in the past to treat and solubilise Tyrian purple, prior to HPLC analysis. Our goal is to investigate (i) the efficiencies of these solvents to treat true purple and (ii) the effects that they have on the results for the relative composition of the dye. To achieve our objective, samples of Tyrian purple are treated with the aforementioned solvents at various temperatures and time periods. Solutions are then analysed with HPLC. The following compounds are monitored at 288nm to compare the three solvents: indigotin (IND), indirubin (INR), 6'-bromoindirubin (6'MBIR), 6-bromoindirubin (6MBIR), 6-bromoindigotin (6MBIR), 6,6'-dibromoindigotin (DBI) and 6,6'-dibromoindirubin (DBIR). The comparison leads to the conclusion that DMSO gives, overall, the best results.

The improved treatment method is then applied to archaeological and historical samples which have been analysed -and presented in DHA meetings [4,5]- in the past. The new method provides better results with respect to the number of extracted compounds, as detected by HPLC.

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An Integrated Microscopic and Chromatographic Analysis of the Molluscan Purple Yarns in the Katoen Natie KTN 1475 Coptic Textile

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The red-purple and blue-purple yarns excised from a 1,500-year old Coptic textile in the collection of Katoen Natie were analysed by means of an integrated physical and chemical approach. The yarns were first examined under a stereo microscope in order to determine their physical construct. It was observed that the red-purple yarn was produced from homogeneously dyed fibres. The blue-purple yarn was dissected and found to consist of fibres possessing three different colours: undyed, red-purple, and blue-purple. Subsequently, high-performance liquid chromatographic (HPLC) analyses were individually performed on the whole red-purple and blue-purple yarns as well as on the fibres dissected from another sample of the blue-purple yarn.

The dye component present in significant quantities in all of the samples was MBI (6-monobromoindigo) and since it has been previously established by Koren [1] that only the *Hexaplex trunculus* species produces such appreciable amounts of that dye, it can be concluded that this species was the primary snail used for all the dyeings. However, the additional minor use of another molluscan species in some of the dyeings cannot be excluded, as mentioned below. The other dyes detected were IND (indigo), purple DBI (6,6'-dibromoindigo) and its redder isomer DBIR (6,6'-dibromoindirubin). By comparing the relative compositions of the various archaeological dyes found with those pigments from various sea snail species, this study has found that the ancient expert dyer knew to differentiate between DBI-rich and IND-rich *H. trunculus* snails. Thus, to produce the red-purple yarn the dyer selectively used the DBI-rich *trunculus* snail, with possibly a minor amount of *Bolinus brandaris* or *Stramonita haemastoma* species to top off the reddish coloration. The dissected blue-purple yarn showed the presence of blue-purple and red-purple fibres, the latter being different in colour (bluer) and in dye compositions from those of the red-purple yarn mentioned above. These dissected red-purple fibres would have been produced solely from a DBI-rich *trunculus* snail, whereas the blue-purple fibres originated from an IND-rich *trunculus* snail. Thus, the spinner of these purple yarns used a total of four different fleeces, one for the red-purple yarn and three distinct fleeces for the blue-purple yarn.

This study shows that a combined micro-physical and micro-chemical approach is essential to the determination of the specific malacological provenance of purple dyeings. Furthermore, only an HPLC method can provide the full chromatographic fingerprinting needed for such dye analyses, and no other spectrometric technique – as ostensibly sophisticated as its name may imply – can compete with the chromatographic method.

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Royal purple in historical, analytical and technical context

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The detection of royal or real or murex purple in samples taken from objects of cultural and artistic value remains rare and exciting. The production of dyes of purple hues from muricid hypobranchial glands and the study of dye components detectable with various instrumental methods, after various recovery procedures and natural ageing conditions has been studied intensively over the last decades.

A recapitulation of (only) nine royal purple detections made by the first author over the past twenty years and spanning an object's production period from the second century BCE through the eighth century CE reveals the following. Royal purple components may be recovered from their substrate by the traditional hydrochloric acid hydrolysis method, by extraction in pyridine or dimethylformamide and by the more recently developed mild acid hydrolysis using oxalic acid. The recovery method may have an influence on the composition in terms of components found as well as their relative proportions. Indigotin is almost always present but should of course be accompanied by at least one, preferably more purple-specific brominated indigoid components. Royal purple may be combined to other biological sources such as a cochineal type and kermes.

Murex purple, together with scale insect reds (cochineals, kermes and lac), belong to the group of natural organic dyes of animal origin. Such dyes seem to have been used for higher quality, hence more expensive fabrics. An on-going study has revealed possible relationships between weaving technological features and a biased use of animal dyes on tapestry woven ornaments of 1st through 9th centuries CE Egyptian linen and woollen fabrics belonging to the textile collection of Katoen Natie, Antwerp, Belgium. Out of 33 samples of Z-spun weft woollen yarns, 15 (45%) were found to have been dyed with animal dyes (6 with a cochineal type, 5 with kermes and 4 with murex purple; none with lac), whereas only 1 (murex purple) (2%) out of 61 S-spun weft woollen samples. The latter percentage amounts to 18% if also lac is taken into account. Out of 7 silk wefts from ornaments, 2 (29%) were dyed with a cochineal type, 3 (43%) with lac, hence a grand total of 72% with animal dyes. Possible relationships between the twist of woollen weft yarns, dyes present and value of fabrics will remain a major topic for further investigations.

Identification of anthraquinone markers for distinguishing *Rubia* species in madder-dyed textiles

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The anthraquinone components of the roots of various species of madder (*Rubia* spp.) have been used for millennia as red colorants in textiles, carpets and other objects. Although many species of *Rubia* are known, only a few of them have been used widely for dyeing. Furthermore, though nearly 70 anthraquinones have been found in *Rubia* species, only a few of these occur consistently at relatively high levels. Knowledge of the plant dyestuffs is helpful for establishing the production location, production method and/or history of the dyed object. Using plant material and dyed textile fibers obtained from a number of sources, and HPLC with photodiode array and mass spectrometric detection for analysis, we have been able to identify marker anthraquinones that permit differentiation of the more common species of madder used for dyeing in Eurasia. Textiles dyed with all of the species examined contain varying amounts of purpurin, but only those dyed with *Rubia akane* contain large amounts of 6-hydroxyrubiadin (1,3,6-trihydroxy-2-methylantraquinone) or its glycosides. Textiles dyed with *R. tinctorum* contain primarily alizarin, whereas those dyed with *R. cordifolia* and *R. peregrina* contain mostly purpurin, munjistin and pseudopurpurin, but little or no alizarin or 6-hydroxyrubiadin. The latter two species cannot reliably be distinguished from each other, however. The plants themselves often contain glycoside precursors not usually seen in the dyed materials.

In recent years we have analysed the dyes in a number of madder-dyed textiles. These include silk textiles (~700 CE) from Japan (*R. akane*), several wool specimens (~1000 BCE) from the Tarim Basin region of Xinjiang (*R. tinctorum*), a ~200 CE Xiongnu silk funerary textile (probably dyed with *R. cordifolia*; tribute from China?), and woolen Tibetan monastic seat mats (*R. cordifolia*). More recently we analyzed a multicolored woolen object dated at 200-400 CE from near Lop Nur in Xinjiang in which the red yarn was dyed with *R. tinctorum*, but the purple contained, besides indigo, only laccaic acid, from lac, which grows in South and Southeast Asia. This finding suggests the use of both local and imported dyestuffs, but may have other explanations.

Characterisation of once-black Queen Victoria's Privy Council dress c.1837

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Queen Victoria was only 18 years old when she wore this dress on 20 June 1837, the first day of her reign. On this day, she held her first meeting of the Privy Council at Kensington Palace, only five hours after being woken with the news of the death of her uncle, King William IV. The dress was black for mourning. Appearing youthful and graceful in this barely adorned simple black silk dress, Queen Victoria stunned all those who witnessed that historic occasion with her perfectly calm, self-possessed manner and behaviour[1].

This historic dress now appears in a 'blotched' brown colour overall showing no evidence of the original black. Severe discolouration is not an unfamiliar problem for silk dyed black using natural dyestuffs in past centuries. Our puzzlement lies not in the extent of the discolouration itself but in the fact that the silk has faded to brown and light brown in this unique mottled pattern throughout the dress on both inside and out to the same extent, even in the most hidden areas of the inside of the dress.

Dye analyses[2], conducted using HPLC and SEM-EDX, has confirmed that the silk fabric was dyed using logwood (haematoxylin) combined with tannin using copper and iron mordants. Additionally, the presence of a yellow dye source from a type of chamomile (*Anthemis* species) was detected. These results suggest that the black mordant dye logwood was suitably fixed to the fibres using both organic and inorganic mordants. Why this unique extensive discolouration then occurred throughout the dress still remains a conundrum.

The results from the SEM analysis further added another piece to this puzzle. The images revealed the severe degradation of the silk fibre appearing hollow and skeletal with many holes. In this destructed state of the fibre, one would expect the silk fabric to be very brittle to touch. However, the dress is still sound and flexible requiring only minor conservation treatment and was able to be mounted safely on a mannequin for display.

