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Departamento de Conservação e Restauro & Requimte, Universidade NOVA de Lisboa

with

Instituto de Estudos Medievais, Universidade NOVA de Lisboa
Instituto Superior Técnico, Universidade de Lisboa
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With the collaboration of

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Acknowledgements

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WELCOME

We are very happy to welcome you to the **37th Dyes in History and Archaeology Meeting**, hosted by the Faculty of Sciences and Technology of the *Universidade NOVA de Lisboa* (NOVA FCT) hand in hand with *Instituto de Estudos Medievais* (NOVA), *Instituto Superior Técnico* (UL) and *Museu Diocesano de Santarém*.

This conference will focus on all issues concerning historical dyes, namely their production, properties, conservation and historical implications.

We would like to thank all the participants for their contributions and our sponsors for their support in making this meeting a rewarding and enjoyable experience. A special note of thanks is extended to the *Mosteiro de Alcobaça* as well as to the students and administrative staff who have worked behind the scenes to make this meeting possible.

On behalf of the Scientific and Organizing Committees
Maria João Melo

LECTURES

Unpacking a 19th century dyer's notebook

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This notebook came into the possession of the current owners in the 1930s when one of the family worked for Paton's and Baldwin's; it was salvaged because it was believed that the book was on the verge of being thrown away. The notebook contains a large number of dye recipes, each with its swatch of dyed wool or fabric.

The family brought it to me because they read of my research into the 19th century Halifax dyer David Smith. On the flyleaf of the notebook are the words *Dyer Instructer [sic] by Daved [sic] Smith pattern Dyer*. The questions I was asked were: what is the connection between David Smith and his book *The Dyer's Instructor* and this book? Was the notebook written by Smith and/or did the recipes feature in *The Dyer's Instructor*?

This presentation will describe the analysis that was undertaken to discover whether or not the book had been written by Smith and/or used in *The Dyer's Instructor*, including the transcription of the pages, visual analysis of sample degradation, comparison of recipes and comparison of hand writing. It will also examine the dating of the notebook and the variety and nature of the dye recipes in relation to dyeing education in 19th century Yorkshire.

Thursday 25 October

Lakes on the large scale. The production of brazilwood lake pigments in 19th c. paint industry

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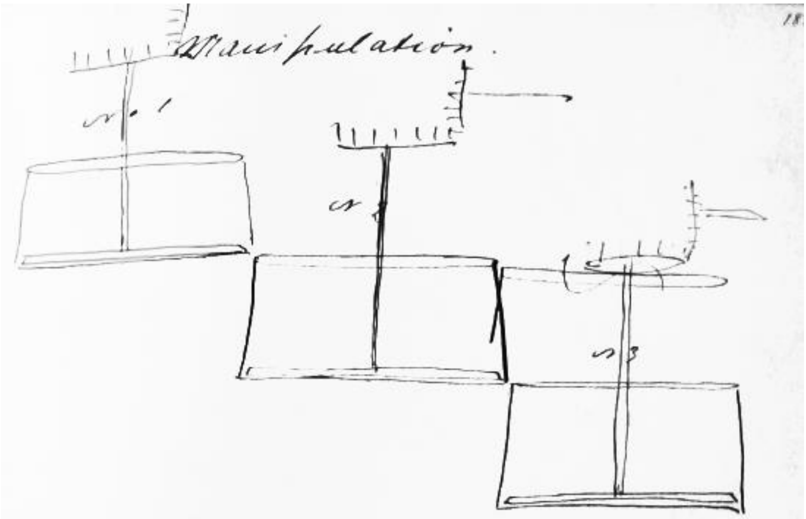
During the 19th century the production of pigments and paints has undergone a considerable change. While pigments and paints had previously been made by colourmen or small-scale manufactories, they were now produced in large, industrially organized factories. The rise of the pigment industry went hand in hand with many new discoveries. The invention of synthetic dyes is often regarded as a main factor causing this "colour revolution" and many natural dyes were just replaced with a synthetic equivalent.

But while some natural dyes were almost completely driven out of the market by the new brilliant and colourful synthetic products, a few natural dyes were still used until the early 20th century. Literature as well as hand-written sources indicate that brazilwood not only was among those few persisting natural dyes, but also played quite an important role in 19th century pigment manufacture – at least in Germany. Evaluation of recipes of several manufacturers shows that brazilwood lakes were produced in astonishingly large amounts throughout the 19th century. Beside pale rose coloured lakes with large amounts of fillers the sources also mention intense reds, deep purples or dark, brownish shades.

While late 19th century recipes indicate that lake pigments from synthetic dyes were made in relatively small batches, production of brazilwood lakes went into larger scale. Towards the end of the century, industrial production techniques were efficiently applied to make lake pigments from natural dyes. The presentation will show examples of such recipes and will point out difficulties with their reproduction. With these recipes, ingredients cannot easily be scaled down to laboratory amounts or their production may require quite a complicated experimental build-up.

The results from these experiments and the research into 19th century literature on brazilwood lakes bring up more questions than answers. The amounts mentioned in the sources make one wonder what those large amounts of lake pigments were used for? Was making a brazilwood lake really that much cheaper? And why were they made and used at all, even though lake pigments from synthetic dyes were more brilliant, much easier to produce and more consistent in colour?



Vat set-up for lake pigment production (around 1890)

Studies on *Origanum vulgare* L. as a traditional dye plant in Latvia

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Exploring the traditional cultural heritage, including the natural dyeing, it is essential to investigate exactly the use of local resources. In Latvia dyeing using natural dyes continued to be practiced for more than 150 years after the discovery of synthetic dyes.

In traditional culture both artistically and symbolically, the red colour carries special significance. So far in the world, there have been more studied the most commonly used sources of red: *Rubia tinctorum* L., brazilwood, cochenille. However, in the traditional dyeing practices of peasants, there were known also other sources of obtaining the red colour. In each region to a large extent, they are related to the local natural conditions. However, these colorants are not always well explored. In the traditional Latvian culture, *Origanum vulgare* L. is like that.

Scientific literature provides extensive information on *O. vulgare* as a pharmaceutical plant containing valuable essential oils. However, information on *O. vulgare* pigment content and dyeing technologies is hardly found in the international scientific environment. At present the University of Latvia, in cooperation with the Institute for Environmental Solutions, has launched studies on *O. vulgare* as a dye plant used in Latvian traditional culture. The report will present the preliminary results obtained by combining both information from ethnographic and folklore sources and reconstruction of dyeing methods and chemical analysis of mass spectrometry, determining the content of pigments in *O. vulgare* dyeing solution and in samples of textiles dyed nowadays.

In Latvian folk songs, which cannot be exactly dated, although their estimated time of origin would be the 16th century, for dyeing the yarn in red are mentioned 'sarkane' *O. vulgare* ('sarkane' = from the Latvian word 'sarkans' = 'red') and 'madara' *Galium* L. In the descriptions of the use of plant dyes given in ethnographic sources about dyeing of wool or yarn in red, *O. vulgare* has been mentioned also alone or in combination with the leaves of apple tree *Malus* spp.

Research is hampered by the fact that the local, ancient dyeing technology is not precisely known. Technological reconstruction with experimental method is still in process. It is not currently known what the red tone obtained from *O. vulgare* in historical textiles looked like. In ethnographic records there has been mentioned a dark red or red colour.

To recognize the source of colorant used in historical textiles, it is necessary to find out the pigments gained from *O. vulgare* in textiles, dyed nowadays.

Liquid chromatography coupled with UV/visible diode-array detection (DAD) and high-resolution mass spectrometry (HRMS) detection were used in this research for the identification of plant pigments extracted from textiles coloured with *O. vulgare*.

This powerful technique provided abundant information for structural elucidation of the extracted plant pigments and facilitated rapid and accurate identification of some extracted chemical compounds, derived from *O. vulgare*. Sixteen different natural dye components were extracted and identified in all analysed samples, mainly flavanols giving the yellow colour, as well as anthocyanins, which give red, were found.

The use of dyes in the Qing dynasty textiles

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Dye analysis of five pieces of Qing dynasty textiles (Figure 1) treasured in China National Silk Museum were carried out by high performance liquid chromatography coupled with mass spectrometry. Dyes from pagoda tree buds, sappanwood, Amur cork tree, safflower, young fustic, turmeric and indigo were identified; ellagic acid and carminic acid were detected in a piece of crimson robe material, indicating that a tannin-type dye and cochineal were also used during the period from the 18th century to the 20th century. An interesting finding was that methyl violet and fuchsine were identified in a piece of purple gauze dating to the late Qing dynasty, thus demonstrating that early synthetic dyes had been exported to China from Europe by the end of 19th century. The results of dye analysis for these Qing dynasty textiles give scientific evidence for the range of colorants used in late Qing textiles.

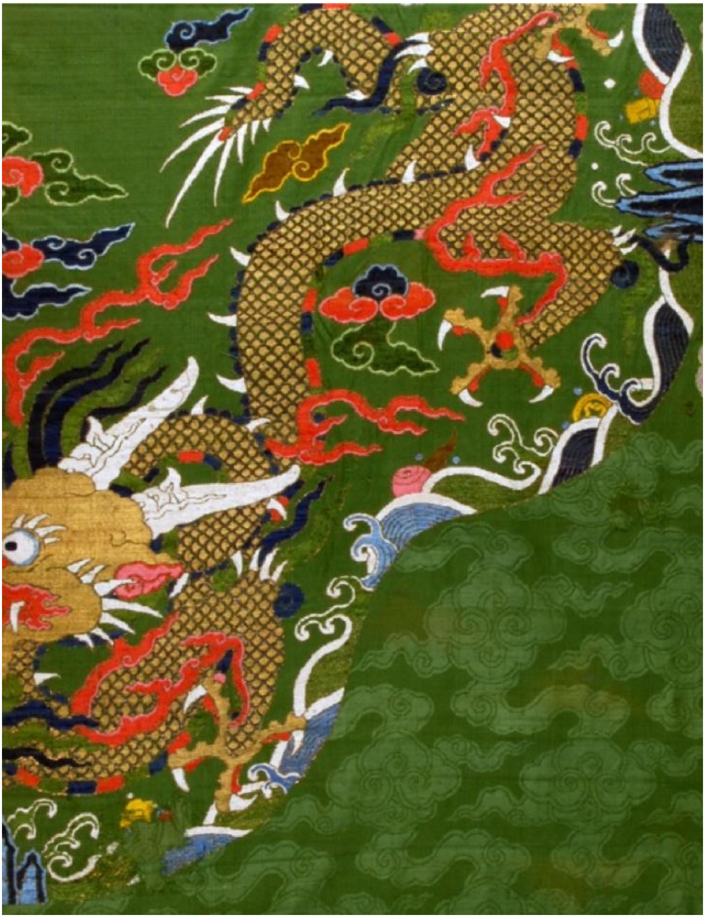

Figure 1. Brocaded robe textile with python pattern in green, China National Silk Museum

The Pazyryk Purples: a reinvestigation

Zvi C. Koren

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The polychrome Pazyryk saddle cloth, together with other textiles from that culture, show the advanced state of textile dyeing and weaving of the peoples inhabiting the Altai Mountains of Siberia and Central Asia from as far back as nearly 2500 years ago. Some of the dye analyses of these textiles were published in a scientific journal (1) whereas other analyses have appeared in the Russian book publishing these results (2).

It has been reported that a molluskan purple dye has been identified in a number of the coloured yarns in the saddle cloth. This finding is of primary importance to those analysts who research molluskan purple dyes since such dyeings are not nearly as common as other plant-derived dyes, and such molluskan-based dyeings shed important light on the high status of the wearer or user of these textiles. Specifically, the differently dyed yarns that are discussed consist of blue, violet, and reddish-purple hues. Some of the questions regarding the results of the analyses are as to which colours were in fact produced from molluskan species and which from flora sources alone. An additional question is which molluskan species is (or are) believed to have been used for these dyeings. To complicate the situation, certain end-users of the Russian results have used the Pazyryk blues to show that a so-called "pure-blue" colour was produced in antiquity from molluskan species. Is this reporting correct or have the Russian results been misinterpreted by others.

About 7 years ago, this author was granted permission from the relevant authorities at the Hermitage in St. Petersburgh to have representative samples removed from the saddle cloth and to re-analyse these yarns with the HPLC methodology that the author has been using for over two decades.

This talk will highlight the surprising results from the author's analyses of these yarns and should set the record straight, once and for all, regarding the true nature of the dyestuff sources used for those colours.

(1) G. G. Balakina, V. G. Vasiliev, E. V. Karpova, V.I. Mamatyuk, *Dyes Pigm*. 2006, 71, 54-60.

(2) N. V. Polosmak, L. L. Barkova, *Costume and Textiles* (Russian), 2005, Novosibirsk.

Organic reds in El-Andaluz: a study on medieval Islamic manuscripts

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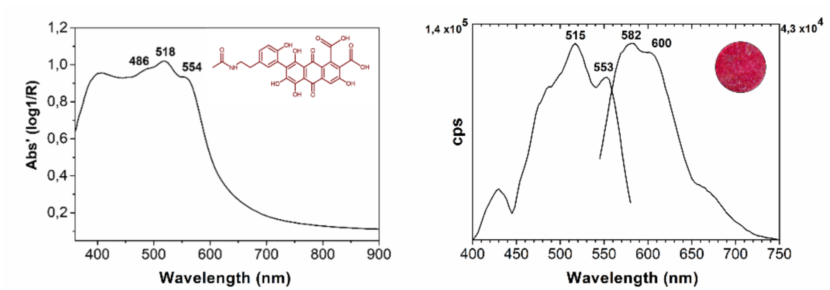
The rescue and possible restoration of a group of Islamic manuscripts from Timbuktu, Mali, created the opportunity to study the materials and techniques used to illuminate these medieval books. Organic reds, that we describe as a carmine colour, were applied in all five manuscripts studied, dated between the 11th. c. and the 15th c., which include a Coran, a mathematical treatise, a book of poems from al-Sarishi, a biography of the prophet and a theological treatise. With the exception of the Coran, applied on parchment, all were on paper.

The dark reds were characterized using FORS (VIS), microspectrofluorimetry, infrared spectroscopy (μ-FTIR) and SERS. Microspectrofluorimetry detected the presence of lac dye chromophore and disclosed the diversity of the recipes used. In this presentation, we will compare the data from the original Islamic colours with our references for medieval lac dye paints to ascribe specific recipes for each of the different carmines studied (1). μ-FTIR enable us to identify fillers and to further pinpoint the process used to create these medieval paints. It also showed the presence of oxalate compounds, possibly, resulting from the binding media degradation, a mark of the dramatic recent history of these books.

The rich variety of organic red recipes contrasts with the absence of an inorganic red; in fact, vermilion was only detected in one manuscript to create an orange hue, admixed with orpiment.

Finally, the carmine colours are compared to lac dye colours found in our systematic study on 12th-13th c. Portuguese manuscript illuminations (2). From Mali to Portugal, tracing the precious heritage legated by medieval Arab culture.



(1) R. Castro, A. Miranda, M. J. Melo, in *Sources in Art Technology: Back to Basics*, S. Eyb-Green, J. Townsend, K. Pilz, S. Kroustallis and I. van Leeuwen (Eds.), London: Archetype Publications, 2016, pp. 88-99.

(2) M. J. Melo, P. Nabais, M. Guimarães, R. Araújo, R. Castro, M. C. Oliveira, I. Whitworth, *Phil. Trans. R. Soc. A* 2016, 374(2082), 1-20.