The dress is now on display in a sealed showcase in a new exhibition at Kensington Palace – '*Victoria Revealed*'. To ensure the long-term preservation of this dress of historic significance, in particular to prevent it from further discolouration, the most appropriate conservation practices for this dress need to be established for both display and storage. This paper will explore the possible cause of this discolouration, inviting discussion on the chemical impact of these changing dyes on the fibre and what factors could potentially be most harmful for the dress.

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Unravelling the colour palette of 19th century furniture: Reconstruction and analysis of synthetic dyes used as stains.

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In the last decade, several pieces of furniture were studied which were stained using synthetic dyes. Dyes such as methyl violet, indigo carmine, orange II, diamond green and nigrosin were found in objects from the late 19th and early 20th century as in remaining marquetry pieces preserved by the Amsterdam museum [1]. The number of objects studied so far is too small to determine how fast the furniture manufacturers adapted to the new, brilliant colourants but at least it is certain that they were using them.

In general, the first reason for studying the organic colorants used is to learn more about the dating and the (making) history of the object. However, a very important question is what the pieces of furniture originally looked like. These objects are often severely faded and in many cases the original layer has been removed as fashion changed. But even if some of the original dye could be identified, it is still difficult to determine the original colour, as, in the recipe not only the colourant used is of relevance but also other parameters such as temperature, concentration, pre-treatment of the wood, the colour of the wood itself and so forth. All of which could affect the final colour. Additional reconstruction research was necessary to draw better conclusions about the original appearance.

As well as the problem of the determination of original colour, a second problem occurred:-. In general, the concentration of dyestuff found in samples taken was extremely low when analysed by High Performance Liquid Chromatography, coupled with Photo Diode Array detection (HPLC-PDA). This could be due to fading, but, in many cases we were able to sample areas which were well protected from light so still showed their colours. The reason for this low response could be that either, the concentration of dye needed to give the wood a strong colour is very low, or, that the extraction technique to dissolve the dye prior to analysis was not suitable for these types of samples. It must be noted that the extraction technique used, boiling in concentrated methanolic hydrochloric acid, was evaluated for synthetic dyes applied on textiles which works very well [2]. However, wood is another material and the interaction of the dye with the wood could be different.

Facing these two problems, a project was developed creating reconstructions of wood stained with synthetic dyes based on historical recipes. The aim of this project was twofold:

- 1- To achieve a better understanding of different parameters in the recipes and their final effect on the overall colour to support conservators and curators when working with furniture from this period
- 2- To use these reconstructions to evaluate and if necessary improve the extraction procedure used prior to HPLC-PDA analysis.

Within this presentation, the outcome of the results will be presented and discussed and the reconstructed materials will be shown. The presentation will focus in particular on the effect of different parameters in the recipes used on the overall colour. In addition, the extraction procedure finally used will be briefly discussed.

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Identification of dyes in Persian manuscripts

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Persian manuscripts are among the most beautiful artistic productions in the field of miniature painting. The term "Persian" applies mostly to the linguistic-textual aspect rather than to the palaeographic-codicological one, so that under this term we can include manuscripts of Turk-Ottoman, Moghul Indian and sometimes European geographic provenance, coming from what is now the area comprising Turkey and Northern India across modern Iraq, Iran, Afghanistan and Pakistan.

Knowledge of the colorants used by Persian artists, though, is not so deep as the knowledge of pictorial materials used in Western manuscripts. It is only recently that diagnostic studies have been applied to Persian miniatures [1,2], apart from the pioneering work by Purinton and Watters [3]. In particular, very few diagnostic information is available for what concerns the use of organic colorants in the palette of Persian artists, so that our knowledge on this aspect relies mostly on bibliographic sources such as *Qanun us-Suvar* (Canons of Painting) by Sadiqi Bek, a royal painter in XVI century Safavid Iran, or *Gulistan-i Hunan* (Rose Garden of Art) written by Qadi Ahmad at early XVII century. According to some scholars, only inorganic pigments were employed in Persian painting [4]. It is obvious that artists considered inorganic pigments for their superior covering power and their better resistance to pollutants, but this hypothesis could be a result of lack of diagnostic information and it must therefore be checked in the light of technological improvements in the analytical instrumentation.

In fact, evidence of use of dyes on Persian manuscripts has been provided by non-invasive analysis of some volumes kept in Northern Italy libraries. UV-visible diffuse reflectance spectrophotometry (FORS) and spectrofluorimetry were applied *in situ* on these volumes; results showed that dyes were used in two ways: a) to dye the paper support, a practice relatively common in Islamic manuscripts but rare in Western manuscripts; b) to impart delicate hues to particular details in miniatures. For what concerns paper dyeing, different colours could be obtained, frequently inside the same manuscript: dark blue (obtained with indigo), pale green (a mixture of indigo and a yellow dye), red (henna) and yellow. The practice of dyeing paper can be possibly explained with the desire of highlighting text over a proper background, such as gold text on a dark blue surface, but sometimes this is not the case. For what specifically concerns miniatures, it has been found a wide use of anthraquinone dyes; according to the spectral features of both FORS and fluorimetry spectra, these seem to be of animal origin, though using non-invasive techniques only it has not been possible to distinguish among the different scale insects possibly employed. Nevertheless, historical considerations make Armenian cochineal or lac dye, imported from India, the most suitable candidates. In yellow painted areas, the evidence of saffron was found, which is not surprising considering that *Crocus sativus L.* was cultivated in the Iranian area since Sasanian times.

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Materials in Romanian historical parchment documents: dyes, pigments and inks

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Historical documents on parchment, dated between the 15th and 19th centuries, are among the most valuable objects preserved in Romanian museums, monasteries and archives [1,2].

Several studies have been dedicated in the last years to these objects, aiming (i) to contribute to their preservation, by research projects which evaluate the environmental factors contribution to parchment degradation and (ii) to enrich the existing knowledge of the materials used on the Romanian territories in the mentioned period. The first scope was approached by analysis of new, artificial aged and historical parchments, based on the information provided by FTIR, thermal and micro thermal analysis, as also resulted from the information accumulated at European level within projects such as IDAP and OPERA [3,4].

In order to contribute to a better knowledge and understanding of the materials and techniques used, identification of pigments, inks and dyes was indeed an obvious step, results being correlated with those provided by literature [5,6]. XRF and FTIR were used for pigments, binders and inks identification while LC-DAD-MS was used to identify the biological sources used in the (red) fibers which bound seals to parchment documents.

The lecture presents an overview on the pigments, inks and dyes identified together with information provided by (old) written sources.

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Alkanna tinctoria (L.) Tausch as Purple Dye in the Recipes of *Papyrus Graecus Holmiensis* and *Papyrus Leidensis X*

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In the beginning of the 19th century two papyri were found in Thebes (Egypt) which are nowadays treasured in the National Museum of Antiquities in Leiden/Netherlands (Inv. AMS 66; *Papyrus Leidensis X*) and in the National Library of Sweden in Stockholm (dep. 45, *Papyrus Graecus Holmiensis*). They were written in the 3rd or 4th century in the Greek language and provide a vast range of recipes for colorants, wool dyes – especially for vegetal purple –, and metal working. The obvious importance of the texts for our knowledge about ancient technology, chemistry and alchemy had been clear from very early the *Papyrus Leiden* being edited for the first time by Leemans [1] in 1843, the *Papyrus Holmiensis* by Lagercrantz seventy years later [2]. An English translation of both papyri followed in 1926 by Caley [3, 4] and a complete new edition by Halleux with a french translation in 1981 [5]. A first attempt of a technological translation of the texts was made by Reinking in 1938 [6].

These recipes have mainly been ignored and simply quoted as evidence for alternative purple dyes, mostly being declared as false. In contrast to this the latest studies by Steigerwald [7] have made clear the 'purple' was used for a wider spectrum of colours and colorants than just true murex purple.

A convincing translation of the recipes can be achieved neither by a philological nor technical approach alone. So the aim of a project promoted by the Fritz Thyssen Stiftung, Cologne, was to develop the texts as a source for dyeing technology and textile colours in the eastern Mediterranean in Late Antiquity within an interdisciplinary approach. One challenge was the fact that many substances used could not now be positively identified. Therefore the recipes were assembled together with the translations hitherto available. Considering the described characteristics the unclear terms were narrowed down as far as possible. In a second step the recipes were reproduced in the lab. As all these recipes have no precise instructions comparable to modern laboratory prescriptions but notices of ancient dyeing experts. Thus many parameters such as temperature, dyeing period or liquor ratio had to be concluded from recipes complementing one another.

The topic of the proposed oral presentation will be the interesting and sometimes surprising results of these experimental wool dyeings with *Alkanna tinctoria* (L.) Tausch.

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Κόμμαρι; some hypothesis about an enigmatic dyestuff described in certain recipes of Greek alchemical papyri.

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In his article *Teinture et Alchimie dans l'Orient Hellénistique* (1935) [1], Pfister wrote about κόμμαρι, an enigmatic matter that Berthelot transcribed as *Arbutus* sp. and Lagercrantz associated to *Comarus palustre* L. The dissolution of the κόμμαρι is prescribed in some of the recipes to obtain a vegetable purple dye described in the Leyden Papyrus X and the Papyrus Graecus Holmiensis as well as in another alchemy recipes reserved for the dyeing of fabrics, present in Genève 122 Papyrus. We can trace its use in later periods in Syrian alchemy recipes handed down from Antiquity to the Middle Ages. By the study of the classical sources, current knowledge regarding the chemical composition of substances, and the actual experimentation of such recipes, our purpose is to demonstrate that this enigmatic substance corresponds to the strawberry tree, *Arbutus unedo* L., its leaves or its bark, as postulated by Berthelot. We discard the hypothesis of an association to *Comarus palustre* L. since it is endemic of the Northern European countries and possibly unknown by the craftsmen who made use of these recipes in 3rd-4th century A.D. Egypt

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A Flemish dye recipe manuscript from the 1620's.

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The dyeing literature in Dutch, now known to be from before the 18th century, consists of 9 manuscripts and 7 printed books, and most of the MS have been published. Between 1619 and 1623, the Flemish dyer Henric Coghen, living and working in the Brabant town of Leuven, wrote down 168 dyeing recipes in his book *Conste des Ververs* (Art of the Dyer). Except for the transcription of a few of these recipes published eighty years ago, that have passed almost unnoticed [1], the contents of the book have remained unknown. The general lines of this MS will be presented here.

In contrast to all other known dye recipe books, this MS is rather specialized concentrating on the dyeing of one branch of textiles: stockings. Unfortunately, Coghen does not tell us clearly which kind of stockings (woven, knitted; which fibre?). The fibres Coghen was dyeing were wool, linen, silk, cotton(?); in such textile qualities as *laecken* (broadcloth), *lijwaet* (linen), *syde* (silk), *bombesyn* (mixed weaving with silk warp), *fruweel* (velvet), *lint* (silk ? ribbon).

His choice of dyestuffs does not really place him with the dyers *Grand Teint*, although solid dyes as cochineal, indigo, kermes are mentioned a few times. Much more frequent are madder (*mee*, *meecrappe*, *crap*), brazilwood, logwood, weld, fustic; and *lackmoes*, *purper*, and dyes identifiable as *safflower* (*Carthamus*). The rather poorly known recuperated dye *follegreyn* is not unusual in this MS. Because of the use of phonetic spellings, corrupt spellings and writing errors, the dyestuff terminology used sometimes asks for some interpretation.

Some of Coghen's dyeing methods can hardly have given well-dyed textiles: several recipes prescribe putting the textile in the bath, and *terstont* (at once) it will be dyed; but the dye cannot possibly have had a sufficient penetration into the fibre.

The colour shades dyed by Coghen are: *arsienty* (silver grey ?), yellow, orange, red and its shades (*carmosyn*, *carmosyn violet*, *carmosyn grau*, *incarnate*, *lyfverve* (skin colour), *follegreyn*, *rooset* (rose ?), blue, *columbine* blue, *lavende* (lavender ?), green, *peers*, purple, violet, *terneyt* (French: *tanné*), grey, black.

Unlike the one-century older printed Flemish *Bouck van Wondre* (Brussels, 1513), this MS is not a mixture of all kinds of wonderful recipes for the layman, in the style of the Italian *Secreti*. It is a compilation of rather solid recipes for the professional dyer. This MS forms an interesting addition to the corpus of dye texts in Dutch, that exceed in number and importance what would be expected from a relatively small language area, seen on the European scale.

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Beyond the eye-sight: the puzzle of a Japanese *manchira*

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In the framework of a collaboration between the Opificio delle Pietre Dure and the Stibbert Museum (Florence), a Japanese *manchira* was subjected to a multi-analytical diagnostic campaign. The diagnostic campaign entailed both non-invasive and micro-destructive techniques, such as FORS, FT-IR, XRF and HPLC-DAD analysis. The main goals of the study were:

- characterizing the materials employed and the assembly;
- assessing the state of conservation in order to plan a thorough cleaning and consolidation strategy;
- dating the object and clarifying the context of its production (e.g. the social status of the owner, the quality of the constituting materials, etc.).

Reference mock-ups of dyed textiles were prepared according to Japanese recipes, by using local raw materials. The results obtained by the diagnostic campaign were interpreted with the help of Japanese costume and textile historians and allowed us to clarify the nature of the constituting material and to characterize the object under study.

In this paper, the main results obtained by non-invasive and micro-destructive techniques will be presented. The dye analyses and the study of the impact of the dyeing technique on the state of conservation of the object will be discussed in detail. The impact of the diagnostic campaign on the adopted restoration procedure will be also discussed in detail.

Provenance Analysis of Protoberberines in Amur Cork Tree in Historical Textiles: An Approach for Origin of the Textiles in East Asia

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The Amur cork tree is a traditional yellow dye used widely in East Asia. Non-destructive detection of this dye is easily achieved by spectroscopic methods on the basis of their characteristic properties of major ingredients: protoberberine alkaloids. Last year, we have reported new chemical methodologies for provenance analysis of historical textiles to discriminate between Japan and China [1]. HPLC analyses of the dye showed that the relative ratios of Palmatine (P) and Jatrorrhizine (J) to Berberine (B) (J/B and P/B ratios) in Amur cork tree, strongly reflected the difference in the species between Japan and China, presumably *Phellodendron amurense* and *Phellodendron chinense*, respectively. The provenance could be easily determined using scatter gram of J/B and P/B ratios. This methodology was applied to the provenance analysis of Chinese style 14thC *Kasaya* stored in *Donke-in* temple at Kyoto, and six Japanese style 18thC *Kimono* fragments (private collection). HPLC analyses were performed for yellow extracts from yellow, green and red threads with characteristic fluorescence behaviour of protoberberines. The J/B and P/B ratios were determined by their relative area monitored by 350nm absorption. The pale green thread of Chinese style *Kasaya* clearly appeared in the Japanese region of the diagrams, leading to the conclusion that manufacture was in Japan in spite of having typical Chinese style in the textile design. Japanese style *Kimono* fragments were analysed similarly. The J/B and P/B ratios of two samples (embroidery threads) were unexpectedly showing the typically Chinese regional dye. These results provide direct evidence of trading of dyed threads from China to Japan in the 18thC. Thus, quantitative analysis on the basis of the composition of Amur cork tree will be a useful methodology for historical information for technique and trading of Japanese textiles.

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HPLC-PDA analysis of safflower red and -yellow, cape jasmine and gromwell in mild-acid hydrolyzed samples of Asian historic textiles

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Biological sources such as *Carthamus tinctorius* L. (safflower), *Gardenia augusta* L. (cape jasmine) and *Lithospermum erythrorhizon* ZIEB. & ZUCC. (gromwell) must be expected to have been used predominantly within an (East) Asian geographical context. The research project on Asian organic colourants carried out at the Getty Conservation Institute (Los Angeles, USA; 2006-2010) and two analysis campaigns on selected items of the Asian textile collection of the Abegg-Stiftung (Riggisberg, Switzerland) have generated updated information on the use and detection of these sources in historical fabrics. All results reported here were obtained on hydrolysates following the oxalic acid procedure [1] and these were analysed at the laboratory of the second author.

Safflower contains both a red and a yellow dye. The former is mainly composed of carthamin, but safflower red can still be detected with the help of four non-colouring components (Ct1, Ct2, Ct3 and Ct4), even when carthamin has completely faded [2]. The latter is composed of several quinochalcons with characteristic absorption maxima at 405±4 nm, and of flavonoids. In a textile, originating from 8th century Bagdad, evidence was found for the specific use of either safflower red, safflower yellow or a mixture of both that have produced present-day yellow, orange and pink hues. These hypotheses could be put forward by looking at relative proportions of all safflower-specific components (carthamin, the four Cts and the quinochalcone yellows) in the analyses.

The detectability of one or more safflower components, often at trace level, is important to identify the presence of this dye within a controversial historic context. This was clearly an issue in a process of demystification of the dating of a Chinese shoe by a dealer to between the 1st century BCE through the 2nd century CE. Whereas no historical evidence exists for the use of safflower in this period, the detection of safflower components in three dyes of this object underpinned the suggestion by the collection's curator of the production period to be rather Jin (265-420 CE).

The dye of *Lithospermum erythrorhizon* originally consists of a series of esters of shikonin. When using mild acid hydrolysis, these esters are likely to remain unhydrolysed and will show up in the chromatogram. In the Asian organic colourants project and the recent analysis campaigns we were able to list up nine gromwell ester components. An example of a multi-component gromwell detection will be given that refers to the textile from Bagdad that was mentioned above

Colourants of cape jasmine, based on crocin and crocetin, are destroyed in the traditional hydrochloric acid hydrolysis, but survive the mild oxalic acid hydrolysis method. The detection of five cape jasmine components together with berberine and alizarin will be illustrated in a sample taken from a late Han (25-220 CE) radiocarbon dated shirt (80-260 CE).

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A discussion on the biological sources identified in kilims and knot carpets belonging to the National Art Museum of Romania

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A large number of Islamic textiles are preserved in Romanian collections, including kilim - karamaniu rugs and knot carpets. The presence of these pieces in local collections may be explained by either (i) accidental introduction to Western Europe, as a result of the military conflicts and trade routes position; (ii) manufacture in local workshops - possibly established by the Ottomans to reduce the manufacturing costs, such pieces being sold in Western Europe; (iii) acquisition by the Romanian noble families, to display their luxury (starting with the 19th c.) [1]. At the beginning of the 20th c., in their interest to build collections of art objects, the rich families in Romania co-opted well-known specialists at that time, among others Theodor Dumitru Tuduc. Such specialists started to embellish the existing textiles which resulted in high quality reconstructions on more than 50% of the objects surface. Gradually they executed replicas of the original carpets and sold them as originals, the only difference being in the materials (dyes) used. As result of his activity, Tuduc is nowadays considered one of the best restorers and at the same time one of the best rug fakers. His works, even when known as fakes, produced between 1919-1945, in his workshop (in Brasov), became art objects in their own right.