Acknowledgements

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Textiles, trade and taste - Portugal and the world: what happened after 8 years

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Museums, religious temples and private institutions around the world house very fine and diverse textile collections. Their significance has been highlighted in the past decades by new research methods, which have greatly contributed to an increased awareness of their artistic and historical value. In Portugal, the interdisciplinary method developed in 2005 involving historians, art historians, museum curators and conservation scientists towards the historical and artistic study of a textile was particularly significant. This study was developed towards the conservation of an Iranian carpet belonging to the collection of the Museu Nacional de Machado de Castro (Coimbra) and which origin can be traced back to the Portuguese Expansion.
In this context further interdisciplinary projects came to promote the dialogue between researchers from distant fields of expertise, thus generating knowledge and contributing to the preservation of this Cultural Heritage. Furthermore, leading to the creation of *Textiles, Trade and Taste - Portugal and the World* (TTT) a multidisciplinary project on the global circulation of colour and textiles in 2011. One of the TTT's goals

was to establish a network of researchers working independently but also in cooperation. This has been encouraging the interdisciplinary combination of science, conservation and art history, providing systematic studies on the rich textile heritage, in Portugal and in the world. Moreover, disseminating the research undertaken by its members, TTT aspires to create new synergies in the field of textile studies and encourage collaboration among international researchers and institutions.
This communication presents the work that has been done so far by TTT and its collaborators. Textile research within TTT has ranged from assembling inventories to conducting stylistic, iconographic and archival studies, aiming to place objects in their historical, artistic, technological and socio-cultural contexts. Analytical interdisciplinary collaboration has been developed as well: textile fibres identification and metal threads or dyes characterization, provide useful data to identify geographical origins of raw materials and finished textiles, to establish a connection or not between textiles, or to develop improved conservation treatments for their preservation. This communication also presents various research projects, in which the study of colours and dyes turned fundamental to successfully establish questions of origin, date, trade and taste of historical textiles within the scope of TTT and the Portuguese Expansion.

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

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The studies on yellow dye plant sources, in the past ten years, provided further support for the hypothesis that yellow dyes are more regional than reds or indigo blues (1-3). We intend to cross Portuguese national territory collecting plants which could have been sources for yellow dyes. To assess their use, we intend to create a database of reconstructions which will allow us to develop techniques that will allow for the identification of these “lost yellows” in medieval manuscripts and textiles.
Coordinated by botanist Adelaide Clemente, nine plants were collected in botanical field expeditions in Portugal. The selection was based on the plans described in (4); when a particular plant is not native to Portugal, such as *Anthemis tinctoria*, the species from the same family were also collected. The collection in field expeditions is important to guaranty that plant collection occurs during the appropriate phenological stage (e.g. flowering). An herbarium voucher was collected for each species, and stored at the LISU Herbarium, University of Lisbon.

The raw materials were extracted, fresh or naturally dried, and characterized by HPLC-DAD-HRMS to obtain a full profiling and to identify signature markers. These data were compared with previous studies, such as *Reseda luteola*, where the glycosides of luteolin, known specific markers of the species, were found. The plants were then used to dye textiles, specifically wool broadcloth, according to a recipe selected by Dominique Cardon, based on compiling 18th century broadcloth dyers' recipes for yellows and greens.

A discussion on the dyeing procedures as well as a full characterization of the plant extracts compared with extracts from dyed textiles, will allow to ascertain their use as a possible source for yellows in Portugal.

Finally, the dyed textiles were preliminarily analysed by microspectrofluorimetry, to set the foundations for a database of reconstructions of yellow dyes that will be built and analysed through a methodology already used in the identification of red lake pigments (5).

Figure 1. *Genista tournefortii*, from *right* to *left*: in the; flowering branches were used to dye; and broadcloth dyed with the plant extract.

(1) X. Zhang, R. Laursen, *Analytical Chem*. 2005, 77, 2022-2025.

(2) T. Devièse, T., CHARISMA project 2014, 228330.

(3) Zhang, X., K. Corrigan, B. MacLaren, M. Leveque, R. Laursen, *Stud. Conserv*. 2007, 52(3), 211-220.

(4) D. Cardon, *Natural Dyes*, London: Archetype Publications, 2007.

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Madder or alizarin: which dye for the French *pantalon garance* from 1850 to 1914?

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Beginning in the 1980s, studies in 19th and 20th centuries textiles in French museums have essentially followed the organization of major exhibitions. Although some exhibitions dwelt on colours, very few investigated dyes. Based upon Anne-Rose Bringel's knowledge of the archives being collected since the 19th century by the *Société Industrielle de Mulhouse* (*SIM*) and housed in the town museum (*Musée de l'impression sur étoffes*), a first textile item has been in 2013 described as made with "violet synthétique (d'aniline?)" within the exhibition catalogue untitled *Folie textile: mode et décoration sous le second Empire*. It remains a unique example and therefore symbolizes the huge research and work still to be done in France on the transition process in dyes during the second half of the 19th century. Gathering academic researchers and museum scientific staffs, the *Institut national d'histoire de l'art* (*INHA*) located in Paris, launched in 2017 a new research program dedicated to synthetic dyes in France between 1850 and 1914. One of the main aims of the research program is not only to go further in the knowledge of early synthetic dyes but to document this knowledge by linking it to precise textile items housed in French public collections.

Having been discussed by the program scientific committee which comprises chemists, historians, art historians, curators and dyers, the research field has been limited to silk and wool. We also chose to investigate primarily the early years (aniline dyes, from 1856 to 1870) and the end of the period (beginning of the 20th century). Regarding the latter, it has long been written that the French Republic was willing to sustain the production of madder around Avignon by maintaining our soldiers' *pantalon garance* until the end of 1914. As a matter of fact, the *pantalon garance* did exist until 1914 but had long been produced not with madder but synthetic alizarin. A comprehensive study of the *Statistiques de la France* shows without question that madder totally ceased to be grown in 1882.

At the same time, while researching on French regional wool centres, we found unknown archives in Bischwiller, a small town 30 kilometers north of Strasbourg having hosted madder producers as well as wool manufacturers. These archives keep unvaluable materials documenting the *Ministère de la Guerre* buying huge amount of different kinds of wool and verifying the quality of the dyes. These unexpected archives also demonstrate a major evolution in the way of perceiving dyes during the second half of the 19th century.

During the talk, after introducing the INHA research program on synthetic dyes, we will present these new archives as well as the work engaged with French museums.

Mapping degradation pathways of natural and synthetic dyes LC-MS: influence of solvent on the degradation of eosin and carminic acid

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To conserve the vast array of (combinations of) dyestuffs, pigments, cultural-heritage objects and application materials create, a quick and easy method for dye-degradation research is required. In previous research, we investigated the degradation mechanism of methyl violet in an aqueous solution, illuminated with a strong UV light [1]. By this it was possible to overcome laborious extraction procedures when such dye is for example applied as ink on paper or as textile dye. It also guarantees that the extraction procedure does not affects the composition of the degradation products. By an application of methyl violet on paper, we demonstrated that the degradation of methyl violet in solution was comparable with the process on paper [2].

Degradation in a strong solvent as DMSO can potentially be interesting compared to other solvents such as water. DMSO will have the advantage that almost all dyes and most organic pigment will dissolve and can be studied as such, while in water several dyes and in particular organic pigments will precipitate. But obviously, the degradation mechanism should not be affected by the solution. Therefore, the degradation of eosin and carminic acid under the influence of light in DMSO and water was investigated. An LC-MS method was developed for analysis of the degraded samples and identification of the individual components. This method uses a LC gradient capable of analysing natural and synthetic dyes, both acid and basic, in a single run being the first universal chromatographic method applied within the field of cultural heritage. The UPLC method will be discussed in detail during a poster presentation [3].