The National Art Museum of Romania (NAMR) has now in its collections very interesting kilims – karamaniu rugs and knot carpets, some of them raising specialists' suspicion regarding their authenticity. The objects have never been restored since they became part of the museum collection. Part of the study started in 1997, which aims to enrich the existing knowledge on textiles in Romanian collections by the help of dye analysis, the work presents the results obtained by LC-DAD-(Ion Trap)MS dye analysis on 11 knot carpets (~120 samples) from the NAMR collection. Analyses were performed according to an analytical protocol recently developed in Romania [2]. Results are discussed together with data previously obtained in the same research group on 17th-19th c. textiles from Asia Minor (kilim, sumak, knot carpets) as well as compared with data available in literature on similar pieces.

Natural dyes only were detected in six knot carpets from the present set, both natural and synthetic dyes were identified in four pieces while in one carpet only synthetic dyes were identified. Madder (*Rubia tinctorum L.*), weld (*Reseda luteola L.*) and indigo (*Isatis tinctoria* or *Indigofera sp.*) were the most used biological sources identified while other sources such as redwood (*Caesalpinia sp.*) and quercetin based dyes were also detected in some pieces. These results are in very good correspondence with those previously obtained in the same research group as well as with data available in literature [3-5].

The contribution discusses in detail some case studies in which dye analyses supports preliminary observations regarding the objects' authenticity.

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Dyestuff, metal and technical analyses of some historical Silk objects from Topkapi Palace Museum

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This study encompasses more than one hundred historic, richly decorative Ottoman textile samples made in coloured silk, which was wrapped with a gold or silver thread, and stemming from the famous Topkapi Palace Museum Collection. To characterize the metallic covered textile fibres and to get some information on the techniques in former times the following methods were used: HPLC-DAD (High performance liquid chromatography coupled with diode array detection) was applied for the identification of dyestuffs and dyeing components of these ancient objects (Table 1). Before HPLC-usage all samples had to be extracted with a 37% HCl/methanol/water (2:1:1, v/v/v) solution. The most important dyes analysed were cochineal, oak, weld, woad, dyer's greenweed, Anatolian buckthorn and Rumex.

| Object number | Garment | Colour | Dyeing components | Biological source |
|---------------|-----------------|-------------------------|---|---|
| 13/838 | Caftan | Red (inside) | Carminic acid, gallic acid and ellagic acid | Cochineal + oak or gall oak |
| | | Green (side of textile) | Luteolin, apigenin and indigotin | Weld + woad or indigo plant |
| 13/1665 | Silk brocade | Yellow | Luteolin and apigenin | Weld |
| 13/399 | Shalwar | Green | Genistein and indigotin | Dyer's greenwood + woad or indigo plant |
| | | Yellow | genistein | Dyer's greenwood |
| 13/2070 | Dress of Sultan | Yellow | Luteolin and apigenin | Weld |
| 13/574 | Caftan | Yellow | İsorhamnetin, rhamnetin and emodin | Anatolian buckthorn |
| 13/1089 | Dress of sultan | Yellow | Emodin | Rumex |
| | | Green | Emodin | |

Table1. Dyestuff compounds and colouring materials identified by HPLC-DAD.

By means of both, FESEM-EDAX (Field emission scanning electron microscopy with energy dispersion spectroscopy) and SEM-EDX (Scanning electron microscopy with X-ray microanalysis), the morphology of the silk (four fibre states: unharmed, frayed out, bent and broken) as well as the elemental composition of the metal threads including the contaminations found upon it were investigated. Metal mixtures in weight percent characteristic for the surface of the threads were: Ag/Cu (36/32, 38/18 or 9/69), Cu (75), Cu/Zn (55/27) and Ag/Cu/Au (41/6/42). Also other elements like Na, Ca, Mg, Cl, S, C and O could be found. Moreover the coordinates of the L*, a*, b* colour space of all historical objects were measured with Gretag Macbeth SpectroEye spectrophotometer.

Thorny Questions About the Athapaskan Porcupine Quill work Collection at National Museums Scotland

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Dyed porcupine quills were used by Native Americans to decorate leather goods and baskets, [1] but little work has been carried out on the extraction and analysis of the dyes used in this medium. [2] Within the collection of the National Museums Scotland (NMS) is a unique set of dyed raw quill samples and Athapaskan objects that were collected from North America in 1862. These examples of Indigenous Art are often described as dyed with early synthetic dyes, although the exact nature of the dyestuffs has never been scientifically investigated. [3, 4]

Prior to sampling the valuable historical material we developed a methodology to clean and then dye raw porcupine quills in the laboratory and prepared a set of dyed porcupine quill references using natural dyes and a few early synthetic dyes in order to compare and contrast with the NMS collection. The dye extraction was carried out using the classical hydrochloric acid hydrolysis used at NMS for the investigation of historical textile samples and was successful in recovering both natural and early synthetic dyes. [5] In order to shed more light on these unusual materials a multidisciplinary analytical approach was developed for the historical samples. The characterisation of the dyestuff was carried out using Ultra Performance Liquid Chromatography (PDA-UPLC) at the University of Edinburgh. The concentration of the metallic mordant was evaluated using both Proton Induced X-Ray Emission (micro-PIXE, AGLAE beamline) and ICP-MS analysis and calibrated against a set of porcupine quill standards treated in-house with dyebaths containing *Dactylopius coccus* Costa and various concentration of tin and copper salts. [6]

The results showed that the Athapaskan collection at NMS is based on natural dyes imported from Europe. The most interesting find is probably that tin and copper mordants were used to achieve the different hues observed, although all the dyes characterised were direct dyes. Finally, the acid hydrolysed extracts of porcupine quills dyed with *Dactylopius coccus* Costa show significant differences to those typically obtained from historical textiles. [7] This study highlights how small differences in the concentration of mordant in the dyebath can greatly affect the uptake of cochineal dye components on the porcupine quills, resulting in perturbation of the normal dye-profiles.

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Dyes and Textiles from Shipwrecks

Case studies *Vrouw Maria* and *St. Michel* from the Age of Enlightenment

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Merchant ships *Vrouw Maria* and *St. Michel* were on their way from Amsterdam to St. Petersburg, when they shipwrecked on the brackish coast of Finland because of poor marine charts, bad weather conditions and perhaps misfortune. According to the Sound toll registers *St. Michel's* cargo consisted of tobacco, sugar, cinnabar (100 pounds), thread and 45 bolts of calico among different kinds of food products and unspecified cargo of high – value. *Vrouw Maria's* cargo consisted of sugar, dyes like madder (more than 8000 kg), indigo (approximately 1500 kg), brazil wood (approximately 2300 kg) and textile raw materials like cotton (600 kg) and fabrics like woolen cloth, calico, Dutch plain weave textile among other commodities, and also some high- value goods.

There are more than 600 objects lifted from the *St. Michel* since she was found by chance in late 1950's and amongst these are several items like socks and pieces of cloth and fragments of textile. These are now analysed to identify the dyes used in them. *Vrouw Maria* was found after a systematic search operation in 1999 and the identification was verified by combining archaeological and historical research. She did not sink immediately, so the crew managed to salvage some goods and there is also very much written information concerning the salvage operation and salvaged goods. Among the goods are several packages or barrels of indigo and different kind of fabrics and textile products. *Vrouw Maria* carried also valuable pieces of art for the Empress Catherine the Great, but most likely the crew did not manage to salvage them. In the archaeological research there are now several samples taken from the barrels and wooden boxes which are still inside the cargo hold of *Vrouw Maria* and the results are both interesting and promising. One of the most remarkable find is a red woolen textile, which was analysed by Maarten Bommel and Ineke Joosten at the Netherlands Heritage Agency [1]. MA, PhD student Krista Vajanto at Helsinki University has studied the materials of these textiles from the fibre samples. Despite the deterioration of fibres, dyes are still traceable.

The aim of this presentation is to tell about this rich and remarkable source material from the Baltic Sea and what archaeological research combined with different kinds of analysis methods can give to the research of dyes and fabrics used in the Age of Enlightenment.

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Central coastal textiles from the Chancay culture: dye sources and technologies

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The British Museum (BM) houses one of the largest collections of Andean textiles outside Peru comprising pieces ranging in date from the Early Horizon through the Colonial Period. A detailed study of the organic colorants and dyeing technologies represented in this collection is currently underway, through the project *Andean textiles: organic colourants, biological sources and dyeing technologies* funded by the Leverhulme Trust, to complement and extend standard approaches to the study of garment form and function, weaving materials and techniques as well as iconographic analysis [1]. The BM collection encompasses a representative range of all the major techniques, structures and designs from the North, Central and South coasts, but the collection's strength is particularly focused on the Central coast and more specifically on the late intermediate period textiles from the Chancay culture.

At the DHA30 meeting, the preliminary work to develop the methodological approach and to optimise the analytical procedures was presented, including soft extraction techniques for HPLC [2]. In this paper we will present the results obtained applying these methods to a selection of Central coastal textiles from the BM collection and on materials drawn from a group of weavers' work-baskets originating mainly from the Ancon necropolis and now in the collections of the BM and the Musée du Quai Branly, Paris. The textiles examined include examples of naturally coloured and dyed fibres, and were produced using both cotton and camelid fibres. A similar range of fibres are found associated with the workbaskets, along with tools and other materials linked to textile production. The main analytical focus has been on the characterisation of the organic colorants using HPLC analysis, but the fibres and mordants have also been examined and will be discussed.

The availability of a large range of comparative reference materials, many collected in coastal regions of Peru around Nazca and Ica in October-November 2011, has been key in interpreting the results obtained from the archaeological materials [3]. The inclusion of reference materials produced by local dyers in Lima and Cuzco and dyed samples produced under laboratory conditions has been particularly revealing. The comparison of the range of different evidence obtained from the reference materials, the fibres and tools associated with the work-baskets, and the finished textiles is starting to offer new insights into coastal spinning traditions and textile production methods and dye sources and technologies.

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Dyes and dye plants of Bronze and Iron Age Europe

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In 2002 the investigation in the dyes of prehistoric textiles from the salt mine of Hallstatt in Upper Austria started. The first results were discussed at the 1st International Hallstatt Symposium (Hallstatt 2004) [1], at DHA 23 and at ICOM-CC (2005) [2]. During 2008 and 2012 an interdisciplinary research project on 'Dyeing techniques of the prehistoric Hallstatt textiles' was supported by the Austrian Science Fund (FWF, L 431-G02). In this project, teams of archaeologists, artists and scientists collaborated in enlarging the knowledge about prehistoric dyes and dyeing techniques and in transforming this knowledge in modern times. They produced replications of Iron Age ribbons and created objects of textile art. Preliminary results of this research were presented at NESAT IX [3], at ISEND 2011 and DHA 30 and discussed at the 2nd International Hallstatt Symposium (Vienna 2012). The project led to the exhibition "Colours of Hallstatt" at the Natural History Museum Vienna [4].

This presentation will focus on the beginning of textile dyeing in Europe. What do we know about the used dyeing materials? The dyes of Bronze and Iron Age Hallstatt textiles were analysed by high-performance liquid chromatography coupled to photodiode-array detection. The results will be summarized and supplemented by analytical results of textile finds from other sites. The possibilities and limitations in identifying the dye material will be discussed. Was there a difference in the textile dyeing between Bronze and Iron Age? Did they only use wild plants or did they already cultivate plants? Taking into account archaeobotanical evidence on dye plants across Europe, the use and possible cultivation of dye plants will be discussed.

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Poster Presentations

(In alphabetical order by author)

Pink-violet residues from pottery recovered in Sumhram (Oman): chromatographic and mass spectrometric investigations

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Since 1997 the Italian Mission to Oman, directed by prof. A. Avanzini (University of Pisa), has been working in the area of Khor Rori (Oman). In particular, the archaeological excavations carried out in Sumhram, the most important pre-Islamic harbour in the area, brought to light a large number of findings. Of particular interest were several ceramic fragments (I-II cent AD), all showing residues of a pink-violet substance (Figure 1).



To reveal the origin of the colour, an approach entailing the use of analytical techniques based on chromatography and mass spectrometry (HPLC-DAD and DE-MS) was used. The analytical investigations provided detailed molecular compositions, highlighting the presence of a wide range of compounds: 6,6'-dibromoindigotin, monobromoindigotin, indigotin, 6,6'-dibromoindirubin, monobromoindirubin and indirubin.

Figure 1

The compounds identified allowed us to assess that shell-fish purple, the so called Royal or Tyrian purple, was the source of the pink-violet substances found in the ceramic fragments. This enabled us to draw hypotheses not only on the possible function of ceramics in connection with the storage/trade of purple, but also on the possibility that Sumhram was a centre for the production of purple.

The Short Life of Tannins – an innovative approach to the study of ageing processes in tannin dyed textiles

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We present an innovative project on the study of tannin-based dyes (VAT, “The Short Life of Tannins”) funded by the Regione Toscana, Italy (FAS grants). The project involves the Department of Chemistry and Industrial Chemistry (Pisa), the ICCOM-CNR (Pisa) and the Opificio delle Pietre Dure (Florence). This project aims at modelling ageing processes undergone by textile fibres dyed with iron-galls and at identifying suitable conservation protocols.

Textile reference specimens were prepared with iron-gall dyes following historical recipes, with the support of the Settore Arazzi and Settore Tessili of the Opificio delle Pietre Dure. During the first year of the project, the morphology of the samples, also artificially aged, was characterised by optical microscopy and SEM analysis. Moreover, the suitability of SEM-EDX and Laser Induced Breakdown Spectroscopy (LIBS) for the identification of the mordant was evaluated. The dye components were analysed by chromatographic and mass spectrometric techniques. In particular, HPLC-ESI-MS/MS was exploited to characterise the raw materials and also to study the degradation products in order to detail the ageing processes. A method for the HPLC-MS/MS analysis of phenols, including phenolic acids, with an amide-embedded phase column (Ascentis Express RP Amide, Supelco) was developed and compared with the ones using classical C18 stationary phase columns. RP-Amide is a new generation of polar embedded stationary phase, whose wetting properties allow us to work with an high percentage of water as eluent, up to 100 %. The increased retention and selectivity for polar compounds and the possibility of working in 100 % water conditions make this column particularly interesting for the HPLC analysis of phenols. Chromatographic separation and detection parameters were optimised allowing us to obtain the separation of 12 standard phenols. The performance of the method was evaluated on the basis of different parameters: linearity, sensitivity, precision, accuracy and repeatability.

At the same time, fundamental research is in progress in the field of developing proper molecular modelling strategies aimed at studying the physical properties of the compounds involved in the textile-dye system. In particular, the characteristics of the gallic acid-iron-amino acid complexes was evaluated, leading to the final modelling of the dye-iron-protein interactions.

The results achieved by HPLC-MS analysis of raw materials (lipid and protein analysis) will be herein presented. Moreover, the results achieved by molecular modelling of the iron-gall-amino acid complexes will be presented.

Glass, Vitriol, and Indigo

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The fanciful idea that ancient Britons were coloured blue with woad arose from a remark by Julius Caesar that '*Omnes vero se Britanni vitro inficiunt, quod caeruleum efficit colorem*', plus a reference by Pliny to British women staining themselves with a plant known in Gaul as *glastum*. Past discussions of this question have not acknowledged four key linguistic facts: that *vitrum* 'glass' was a relatively new word in Caesar's day, that only one of the four parts of ancient Gaul definitely spoke Celtic, that woad started out as a fairly general word for dye-source plants, and that ancient names of colours often did not mean what modern readers assume.

With backgrounds in science and place-name studies, we can resolve some parts of this classic puzzle. Caesar was probably referring to tattooing, with ink formulated using vitriol (metal sulfate salts). However, we hope to trigger a discussion that brings in people with a wider range of expertise, from botany to ancient Coptic. Is it possible to make progress in identifying which plants, pigments, or colours ancient authors really meant when they referred to *isatis*, *glastum*, *indicum*, *terneken*, etc?

Rithons – semantic and dyestuff analyses

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The rithons differ from the everyday life and household vessels made by glass, metal and clay. The early variations of rithons found from the Bronze and Early Iron Age monuments. This research related to the Antique rithons and their semantic analyses found from Azerbaijan. Antique rithons mostly found from the pitcher and ground graves. Deer, horse, sheep, goat and other animal shape rithons decorated with red, dark red, brown and yellow dyes. The results of the dyestuff analyses included to this research as well.

Dyeing of Silk Fabrics with Madder (*Rubia Tinctorum* L.) and their analyses

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Madder has been used for dyeing textiles since the Stone Age. Common madder produces pigments in its roots, such as alizarin, pseudopurpurin, purpurin, munjistin, rubiadin, xanthopurpurin, purpuroxanthin, lucidin, chinizarin, christofin, anthragalol. Madder gives a unique red colour to textiles. The aim of this study is to understand the effect of different mordant concentration on silk dyeing using madder extract. Degummed and bleached, woven silk fabric (51 ends/inch, 46 picks/inch) weighing 89.6 g/m² was used. Madder was obtained from the Turkish Cultural Foundation, Natural Dye Research and Development Laboratory, Istanbul, Turkey. Alum (KAl(SO₄)₂•12H₂O) was used as the mordant. All reagents were analytical grade. Silk fabrics were scoured by soap (35 % w/w) at 90 °C, for 1.5 hour. Liquor ratio was 1:100. Dyeing was performed at 65 °C, 100% wof, for 2 hours. Mordanting procedure was achieved at different mordant ratios, for 2 hours, at 65 °C. All colour measurements were performed using Minolta 3600D spectrophotometer (D65 illuminant, specular included, 10° observer angle) (Table 1). Colour fastness to washing, light, perspiration and rubbing were performed according to ISO 105 C06, ISO 105 B02, ISO 105 E04 and ISO 105 X12 respectively. Each dyed silk fabric was analysed RP-HPLC-DAD. The quantity of colouring compounds were determined in the dyed silk fabrics, depending on the amounts of mordant metal.