Degradation in solution proved to be a straight-forward method which can indicate possible degradation routes of colourants applied in objects. While also different products were formed, the presence of DMSO generally facilitated relatively quick degradation, which, in combination with its universal solvating properties are advantageous. Degradation pathways for eosin and carminic acid are proposed and we will elaborate on similarities and differences in the degradation mechanism in both solvents.

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(2) D. Confortin, H. Neevel, M. R. van Bommel and B. Reissland, in *The CREATE 2010 Conference Proceedings - 'Colour Coded'*, G. Simone, J. Y. Hardeberg, I. Farup, A. Davis and C. Parraman (Eds.), 2010, 81-85.
(3) I. Groeneveld, B. Pirok, P. J. Schoenmakers, M. R. van Bommel, *One size fits all – one method for the simultaneous analysis of natural and synthetic dyes by UHPLC-PDA (optimised by PIOTR)*, Poster presentation 37 Dyes in History and Archaeology meeting, Lisbon, 25-26 October 2018.

Quantification of dye uptake and loss by wool during (over)dyeing of weld, madder, redwood and indigo

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It is known from previous research that combinations of dyes were used to obtain different colours for the dyeing of textiles, mostly prepared by overdyeing. For example, green colours were achieved by combinations of weld and indigo, dyeing weld with madder yields different shades of orange, blacks were achieved with indigo and madder and purples were obtained with combining indigo with redwoods or madder [1]. The final colour is much dependent on the depth of the indigo dyeing, on the order of dyeing, and if a mordant is used. Quantitative analysis of the uptake of the different colorants from the first or second dye bath is not investigated well. Qualitative and semi-quantitative research of historical samples suggests that during overdyeing, that the ratios of the adsorbed dyes change [2]. This led to our main research question, how are the ratios of the dyestuff affected when dyes are mixed, i.e. overdyeing is performed using different biological sources. This could be in particular affected by different dyeing conditions.

Overdyeing experiments were performed using standard recipes in which weld wool was overdyed with madder, redwood and indigo, madder was overdyed with weld and indigo, redwood was overdyed with weld and indigo, and unmordanted indigo wool was overdyed with weld, madder and redwood. Samples were taken from the dye baths before and after dyeing and were analysed by UHPLC-PDA. Samples of the final wool were extracted in triplicate using a mixture of oxalic acid and DMF. Analysis showed that most of the overdyeing experiments resulted in significant differences in ratios of the adsorbed dye constituents, compared to the reference dyeing with just weld, madder redwood or indigo. It was also shown that the ratios of the composition of the second dye is most comparable to the reference dyeing, although a lower absolute uptake was observed. The composition of the first dye seems to be influenced most by the temperature of the second dye bath and the binding efficiency of the dye to the mordant, whilst the second dye is mostly dependent on the number of free binding sites and whether the wool is pre-mordanted or not. As these experiments were only performed once, no definitive conclusions can be made and require further research for confirmation. However, based on the present experiments, which serves as a proof of principle, care should be taken during interpretation of chemical analysis from samples which were dyed using different dyes.

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The identification of yellow iron buff dye on Egyptian textiles

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Investigations at the Canadian Conservation Institute have identified iron buff colourant on 5th – 14th century Egyptian textiles, and may indicate a more widespread use of the yellow colourant than currently documented. To date approximately 70 linen, silk and wool threads from both Coptic and Islamic origins have been examined. In addition to iron buff, other dyes such as madder, lac, indigo (or woad), sumac and weld have been identified. This talk will present the results from analyses using gas chromatography-mass spectrometry (GC-MS), scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS), micro-x-ray fluorescence spectrometry (μ-XRF), x-ray diffraction (XRD) as well as staining techniques. On-fibre production of iron buff dye and the structure of the bonded iron (III) coordination complex will also be discussed. In addition to the use of insect and plant dyes, the presented results will illustrate an established knowledge and centuries of use of iron-based dyes on cellulosic and proteinaceous fibres in Egypt.

Iron buff is a lightfast, brownish yellow mineral dye, which was formed after first mordanting a textile with iron (II) salts, such as ferrous sulphate (copperas or green vitriol), and allowing it to dry. The cloth would then be immersed in an alkaline lime bath to produce the yellow iron (III) buff complex. Elemental analysis of textile fibres coated with bound iron buff dye is challenging. Although SEM/EDS is used frequently to detect the possible presence of metal mordants and mineral dyes on textiles, the limit of detection is relatively high for iron (1), and microscopic iron-complex dye clusters can go undetected. The μ-XRF has a lower detection limit and iron was successfully detected using this technique on textiles where it was not found using SEM/EDS.

Iron can be present as a dye or mordant on textiles, but is also frequently present as a soil contaminant on old fibres. When iron has been detected by μ-XRF, logwood dye can be used to determine which of these forms of iron is present (2). Iron (II) mordants and iron (III) buff dye are bound to textile substrates as amorphous clusters. These bound iron species are then able to form black coordination complexes with haematein in logwood dye, turning the fibres black. Conversely, soil contaminants do not coordinate with haematein. Therefore, although archaeological textiles are often contaminated with soil from an excavation site, the presence of iron-containing minerals will not cause the fibres to become black in a logwood dyebath. Logwood staining offers a method for distinguishing between site contamination and applied iron treatments.

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Early synthetic dyes in Romanian red-yellow-blue ethnographical textiles decoration and historical flags

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Within the historical context of celebrating 100 years from the Great Union of the Romanian provinces in 1918 (when Transylvania joined Moldavia and Wallachia), a special attention was given to the objects dating from that period. It was thus observed that in home produced textiles, new symbols and different combinations of colours aroused, among others, the combination of red, yellow and blue, which became the favourite in the rural textiles from Sibiu area, Transylvania. These three colours are the ones of the Romanian flag, adopted after the union of Moldavia and Wallachia, in 1859 (1). The subtle presence of the tricolour (red, yellow and blue) in the patterns of ethnographic textiles in Transylvania, at the very beginning of the 20th century, would thus represent the feeling of the people's beliefs, in the new state (2).

The contribution presents the results of dye analysis of visual red, yellow and blue fibres, of vegetal and animal origins, from homemade textiles in Sibiu area, from the first decades of the 20th century. Dyes in tri-coloured flags from the same period, preserved in the National Military Museum

"Ferdinand I", Bucharest and the National Museum of Romanian History were also investigated. Dye analysis were performed by liquid chromatography with UV-Vis and mass spectrometric detection, according to a procedure established for the identification of natural dyes, described in detail in earlier publications (3,4). Although we were unable to identify many of the dyes detected, the results obtained on 80 samples from 23 objects evidenced similarities between dyes used in objects within each group (ethnographical versus flags) and differences between those responsible for the colour in homemade textiles, as compared to the Romanian flags.

From the analytical point of view, the present work should be considered as preliminary, much more experiments and a dedicated database being absolutely necessary in order to be able to undoubtedly identify synthetic dyes, as also considering the high number of dyes in use at the beginning of the 20th century. As far as the historical approach is concerned, apart from the preference for certain dyes in ethnographical textiles versus Romanian flags, the availability of a large variety of synthetic colorants in Romania, in the first decades of the 20^{th} century, is worth to be underlined.

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Photodegradation of triarylmethane and *β*-naphthol dyes in different matrices

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Since mid-19th century, synthetic organic dyes and pigments have been extensively used for dyeing textiles and in paint tube formulations (1). The analysis of the dyes composition is highly challenging due to their complex molecular profile, constituted by several by products or mixtures of homologous species, often differing only for the presence or position of the same substituent on the aromatic rings. Another critical issue to take in consideration is the poor light fastness of these dyes and pigments that is responsible for their severe fading occurring both in historical textiles and in paintings.