Table 1. Colourimetric values of samples.

| Mordant percentage (w/w) | L* | a* | b* | C* | H° |
|--------------------------|--------|--------|--------|--------|--------|
| 0 | 57.151 | 26.875 | 38.681 | 47.101 | 55.209 |
| 1 | 43.539 | 39.285 | 32.810 | 51.184 | 39.867 |
| 2 | 40.488 | 43.541 | 29.809 | 52.767 | 34.396 |
| 3 | 40.218 | 43.751 | 28.927 | 52.449 | 33.472 |
| 4 | 39.882 | 43.643 | 28.450 | 52.097 | 33.099 |
| 6 | 39.740 | 43.517 | 27.511 | 51.484 | 32.301 |
| 9 | 40.268 | 43.435 | 27.218 | 51.248 | 32.079 |
| 12 | 39.266 | 42.424 | 26.480 | 50.010 | 31.972 |
| 14 | 39.672 | 41.771 | 26.078 | 49.243 | 31.977 |
| 18 | 40.688 | 42.048 | 26.824 | 49.876 | 32.536 |
| 21 | 40.702 | 41.738 | 26.441 | 49.409 | 32.354 |
| 24 | 40.065 | 42.789 | 26.426 | 50.292 | 31.699 |
| 27 | 39.803 | 42.994 | 26.605 | 50.560 | 31.749 |
| 30 | 41.439 | 41.551 | 26.930 | 49.514 | 32.948 |
| 33 | 41.430 | 42.819 | 26.866 | 50.549 | 32.106 |
| 36 | 42.097 | 41.129 | 26.917 | 49.155 | 33.203 |

Table 1 shows colourimetric values of samples. Darkest hue was obtained at 12 % of mordant concentration. Redness of fabrics was increased by mordanting. Highest a* value (redness) was obtained at 3 % mordant concentration. Vividness of fabrics was increased by adding mordant.

Study of *Enji*: Red Dyes for Cosmetics, Medicine and Colours

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Enji(胭脂, 胭脂, *Yanzhi*, [rouge]) are red dyes made from safflower that were brought from Central Asia to China in the second century BC[1]. Later, in the eighth century, *enji* made from stick lac (紫釧, *Zikuang*) began to appear[2]. It was made using disc-shaped cotton impregnated with lac dye and plant extracts. This kind of *enji* was called *wata-enji* (綿胭脂, *Mian Yamzhi*, [rouge cotton])[2]. From the eighth century to the beginning of the 20th century, *wata-enjis* were produced in China for use in cosmetics, medicine and for art material throughout East Asia.

Recently, however, the production of *wata-enji* has declined in China as has knowledge of traditional methods for making *wata-enji*. Consequently, stocks of *wata-enjis* produced in China before the 1940s are still being used by restorers and traditional artists in Japan. They continue to need *wata-enji* and are desperate to see it produced again.

The authors have surveyed relevant literature and analysed *wata-enjis* scientifically to develop a comprehensive understanding of the dyes. A number of *wata-enjis* made in China between the 19th and early 20th century have been preserved in Japan. The authors were able to collect samples from them with the cooperation of dye masters, restorers and Japanese-style painters. Sixteen types of *wata-enji* were analysed (including six types collected last year)[3]. In addition, a number of *wata-enji* were observed but not sampled, resulting in total number of types recorded to 22[4]. The authors made use of the 'Siku Quanshu' (四庫全書) database to investigate descriptions of *enji*.

On the basis of our research of the literature, it is possible to reconstruct a history of *enji* and its uses. It is important to recognize that *enji* were used for more purposes other than for painting and dyeing, with other important uses being in cosmetics and medicine. The *wata-enji* that are in use today have largely been designed for use as cosmetics. It is thought, therefore, that *wata-enji* fell into disuse with the influx of Western cosmetics into China, and with broader changes in the Chinese social life after the 1950s. In Japan there is considerable documentary evidence of *wata-enji* being used from the eighth century onwards^[5]. Although these *wata-enji* were used initially in Buddhist art, they became used more widely for painting and dyeing throughout Japan. In terms of the history of *wata-enjis* in the Korean Peninsula, we found evidence in 'the *Nogeoldae*' (老乞大) in the 14th century that *Wata-enjis* were purchased in Beijing and they were taken to Goryeo. These *wata-enjis* were being sold primarily for use as a form of cosmetic.

In addition, *enji* may have been used further afield. The remains of what are thought to be *enji* were discovered in a vanity case excavated from Mawangdui (馬王堆漢墓) in China, and early 20th-century trade records from Guangzhou list *enjis* being exported to Hong Kong^[6]. Therefore, it is possible that *enji* may be found outside East Asia and the authors would like to promote international cooperation in studying the spread of *enji*.

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Decomposition and Analysis of Carthamin in Safflower-Dyed Textiles

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Carthamin, from safflower blossoms, has been used for centuries in Japan and China as a red colorant for dyeing textiles and for making red cosmetics. However, the analysis of carthamin presents some problems because of its instability, although Wouters et al. [1] have shown that the presence of carthamin can be deduced even in faded textiles by the presence of four non-colored compounds (Ct1-Ct4) that copurify with carthamin and also bind to textiles. Carthamin has long been known for its poor fastness to light, but it has also been shown that carthamin is unstable in solution, especially at high temperature [2]. Having encountered what we suspected to be carthamin in several Chinese and Japanese textile specimens, we sought to understand how carthamin decomposes and how we can better analyse for it. There seem to be two modes of decomposition of carthamin: heat-promoted and light-promoted.

If carthamin is extracted from textile fibres at temperatures approaching 100 °C under acidic (HCl), neutral or basic (pyridine) conditions, it rapidly decomposes. Analysis of the decomposition products indicates that carthamin is cleaved into two portions *via* addition of a molecule of water, followed by a reverse aldol condensation. Carthamin can, however, be successfully extracted at low temperature (>50 °C) using a good solvent, such as pyridine, and analysed by HPLC. By contrast, carthamin-dyed textiles seem to be relatively stable to heat. This makes sense considering that reversal of the aldol condensation requires both water (in this case) and the ability of the halves of the molecule to diffuse apart. In a dry, dyed textile, the carthamin molecule is rigidly fixed and the halves, even if they are formed, cannot diffuse apart, but can re-condense to form carthamin.

We propose that carthamin-dyed textiles fade, when exposed to light, by a photo-oxidation process. Exposure of carthamin-dyed textile specimens to sunlight for two weeks resulted in fading and the formation of 4-hydroxybenzaldehyde and 4-hydroxybenzoic acid, as determined by LC-MS analysis using authentic reference compounds. Under the same conditions, a model compound, 4-hydroxy-2,4'-dihydroxychalcone, also produced 4-hydroxybenzaldehyde and 4-hydroxybenzoic acid. Thus it appears that carthamin fades, in the presence of light and air, by cleavage of one or more of its several carbon-carbon double bonds. Assuming that the carthamin is not 100% decomposed by light, the residual carthamin can be detected by extraction of the textile fibres at low temperature as described above.

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Brazilwood and its lake pigments: historic reconstructions

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Redwoods, also known in antiquity as brazil [1], were used as sources of dyes and pigment lakes. It is said that the country Brazil was named after those redwoods, this possibly being the only country in the world named after a tree. The flavonoid reds obtained from the bark of the tree are not so stable as anthraquinone reds, but they were much more affordable and were widely used for dyeing and in medieval miniature painting [1, 2] as well as in cosmetics. Brazilein, the red chromophore that may be extracted from the so-called redwoods, is the oxidized form of the natural precursor brazilin, Figure 1.

In this poster we will revisit the history of the production of the brazil lakes from medieval times to the nineteenth century, based on the information found in written sources and artworks. Historic accurate reconstructions of brazilein lake pigments were produced, following a systematic analysis and rationale of brazil lake recipes dating from 1846 to 1858 from the W&N database (Researcher Edition) and medieval times from the treatise *Libro de como si facem as côres* [3]. The W&N Researcher Edition combines a computer-based indexing system with digitalised page by page images from 85 handwritten books detailing manufacturing practices and recipes for 19th century artists' materials [4].

Finally, selected reproductions of brazilwood lakes, both from the on *Libro de como si facem as côres* and W&N archives, are analysed by FORS (fibre optic reflectance spectroscopy) and microspectrofluorimetry [2]. The information revealed by the two analytical techniques will be discussed.

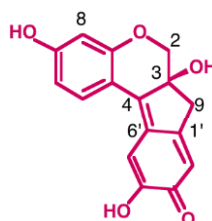


Figure 1: Brazilein

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Study of the influence of black dyes in the physico-mechanical behaviour of silk fabrics

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The aim of this research is to understand the implications of the chemical structure of some natural dyes in the physico-mechanical behaviour and degradation of dyed silk fabrics. More specifically, this study focuses on black natural dyes such as logwood (*Haematoxylum Campechianum L.*), commonly used in dyeing silk fabrics during the 18th century.

For this purpose, a multi-method approach is proposed combining microscopy, spectroscopy techniques and tensile testing in order to characterize the behaviour of silk fabrics as a function of the dyes present in their composition.

According to this, different recipes from treatises dated on the 18th century led to the preparation of different dyed silk samples in order to characterize them physically, mechanically and chemically. Stress strain curves helped to determine the stiffness and flexibility of silk as well as their elongation and strength to failure within specific environmental conditions and dyeing procedures.