In order to shade light on dye photo-degradation processes, the most representative dyes of triarylmethane (Diamond green, Fuchsine and Methyl Violet) and ß-naphthol (PR53 and PR49) chemical classes have been selected and analysed both as standard, and as unaged and aged wool yarns and paint model systems, kindly provided by IPERION network (2). The optimized analytical approach used is based on Liquid Chromatography coupled with tandem high-resolution mass spectrometry or Diode Array and Fluorescence detectors (HPLC-ESI-Q-ToF, UHPLC-DAD-MS and HPLC-DAD-

FD). Our methods were powerful in separating and identifying the several miscellaneous components contained in triarylmethane and β-naphthol dyes and pigments and their relative degradation products. Moreover, high resolution mass spectrometry allowed us to determine specific fragmentation patterns enabling us to distinguish different possible isomers.

Moreover, the investigation of Diamond Green degradation in different kind of solvents disclosed differentiated pathways. The correlation of the kinetic trends of the several degradation compounds identified in solution with those detected in paint model systems and textiles was fundamental to understand the role played by the matrix and the most influent parameters affecting the degradation.

The comparison among the ageing pathway of dyes with similar chemical formula underlined which features in the molecular structure influenced the stability.

In this study we will highlight the potentiality of HPLC-DAD-FD-MS micro-destructive analytical approach in solving and fully characterize complex mixture of unaged and aged synthetic dyes and pigments.

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Natural dyes in madder (*Rubia* spp.) and their extraction and analysis in historical textiles

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Textiles coloration using extracts from the roots of various madder species (*Rubia* spp.) has been performed for centuries. To date, 68 anthraquinone colorants have been detected in *Rubia* spp. used to dye textiles. Many of these dyes are sensitive to hydrolysis and degradation from enzymes, extraction chemicals and processing temperatures (Fig 1), and are often overlooked as colorants in historical textiles. Conclusions in literature of the past 30 years concerning colorants present in planta are being challenged as new analysis methods are developed.

The recent advent of 'soft' extraction techniques has demonstrated that anthraquinone glycosides and other sensitive molecules, such as carboxylated compounds, need to be preserved; this valuable chemical information embedded in the dye structure may be lost if extraction and analysis is too harsh. Some compounds thought to be present in madder and madder-dyed artefacts are in fact degradation products resultant from the extraction process, and degradation pathways have been developed to better understand the reactivity and stability of these compounds. Detailed analysis of dyes in textile artefacts can reveal important cultural and heritage information concerning historical textiles relative to the specific dye species, the area of the world where this may have grown, how and where it was dyed, and, perhaps, where it was traded. 'Soft' extraction techniques are needed in the analysis of madder-dyed textiles due to the sensitive nature of these molecules, and their preservation up to the point of detection is key to unlocking full and valuable chemical information embedded in the dye structure, which otherwise is lost.

Another key aspect is one of preservation, and the aim is to fully understand the nature of these dyestuffs in order to determine degradation patterns and structure-efficient conservation techniques. Understanding the precise molecular structure of these natural dyes and their chemical reactivity is important to provide knowledge of their interactions with physical substrates, such as textile fibres, which could be used to develop superior techniques for analysis of artefacts.

A flowchart is proposed as a decision tool to enable *Rubia* species to be distinguished from one another based on compounds detected in extraction and analysis of dyed fibre samples; this assumes that the extraction methods used are soft and preserve chemical structure integrity to enable a valid assessment, but does take into account very sensitive components such as galiosin and pseudopurpurin.

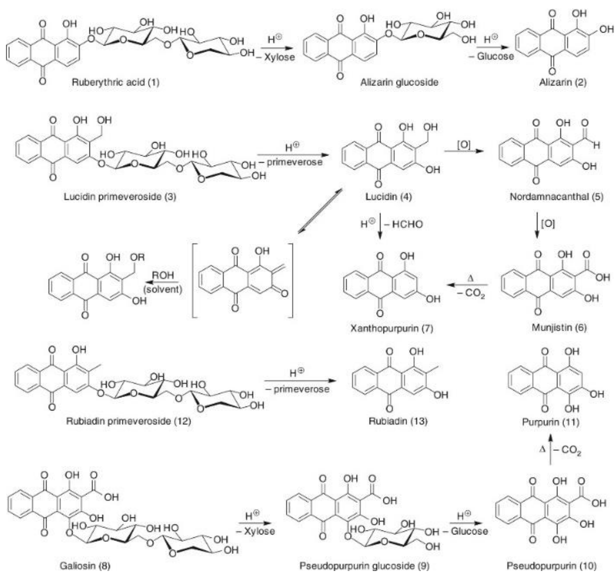

Figure 1. Possible inter-relationships between anthraquinone compounds found in *Rubia* species based on chemical or biochemical interconversion.

POSTERS

Imitation gold made from cornflowers

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Since antiquity, organic blues processed from various plants have been used to dye cloth; made into a dye-pigment for creating a paint source; and historically used as flowers in funerary garlands (1-2). One such plant is the small cornflower (*Centaurea cyaneus*) which has been documented in many medieval technical manuals for suggesting to make a blue coloured glaze and paint (3-4). This paper demonstrates an alternative perspective for processing the cornflower's blue petals to produce a convincing imitation gold colourant when applied over silver leaf. This study will explore the effectiveness of hidden colours buried within historical recipes, showing alternative outcomes compared with the original medieval concepts and transcripts. The theory, through practice, concludes with strong experimental evidence to support the idea of using the blue cornflower juice as a gold substitute rather than using this colourant as a blue dye source.

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P1

Photophysical properties of *β*-naphthol pigments

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In the second half of the 19th century new synthetic organic pigments began to be synthetized, replacing quickly the traditional natural organic dyes (extracted by vegetal and animal sources). Among the several classes of azo pigments synthesized, β-naphthols were considered the first successfully used for printing inks, plastics, paints, artists' colour, tinctorial applications and their historical impact is widely referred in the literature (1-2). Nevertheless, their fastness proprieties are yet to be understood resulting in a general lack of knowledge of the chemistry of these species in modern/contemporary artworks. Found on good conservation condition or severely faded, literature on the photophysical characterization of this class of pigment is contradictory, and it will be necessary to revisit it, experimentally, to have a clear understanding of the factor affecting β-naphthol pigments photostability and fading.

In cultural heritage, photophysics has been successfully used to study photochemical properties of colorants providing new insights into the photochemistry of organic dyes (3-4). Thus, photophysical studies represent a key area of research to understand the organic colorants photostability and fading in artworks and Insights into the fundamental photophysical properties support the comprehensive understanding of the photochemical stability of ß-naphthol pigments in the future.

To understand photodegradation mechanisms of this class of azo pigments, photophysical studies of some ß-naphthols, not so much investigated until now, were carried out. This work aims to discuss preliminary results of their fundamental photophysical properties allowing us to offer a first rationale for their light-induced degradation (cis-trans photoisomerization of the azo group, ESPT and quantum yields of reactions). To support the prediction of their photochemical behaviour in different media, first-principles quantum mechanics calculations are also included.

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A blue can conceal another! Non-invasive analyses of indigo mixtures used in Japanese ukiyo-e prints

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Indigo blue is one of the main organic colours used in the world and through the times. Japanese artworks are not exceptions. Indigo was used as a pigment for the printing of the famous *ukiyo-e*, produced between the 17th and the 19th century from different plants, such as the dyer's knotweed (*Polygonum tinctorium*).

Blue colours were sparsely used in the first coloured ukiyo-e but became predominant during the 19th century, mainly due to the integration of the synthetic Prussian blue in the palette of the printers around 1830 (1). For a long time, researchers have assumed that the Japanese organic blue colourants such as indigo were substituted by cheaper Prussian blue in the woodblock prints. Few analytical studies were conducted on such artworks but the common use of indigo and Prussian blue in Japanese paintings, mixed together or seldom used, has been evidenced (2,3).

In this study, non-invasive analyses were carried out using UV-visible reflectance spectroscopy (spectrofluorimetry and hyperspectral imaging) and Fourier Transform Near and Mid Infrared spectroscopy (FT-NIR, FT-MIR)

(4). A woodblock print attributed to Utamaro (first printed in 1798-1799) was characterised and the analyses performed on the bluish area showed different pigments compositions. Indigo mixed with vermillion could be identified thanks to hyperspectral results but could not be revealed thanks to FTIR spectroscopy, even though its infrared spectrum is well-known. However, infrared analyses on the same bluish area suggested the use of Prussian blue. In this case, Prussian blue could not be detected straightforwardly by visible reflectance spectroscopy.

In order to assess the detection limits for each spectroscopic technique employed, various mixtures of Indigo and Prussian blue prepared with wide-ranging and well-known compositions were analysed. Among the established techniques, UV-visible reflectance spectroscopy, FT-NIR and FT-MIR spectroscopy were selected as they are highly selective and sensitive. Knowing the detection limits of these methods is of great importance. Indeed, missing the identification of one of these two blue pigments can lead to erroneous interpretation on the use of blue pigments, on the technical choices of the printers, and to some extent could induce a wrong chronological interpretation, Prussian blue being used as a chronological marker.

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P3

In Antoine Janot's blue steps

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Is it pertinent to propose the colours of ancient dyers as an inspiration for today's colour lovers? Is it possible to reproduce their colours, following their recipes or with different ingredients and techniques?
To answer such questions, as a case study, we present the first results of our experiments to compare the scale of blues of a French 18th century dyer (1) with the scales of indigo blues obtained today, using different indigo sources and vat processes. Antoine Janot (1700-1778) was a master-dyer in Saint-Chinian (Hérault, France), a centre of production of wool broadcloth for exportation to the Levant. He has left a Memoir - on the processes of dyeing the colours that are consumed in the Levant in the good and fast mode of dyeing, with the quantities and qualities of the drugs from which they are obtained, dated 31st May 1744, preserved in the Archives départementales de l'Hérault in Montpellier. It describes dyeing processes for 65 different colour shades, illustrated by 59 samples of dyed wool broadcloth. The first colours presented are the eight degrees of his scale of blues. This scale might have been looked upon as one among many examples of irretrievably lost technical knowledge, the main reason for this being the process by which these blues were obtained, viz. the woad vat, boosted by an addition of indigo pigment. Nowadays woad is no longer processed into woad balls or couched woad, except in very limited quantities for workshops of experimental archaeology, while in his Memoir, Antoine Janot describes a large-scale process, in a vat containing several

thousands litres of hot water to which are added hundreds of kilograms of couched woad and several kilograms of natural indigo. Could it then be assumed that proportions of ingredients calculated from his description would still be valid for a smaller scale version of the process?

To answer this question and also to propose alternative ways to reproduce Janot's different degrees of blues, expert indigo dyers from different parts of the world have started experiments to reproduce these blues with their local source(s) of indigo and different vat processes, traditional or not, biological or chemical, at different scales. The same quality of fine wool broadcloth was used by all. It presents the same chromatic specifications as an undyed sample of the broadcloth Janot used to dye. Colorimetric measurements of all samples, from the18th century document and from all experiments, were performed with the same instrument in the same conditions. Research is still ongoing, but experiments already show that blue dyes with the same chromatic specifications as the different gradations of Antoine Janot's scale of blues can be obtained in our time, from biological fermentation vats of different volumes, set with indigo extracted from all the indigo-producing plants that have been used on a large scale by indigo dyers, in all parts of the world. This is a welcome discovery, coming at a time when the production of indigo from all these plants is enjoying a significant revival, which makes the sourcing of natural indigo less and less of a problem. In this context, the colorimetric data obtained can be used as references in any attempt to reproduce, not only Antoine Janot's blues, but also all his colours that need a blue ground of one of the degrees in his scale of blues. Moreover, they also allow to check how any indigo-dyed textile, from whatever civilization and of whatever period, compares with the different degrees of this scale

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Logwood blue: dyeing, fading and the possible marker compound for the HPLC-PDA identification by a mild extraction

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Logwood (*Haematoxylum campechianum* L.) contains a mordant dye that gives a wide range of different shades of colour: blues, violets, greys and black. However, logwood is especially associated with a black dyeing and, despite various published recipes (traditional and adapted) on logwood blue, no extensive studies have been carried out up to now on this subject. Through the presented work, different aspects of logwood blue were researched, namely: the dyeing process and the influence of parameters such as pH; the lightfastness; the identification by high performance liquid chromatography (HPLC) using a mild extraction method. The study started with an irregular mosaic pattern of blue and beige that was observed in the border of 16-17th century Safavid carpet belonging to the MMA collection. The analysis by HPLC-PDA showed that an indigo source was used on the blue part. On the other hand, a mild extraction method (involving oxalic acid and pyridine) was used to extract the dye from a sample of the beige part to be analysed by HPLC-PDA. The resulting chromatogram presented a notable peak of an unknown compound (absorbance spectrum with maximum wavelength at around 360, 290 and 250 nm). Interestingly, the same component was detected in some reference samples as well as in further case studies dyed with logwood, indicating that the marker might be associated with this dye source. It

was, therefore, considered that the beige part was dyed with logwood to first obtain a blue shade comparable to that dyed with indigo. However, because of the poor lightfastness of logwood, it was speculated that the dyeing eventually faded, resulting in the beige hue. From the described starting point, the research was further developed pursuing two main objectives. (*i*) To verify if the notable peak is indeed specific to logwood, and then to characterize the compound of the peak. When a mild extraction method is used, this compound may be useful as a maker for logwood while it is difficult to detect hematein in a conventional analytical condition of HPLC (1). (*ii*) To dye “logwood blue” and examine the fading behaviour in comparison to “indigo blue” in order to understand the irregular pattern of beige and blue in the Safavid carpet.

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Vordan Karmir - Evaluating lost Armenian cochineal recipes

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Vivid colours of Armenian medieval manuscripts are the evidence of artistic mastery and ancient knowledge. In the case of Armenian manuscripts, colour making techniques were not preserved on treatises or literature. But there are a few later publications containing the collected recipes from different manuscripts (14th c. - 18th c.). We have studied one of those publications (1).

The book, named “The Use of Paints and Inks in Ancient Armenian Manuscripts”, was published in 1941, in Yerevan (Armenia), in Armenian and Russian languages, by Ashkhen Harutyunyan, Doctor in Chemistry. It contains 100 recipes from original Armenian manuscripts produced between 14th c. and 18th c., which are preserved in the Institute of Ancient Manuscripts known as Matenadaran, in Yerevan (1). The language of the recipes is Armenian in its ancient, medieval or dialectal forms. Our contribution was to translate this collection in English, in order to make it available for the scholars interested in Armenian manuscripts or art in general. The translation was followed by comparison of Armenian and Russian versions and with verification of linguistic literature (dictionaries, terminology in other languages, etc.). It is a work in progress.

The content of the book is organized in the following topics: concept of colour and light; black inks; coloured inks and paints; gold and silver paints; glue making; parchment making.

In this poster, we will focus on the preparation of organic reds, made particularly with Armenian cochineal. According to historical sources, this

scale insect was found in large areas of saline soils of the Ararat valley in Armenia (2).
In the past, carmine was considered one of the most beautiful red dyes, and was used in colouring of royal fabrics and carpets, in paintings and manuscript illuminations. The technique of making cochineal dye was kept for centuries in Armenian scriptoria and is lost today, although there are attempts to restore it (3). However, the search of the lost recipe continues. In the above mentioned collection we have found only one recipe mentioning the cochineal as it is, although there are other recipes of red colours using organic colourants (brazilwood, madder, shellac) and inorganic pigments (cinnabar, red lead, realgar). In the framework of our study, we will reproduce and analyse chemically the unique recipe which is described in the original manuscript: Ms. No 432, Collection, 1818, Matenadaran, Yerevan (4).
The quest of these lost Armenian reds has started in the framework of my PhD thesis in conservation and restoration of cultural heritage (5).