Previous research carried out on the behaviour of silk fabrics allowed the correlation of results and evidenced an increase of silk's stiffness as a function of the type of dye and therefore its chromatism and pH of the bath solutions.

Effects of a textile cleaning method using supercritical CO₂ on dyes

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Cleaning textiles using high pressure CO₂ (liquid or supercritical) has been reported in the open literature. Almost invariably, however, co-solvents and/or surfactants are added to supercritical CO₂ for efficient cleaning [1,2]. In the case of historical textiles very much care must be exercised in finding safe, mild but effective cleaning methods that will remove the unwanted material without causing any deterioration or damage to the textile and the dyes.

Silk and cotton textiles, dyed with turmeric, weld, indigo and cochineal, have been soiled and cleaned using supercritical carbon dioxide, water and fine pulverized limestone as a stabilizer [3-5]. The proposed process gives successful results for polar and non-polar soils. The soiling removal (Figure 1) varies between 80 to 95% depending on the type of soil.

Attention is currently focused on the possible effects of the aforementioned cleaning process on the dyes. Colorimetric measurements showed that the ΔE between unsoiled and washed textile samples is decreased dramatically compared to the ΔE of unsoiled and soiled textiles and in some cases reach the JND limit. Furthermore, dyes showed no apparent loss of color consistency. The results of other measurements using XRF, optical microscopy, SEM and HPLC will be included in the poster to discuss in detail the possible effects of the cleaning process on the dyed textiles.

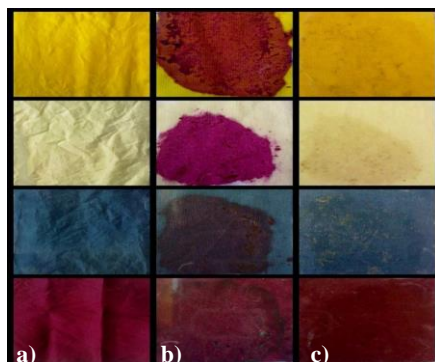


Figure 1: silk textiles dyed with turmeric, weld, indigo and cochineal; a) before the soiling, b) after the soiling, c) after the cleaning

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Re-thinking to Reflectance Spectrometry as a tool to identify some classes of dyes in old textiles and paintings *in situ*. Examples

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Reflectance Spectroscopy (RS) in the UV, visible and IR range represents a simple non-invasive tool that can be easily applied *in situ* to many objects and contexts, surface materials, allowing identifying many pigments and dyes, giving important information on colour and conservation issues [1]. The associated use of non-invasive analyses like RS and vibrational techniques such as Raman and Fourier Transform InfraRed (FTIR) spectroscopies or elemental techniques like X-Ray Fluorescence (XRF) can assure more precise or wide identifications, particularly on paintings [2, 3].

Despite the fact that its use, particularly on textiles, appears to be quite rare, RS allows to identify a very large set of pigments from antiquity to the modern era (up to 20th century), and it can provide a preliminary identification or class-distinction of dyes used in ancient (and sometimes modern) textiles, particularly for blue, green, violet and red dyes, as well as the identification of some lakes used in paintings [4, 5].

The possibility to study a large set of points/areas in a short period of time on one object, contextually obtaining a first interpretation of results, enables a greater precision and significance to choosing the areas on which to perform the more invasive examination, including HPLC and SEM+EDX, or SERS. On the other hand, it permits to extend to larger areas the results obtained on the analysed micro-samples.

In this work, the possibility to use vis-RS in order to detect dyes on textiles as well as lakes and dyes in paintings is briefly discussed, together with some band-shifts and changes experienced by reflectance spectra and the main limits of the technique. The latter regard – above all – the absence of characterizing bands in many dyes, leading to the difficulty in identifying yellow and brown dyes, some red dyes and some mixtures.

Some interesting examples will be discussed, mainly focused on red and blue dyes, including discoloration effects on Chinese ancient carpets [6].

The interpretation of the RS results is based on a database of dyed textiles created in laboratory and also on the field, where many samples from old textiles have been studied by means of this tool and chromatographic analyses: much more test dyes have to be analysed in the near future. 19th and 20th century samples have also been collected and studied, in order to assess RS detection limits.

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Studies of the category „Rheinische Zeugdrucke“

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The motivation for the work was a request by an art dealer (Wolfgang Ruf), who wants to determine the originality of several Rhenish patterns from his collection. The objects were reviewed by Donald King in 1962 on the originality of the class of the objects. At the time, King concluded that these objects must be imitations that must have been produced in the 19th century. Now, these prints should be reanalysed with current state-of-the-art methods. The term “Zeugdruck” stands for patterning of fabrics by block printing. The term “Rheinische Zeugdrucke” refers to printings originating from the Rhine valley, and in particular from the lower Rhine valley. The definition of the “Rheinische Zeugdrucke” was established by Robert Forrer, who published more than 90 works in the literature between 1894 and 1898. He described them as products of the 8th-16th century. For the most part, these patterns appeared at the Rhenish art markets in the years 1890-1900. [1]

Altogether twelve objects have been analysed, of which five exemplars are coming from the collection ‘Ruf’. Another four exemplars are from the ‘Museum für angewandte Kunst Köln’, one exemplar is from the ‘Suermond-Ludwig-Museum Aachen’, and two more exemplars from the ‘Deutsches Textilmuseum Krefeld’. The similarity of all objects is that they all are referred to as “Rheinische Zeugdrucke”. Also, they are all dated to the period between the 12th and 15th century.

In order to characterize the applied pigments, binders, and materials, several state-of-the-art scientific methods have been carried out. The investigation started with a fibre analysis, and was followed by UV-VIS and infrared spectroscopy. Subsequently, the investigation was followed by scanning electron microscopy and an element analysis. On the basis of these examinations, one could for example assert that the assumed gold and silver prints are rather made from tin and brass. For the purpose of typological and stylistic characterization, an art historic analysis was carried out. This included a detailed examination of the weaving construction and manufacturing technique. Finally, for a better age determination and classification, the printings have been compared to silk fabrics from the Middle Ages.

The scientific analysis of the objects does not allow any conclusion that the works might not originate from the Middle Age. For example, all applied materials and pigments were known at the time. However, the results of the art historic analysis suggest the origin of the works in the time of historicism. Although all prints carry the typical conformities with medieval fabrics, they also show several deviations from the usual pattern canon. Therefore, the results of the art historic analysis suggest that these works are indeed imitations of the prints. In summary, however, more research on the question of the originality of the “Rheinische Zeugdrucke” is needed to come to a final conclusion.

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Rare compounds studies in *Reseda luteola* L. and *Rubia tinctorum* L.

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Compounds from weld (*Reseda luteola* L.) and madder (*Rubia tinctorum* L.) plants are the most encountered in dyed textiles and lake pigments in cultural heritage objects from Europe. A few of the components present in these dye plants have been elucidated and are available to research centres from chemical suppliers as standards. However many components in these plants are not available despite the fact that they are often found in the objects and play a role in the colouring mechanism.

Within the joint research work package of the *Cultural Heritage Advanced Research Infrastructures: Synergy for a Multidisciplinary Approach to Conservation/Restoration* (CHARSIMA) project, a method was developed to isolate these rare compounds from the plant material in order to study their behaviour and elucidate their structure if possible.

A large amount of dried weld and madder was purchased. A simple extraction method that consisted of water/methanol (1:1) at 65°C in an oven for 30 minutes was applied. The 250ml extractions were filtered with 0.45µm filter units.

A preparative liquid chromatography system (Prep-LC) was set up to isolate the weld and madder compound fractions. The system derives from the typical high performance liquid chromatography system using a Luna C₁₈ column but with different dimensions. However phosphoric acid in the mobile phase gradient was replaced by formic acid; this because formic acid is volatile so it can be, unlike phosphoric acid, easily evaporated.

These separate compounds were collected with a fraction collector and then concentrated with a rotary evaporator.

Eight fractions of weld and seven fractions of madder were collected. All of them were then kept in a 10% methanol aqueous solution; the fraction's decay was monitored with high performance liquid chromatography with photodiode array detector (HPLC-PDA). Hydrolysis of the fractions was as well performed in order to understand their mechanisms and establish, if possible, its core molecule.

These fractions are also studied by means of electrospray ionization quadrupole-time-of-flight mass spectrometry (ESI-QToF) and nuclear magnetic resonance spectroscopy (¹H- and ¹³C-NMR) for elucidation of these complex components.

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A New Method for Characterizing Dyestuffs with Ultra-Performance Liquid Chromatography

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An interdisciplinary project that connects both disciplines of History and Chemistry has been developed in order to obtain accurate approaches on the real impact of American cochineal, as a red dyestuff, in European and Asian centres of textile production, between the 16th and 18th centuries. This will be achieved through the revision of historical sources, along with the development of an optimised analytical method, which comprises the chromatographic analysis of cochineal species and their subsequent differentiation with multivariate statistical comparison and, consequently, their further characterization in European and Asian historical textiles, dated from the 16th century onwards.

It has been previously shown that High-Performance Liquid Chromatography (HPLC), along with components quantification, cannot provide a precise characterization of the cochineal insect species, and for this reason, multivariate statistical analyses are needed to compare the resulting chromatograms [1]. As good resolution chromatograms are required to ensure the correct discrimination of the components present in cochineal species, it was opted to undertake an optimization of the analysis conditions using Ultra high-Performance Liquid Chromatography (UPLC). This very recent technique presents several advantages over HPLC, as it can provide a better resolution, owing to the smaller particle size columns [2], essential for the low molecular weight from dyestuff components. Therefore, the optimisation of the analytical conditions comprised three main parameters: several UPLC columns of different dimensions and stationary phase composition; different elution gradients, adapted from previously published HPLC methods used for dyestuffs characterization [3]; and mixtures of natural dyestuffs extracts, which included the main components commonly found in historical textiles. The optimised elution method for UPLC was then applied to a HPLC column, hence demonstrating that UPLC analyses provide more accurate results than HPLC. Indeed, the Limit of Detection (LOD) significantly improved with UPLC, which allowed the acquisition of more precise data, extremely valuable for the characterization of minor components present in dyestuffs. Therefore, this research is of upmost importance, as it represents the first application of UPLC analyses into the field of dyestuff analysis related to cultural heritage.

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Microbiological analysis of naturally fermented indigo vat by Korean traditional method

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Indigo is one of the oldest natural dyes for blue color and is traditionally produced from indican by innate enzyme in indigo plant. In Korea, indigo blue extracted from *Polygonum tinctorium* has been very popular and its deep blue colour is called by 'jjok bit'- Korean Blue. As it has been known, indigo is insoluble and, therefore, for commercial dyeing, it is converted to the colourless and soluble leuco-form by chemical reduction using alkaline sodium dithionite. Today, several thousand tons of indigo dye is consumed annually for dyeing jeans by the chemical reduction process [1]. This conventional procedure generates environment-polluting, highly alkaline effluents, in addition to by-products containing sulphur [2]. On the other hand, in the fermentation reduction method which has been used traditionally in Korea, the mixture of *Niram* (muddy indigo) and lye (pH 11-12) is set in a ceramic jar with lid and stirred occasionally, not very often, until the bath has become a yellowish green colour with a coppery film on the surface [3]. The reduction occurs naturally with no additives, but it takes time from one to four weeks depending on seasonal temperature. The traditional process is eco-friendly but not reproducible and rather tedious. This prevented its use as an industrial application. Thus, we expect that the process using microorganism participated in indigo reduction may solve these problems in an environmentally friendly manner, also providing another possibility of improvement for low reliability. In this context, we identify the bacterial population or community resident in well-fermented natural indigo vats following Korean traditional method. 16S rRNA sequences-based meta-genomic approach paves a way for understanding [4] and interpreting the bacterial community related to natural indigo fermentation [5]. This will be a basis for developing the eco-friendly indigo reduction process mimic formulated by the artificial one. Six identified and three unidentified bacterial strains were isolated from the indigo fermentation vat.

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English tapestry workshops in the mid-16th century: characterisation and provenance through PDA-HPLC and UPLC analysis

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This paper presents a recent survey of mid-16th century English tapestries attributed to the Sheldon workshop at Barcheston in Warwickshire. The term “Sheldon” is usually applied to early English tapestries and mainly refers to large tapestry maps representing the English countryside, key examples today being part of the Bodleian collection in Oxford and the Victoria and Albert Museum in London. The assumption was that there was only this one workshop in England in the mid-16th century, although this is being today reassessed through art historical research. [1, 2]

In order to understand workshop practices in England, we studied nineteen small tapestries part of the Burrell Collection in Glasgow, as well as three secure “Sheldon” pieces part of the Bodleian collection in Oxford. Around 300 samples were investigated using High Performance Liquid Chromatography coupled to Photo Diode Array Detector (PDA-HPLC) and Ultra Performance Liquid Chromatography (UPLC). Dye sources were identified by comparing the chromatographic profiles of main, minor and traces components to those obtained from references samples. Special interest was given to the identification of flavonoid-based dyestuffs and several sources were characterised, including weld, dyer’s greenweed but also surprisingly young fustic. Madder species and Mexican Cochineal were identified for red hues but also safflower and lichen dyes. [3, 4]

This study provides new information on this unique group of English tapestries. Safflower dye has only been characterised once on a mid-16th century European tapestry, prior to this study. [5] Thus its presence on all the Burrell English tapestries is particularly notable in an historic context, as safflower would have been traded into Europe.

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Dialogue with folklore and dye analysis – HPLC-DAD analysis of some Finnish folkloristic textiles

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Three Finnish folkloristic textiles were selected for this study: two woven rugs and a pillow case. The rugs from the City Museum of Espoo, Finland were dated to the late 18th century and to the early 19th century according to the motifs of the decorations. The pillow case from a private collection was dated to the early 20th century according to a family history. The rugs were estimated to contain local plant dyes on the basis of folkloristic information whereas the pillow case was expected to contain local mushroom colorants on the basis of family folklore.

In the fibre analysis the wool yarns of the rugs were defined to contain unpigmented and naturally pigmented fibres as well as broken medullas and very shiny fibres, which indicated the wool to be from the early modern Finnsheep. According to the family history the pillow case was made of local materials by a woman who was a folk healer and a weaver.

Several samples were taken from the textiles and analysed using the HPLC-DAD technique. Results of the analyses were interesting [1]. Both of the rugs contained many imported dyes, though almost similar shades could have been obtained from the Finnish nature. Mexican cochineal was found in the red yarns from the 18th century rug while the actually faded red yarns in the 19th century rug were interpreted to contain redwood - no local bedstraws as expected. The green was dyed with indigoid dye, possibly woad, but no yellow compounds were found. However, some unidentified peaks were observed in every dyed yarn of the older rug. Those peaks - showing no absorbance above 255 nm wavelength - could indicate the use of a still unknown Finnish dye and plant mordant but more probably they refer to contaminations. It is known, that this rug had been first used as a wall hanging, then as a horse blanket and finally as a blanket for potatoes in a farmer's cart.

In the 19th century rug the green yarn seems to be dyed with a yellow flavonoid dye together with indigo carmine. The yellow quercetin based dye is most probably local heather, which has been a well known yellow dye source with good light fastness properties [2]. The bright reds were defined to be from two insect dyes, Indian lac dye and Mexican cochineal. One sample was visually observed as beige-purple, however no peaks were detected.

The most unexpected result came from the yarns of the pillow case. It seems that there were no natural dyes present, but synthetic dyes, such as Acid yellow 23, Acid orange 7, Acid red 1 and Acid blue 3. This is in agreement with the dating of the pillow but unfortunately, doesn't give evidence to the use of local mushroom colorants.

The results show that the dye history of Finland is more complicated than expected. It seems that the usage of imported dyes has been common among the folk people regardless of the high price of dyestuffs. The actual variety of dye sources found makes it necessary to find more textiles from Finnish folklore heritage for identification of the applied dyes.

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The *Tekhelet* Project: to revive the industrial dyeing of ancient hyacinthine purple

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The Biblical commandment to tie a tassel (Heb. *tzitzit*) to each corner of garments requires that a cord of violet blue (Heb. *tekhelet*) be attached to the tassel (Numbers 15, 38). *Tekhelet* is synonymous with "hyacinthine purple" of classical antiquity, while Biblical purple (Heb. *argaman*) is "Tyrian purple" [1]. On Judaic ritual prayer-shawls (Heb. *tallit*), the use of this *tekhelet* cord was discontinued in the 7th century, because its source was lost.

The Venetian professor of pharmacy and chemistry Bartolommeo Bizio [2] was the first to identify the Mediterranean shellfish "banded dye-murex" (*Hexaplex trunculus*) as the source of ancient hyacinthine purple. Although contradicted by his contemporaries, this finding was confirmed by later researchers [3]. The dye from *H. trunculus* is characterized by a significant content of 6-bromoindigotin admixed with indigotin, in addition to 6,6'-dibromoindigotin [4]. The authentic dyeing-process is now considered to have required a bacterial fermentation vat [5].

Utilizing these findings, the *Tekhelet* Project [6] aims to re-establish the large-scale manufacture of *tekhelet* in order to reintroduce the use of the coloured cords on ritual shawls worn by Jews throughout the world. The feasibility of creating a sustainable market for *tekhelet* cords has now been proved by the pilot-undertaking of Ptil Tekhelet [7]. The new initiative faces several difficulties:

1. The mollusc must be conserved, as it is threatened by extinction in nature due to pollution of the Mediterranean Sea [8].
2. It cannot be fished for in Israel because it is a protected species.
3. A regular and reliable supply of hundreds of thousands of snails will be required each year.

Therefore the central initiative of the *Tekhelet* Project is an R&D program to investigate how to rear and farm banded dye-murex in artificial pools using mariculture. The goal will be to be able to set up full-scale installations for breeding the snails, producing the dye and dyeing the ritual *tekhelet* cords.

The project may also deal with related subjects, such as:

1. developing a laboratory assay for the content of dyestuff precursors in the shellfish;
2. chemical synthesis of 6-bromoindoxyl and 6-bromoindigotin;
3. clarification of the mechanism of the thermochromic transition of 6-bromoindigotin [9];
4. explaining variations in the colour as obtained from individual snails;
5. defining optimal conditions for the formation of the dye;
6. using a fermentation vat for dyeing;
7. the biology of the fermentation process;
8. alternative biological methodologies for making the dye.

The *Tekhelet* Project will contribute to the interpretation of findings regarding dyes and dyeing.

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