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One size fits all – one method for the simultaneous analysis of natural and synthetic dyes by UHPLC-PDA (optimised by PIOTR)

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Within cultural heritage, the characterisation of organic colorants is a challenging task. Research has been done in which liquid chromatographic techniques were used for the analysis of organic colorants and their degradation products (1-2). Currently, two different chromatographic techniques are used at the RCE to analyse natural and synthetic dyes separately (3). These methods were combined into one single 1D UHPLC-PDA method, partially based on the research done with 2D-LC (2). Since the number of existing colorants is rather large, it is most likely not possible to achieve baseline separation between all compounds within a short analysis time. However, as most dyes' absorption spectra differ significantly this could be used as a second parameter besides the difference in retention time.

It was possible to optimize a 1D UHPLC-PDA method with the help of PIOTR and based on the differences in retention time and absorption spectra it was possible to identify more than 120 natural and synthetic colorants by gradient analysis within 60-minutes. The chromatographic procedure uses a linear gradient operating at a low pH in combination with an ion-pairing agent (TEA) to neutralize charged sulphonated and nitro dye compounds. Two columns were tested, the organic modifier was varied between acetonitrile and methanol, the concentration of TEA was varied between 1 and 5 mM, and it was also tested whether there was an effect if TEA would be present in both eluent A and B. After optimisation, the software tool PIOTR was used to optimise a gradient for more than 120 natural and synthetic dyes. Both linear and step gradients were calculated and experimentally tested. PIOTR proved to be very accurate in predicting retention times for both type of gradients, however, since all peaks were integrated manually (not by PIOTR) the software did not account for 'real' band broadening. This problem could be solved by making PIOTR feasible to read, besides MS data, also PDA data.

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A study in scarlet, and Cerise, and malachite green - Rediscovery of the historical collection of dyes at the Hochschule Niederrhein

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The dyestuff collection of the University of Applied Sciences, Krefeld, Germany turns out to be one of the largest synthetic dye collections in the world, comprising over 10,000 different containers of dye samples as well as additional sample books including the corresponding formulations and teaching materials. Dated back from the 1860s to the late 20th century it represents the rise and use of synthetic dyes.

The collection was gathered in the precursor institution, the School for Dyeing and Finishing, Krefeld (1888 – 1947), and was long time overlooked in the Faculty of Chemistry at the Hochschule Niederrhein. The Project "Weltbunt" – Colourful World formed 2017 for a new scientific focus and an intense interaction with the collection in a cluster of four national institutions. Aim of the research is the historic classification of the collection, chemical analysis of dyes, research in the development and history of dyestuff chemistry and fashion. The education in dyeing and finishing from 1850 to 1915 and the knowledge transfer between chemists and the dyestuff industry and to the practical dyers is in special focus in this project. Furthermore, the development of a collection based conservation concept for the historic dyes is of special interest of this work. First steps and results of both chapters will be presented.

The instrumental-analytic part of the project focuses on the history of the chemical industry by analysing the dye powders. The main method used is FTIR.

We established a preparation and exact measuring method to provide comparability of the spectra in the course of the project: For the sample preparation, either a KBr pellet can be made from the dye or the powder itself can be measured. Concerning the method, three alternatives are available: measuring in transmission mode or in absorption mode, in this case either by using an ATR (attenuated total reflection) unit or an IR microscope. Combination yielded in five different options from which the optimal approach had to be selected and discussed. NIR, TXRF, Raman Spectroscopy and several chromatic analyses will be done as well, in comparison to the results. These first analytical steps will be presented in this talk.

After having decided the ideal procedure, it will be of special interest to look at dyes with historic relevance like Malachite Green or with identical trade names but from different producers. Based on the wide collection several dyes should be exanimated which have not been in the focus in scientific publications yet. The project also aims for findings about the trading of patents which probably already took place in the time before World War I which could be proved e.g. by comparing the spectra of dyes which have been marketed under different trade names but are chemically identical. With the data measured a spectral database of historical dyes shall be established during the project to bridge the gap between the pure dyes, their colouring products which can be found in the sample books and the coloured textiles as final product.

Archaeological experimentation of Iberian iron-gall ink recipes from the 15th - 17th century

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In Europe, iron gall ink recipes are described in medieval treatises that mention the use of plant extracts such as Quercus infectoria that were combined with iron salts (1). The result of this mixture was an iron-polyphenol complex, to which a polysaccharide such as arabic gum was usually added (2). In this poster, five historical inks were selected based on research into Iberian written sources of medieval techniques and their characterization is supported by comparison with 5 different references, which were made combining iron sulphate with different polyphenols (tannic, gallic and ellagic acid, as well as di- and pentagalloyl glucose); as precipitates or prepared as inks by adding gum arabic.

Four Spanish and one Portuguese ink recipe, dated between 15th - 17th centuries, were chosen and are representative of different institutions in which the use of the writing ink was essential, such as universities, notaries, chanceries and the monastic world. A study of the documentary sources and their interpretation has been carried out, for the reproduction of the recipes in the laboratory with as much accuracy as possible (3).

A series of analyses has been carried out with the objective of characterizing the inks, making it possible to build bridges between disciplines such as History / History of Art and Chemistry. Colorimetry has shown that all inks are suitable for writing, having the characteristic black colour intended. The characterization by Raman and infrared allowed to identify these inks, at a molecular level, as an iron-gall ink, as it is described in literature (4).

Historically accurate reconstructions of medieval inks were crucial to bringing new insights into iron gall inks complex structure and compounds formed within it, which will advance future preparations of model inks and new conservation treatments (3).

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A novel micro-invasive dye extraction protocol for LC-MS identification of red organic dyes on watercolour paintings

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Red organic dyes have been traditionally used by different cultural groups, through the years, for various applications, from dying of textiles to colouring of paintings. Identification of these dyes in artworks is very important as it can provide information about the artistic and technological content of the work, as well as about the technological and cultural exchanges, communication and trade through different historical periods. Most of the commonly used red dyes belong to the group of the anthraquinones that includes scale insect dyes (i.e. lac, cochineal and kermes), as well as the plant-derived dye madder.

The non-invasive identification of the anthraquinone dyes is challenging because of the limitations that the various techniques face; for example, high fluorescence in Raman. The development of surface-enhanced Raman spectroscopy (SERS) overcame this limitation, allowing the identification of the anthraquinone dyes by the analysis of tiny sample (e.g. single fibre) – but at the expense of the requirement to extract a physical sample from the artwork. Recent developments in the fabrication of SERS agents enable the identification of red organic dyes, directly on the surfaces of various types of paintings, without sampling requirement. However, these methods cannot be applied on watercolour paintings and therefore the identification of organic dyes on this kind of artworks remains difficult.

We have developed a non-destructive micro-invasive assay for the sensitive detection and high confidence identification of anthraquinone dyes in watercolour artworks. This assay combines a novel microlitre liquid extraction surface analysis (LESA) method with conventional liquid chromatography mass spectrometry.

Our assay produces no visible damage to paintings. However, more than this, we have also evaluated the impact of our micro-invasive sampling LESA method, on watercolour paintings, by a series of more advanced, non-invasive analytical methods; including optical microscopy (OM), fibre optic reflectance spectroscopy (FORS) and optical coherence tomography (OCT). Optical microscopy was used for the observation of any possible dissolution of the watercolour paint due the application of ethanol. The occurrence of any chemical alteration was examined through the comparison of the FORS measurements (350-2500 nm) taken before and after sampling. OCT scanning enabled the monitoring of the application of the ethanol droplet, showing also that it did not result in any structural modifications of the paper substrate. Results from the analysis of dye containing areas of a watercolour painting on pith paper in the style of 19^{th} c. Chinese export painting are also presented.

Reconstruction of the support layer of old master paintings

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Legends to paintings in a Museum subscribe the material of the support layer in an overall term like wood, paper, copper, slate or canvas. When we look at a painting in a museum our focus is most often on the image and fewer consider what lies beneath.

Lab O is a laboratory for the study and reconstruction of handwoven canvases of old master paintings. and is a connection between conservation departments of Museums and a local community, a handwaving studio in Odemira, Portugal.

The presentation will guide you through the journey of handwoven reconstructions of the diamond pattern textiles seen by El Greco before starting to paint *The Burial of the Count of Orgaz*; the canvas Diego Velázquez saw before starting to paint *Saint John in the Wilderness*; and what stood in front of Titian as he painted *The Vendramin Family*, respectively based on a publication in CIETA Bulletin (1) , a diagram in a publication from the Art Institute of Chicago (2) and an reflectogram/ x-rai image in the technical bulletin of The National Gallery London (3)

Having access to a reconstruction as close as possible to the original canvas not only is a contribution to preservation of technical historical knowledge, it also triggers the visitor of a museum to have a closer look at a layer that is often ignored, both in scientific publication as well as by the general public.

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(2) Zuccari, F. et all (2005) Saint John in the Wilderness: Observations on Technique, Style and Authorship, Art Institute of Chicago Museum Studies, 31:2 pp 30-45 + 105-108
(3) National Gallery Technical Bulletin 36, cats 1-4, p 3 + 7

Ibirapitanga: rastros e impressões

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The work to be presented in DHA 37 is a resume of a PhD thesis in the field of Poetics of Visual Arts (University of São Paulo - Visual Arts faculty – 2013/2017). The research, called *Ibirapitanga: rastros e impressões*, updates the possibilities of use brazilwood as a colorant in the contemporary art context. For that, theoretical researches, interviews with artists and specialists, and some practical experiments were made. The final format of the thesis was a publication and an art exhibition (paintings, drawings, prints etc). The poster will present some relevant topics and images of this work.

In Brazilian schools, pupils learn about brazilwood in a historical context but it is curious that we do not learn much about its properties and different uses. It is rare, for example, to find someone in Brazil that has ever seen a tissue dyed with brazil-wood. The exhibition of the experiments made in the research is a way to extend this knowledge.

Several questions emerge from the study of brazilwood, or ibirapitanga, as called by the natives, since its exploration is an important fragment of the history of Brazil. In this research, these questions are addressed and pointed out to the Art field in a free and provocative way, stimulating exchanges and developing new questions.

It was relevant to the process of this research to make a data collection of some recipes that use brazilwood, for dyeing tissues or papers as well as recipes that use brazil-wood to produce lake pigments. Very old recipes were collected and also recent ones to make an overview.

From this collection of recipes some were put into practice, always thinking about ecological aspects, since brazilwood tree is now considered an endangered species (only certified wood was used). These experiments show the different shades that can be made with brazilwood, Fig 1.
With the aim of bringing possibilities of artistic use of brazilwood without major damage to the environment, dyeing experiments were carried out using other parts of the tree and not just the heartwood, as traditionally used. The botanical printing technique also allowed the leaves to be used to produce colours and images.
Seeing and not seeing, appearing and disappearing, presence and absence are some subjective qualities of this thesis and its poetics. In the processes of dyeing with brazil-wood, the pleasure to witness the creation and transformation of colours is itself a way to know more about the history of this material. Colours have much to say.

Figure 1. Process of dyeing with brazilwood: tissues being dried after the dye bath - 2016

The quest for Van Gogh’s inks: 13 years of research at the state heritage laboratory (of the Netherlands)

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For over 13 years, Van Gogh’s drawing inks have been studied at our institute, in close collaboration with the Van Gogh and the Kröller-Müller Museum. Together, these museums possess the world’s most extensive collection of Van Gogh drawings. Due to light exposure, the inks on some of these drawings have faded considerably. Also, inks on some of his letters, present at the Van Gogh Museum and the Pierpont Morgan Library in New York, have been studied. As these have less often or never been exhibited, it was expected that the inks have retained their original appearance. Long term objective is a better understanding of the making and the change in appearance over time of the drawings. During these years, our capability to characterise inks and interpret the results has developed significantly.
In-situ analysis of the metals present in the brown inks on 73 drawings and 20 letters by X-Ray Fluorescence Spectrometry, amended by in-situ Fibre Optics Spectroscopic analysis showed that, during the Dutch period (1880-1885), he mainly used iron-containing inks, presumably iron gall ink, for writing and drawing. During the French period (1885–1890), he mainly used chromium-containing inks, presumably chrome-logwood ink. The violet ink used in several drawings he made during a short period in France (1888) is

containing aniline dyes, mainly methyl violet, as initially was shown by Surface Enhanced Raman Spectrometry (SERS).
The organic compounds in these inks, as well as in the chrome-logwood inks were identified by Ultra High-Performance Liquid Chromatography (UHPLC) with PDA detection. For this, samples were taken with a newly developed micro-sampling method, using magnesium-oxide rods. This sampling method also allowed other techniques to be used, e.g. SEM-EDX to determine the elemental composition.
Van Gogh used commercially available writing inks, therefore, to investigate their composition and know what was available, during the last 5 years, over 150 bottles of writing inks from the period 1890 – 1950 have been collected. Several of the violet inks of this collection have been analysed by UHPLC-PDA and the results were compared to those obtained from the violet inks on the drawings and letters, as well those obtained from our dye reference library, built up by chromatographic analyses of our collection of reference dyes. These comparisons were conducted by automated data visualisation. Most remarkable, besides methyl violet, benzyl violet was present in the violet inks on the drawings.
UHPLC-analysis also showed the presence of methyl violet in chrome-logwood ink on a drawing. According to an early 20th c. description of the extraction process, the ink manufacturers added this to compensate for the decrease in hematein content of the logwood extract during steam extraction. Light-induced fading of methyl violet has caused these originally nearly black inks to turn brown.

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Dyes and pigments used for magic lantern glass slides: a literature review

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With the invention of the Magic Lantern during the 17th century, new perspectives for the pre-cinema universe started to emerge. During the following two centuries, this instrument achieved extraordinary success on all social media with high-impact on entertainment, sciences, education, religion, and advertisement (1, 2).

One of the first stages of the production of glass slides for projection with magic lanterns was the hand-painting technique that nowadays represents a great challenge for conservation professionals due to the diversity of painting materials used and their exposure to aggressive conditions of temperature and light during the projections (3).

The aim of this literature review was the identification of most common dyes and pigments used for painting on glass slides to make it easier the analytical characterization of magic lantern glass from several Portuguese collections, that will be studied in the project "Lanterna Magica – Technology and preservation of painted glass slides for projection with Magic Lanterns".

Since the production of glass slides increased and several books, with instructions of how to paint on glass for magic lanterns, were published during the nineteenth century, written sources of this period were consulted (4).

According to historical literature, painting on glass represented a great challenge for painters given the major importance of transparency and vivacity of the colours and details magnification, which lead to the use of both watercolours and oil paints, separately and combined, to obtain the best results. It was also possible to understand that a great diversity of dyes and pigments can be found on historical magic lantern glass slides.

Hand-painted magic lantern glass slide from Ana David Mendes' private collection.

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P14

Research on indexing of deterioration state of silk cloth dyed with amur cork tree

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If the deteriorated state of the cultural textiles can be expressed as a numerical value, it will be very meaningful information for preservation, repair, and exhibition etc of them. In previous studies, we have analysed the components of Amur cork tree extracted from cultural textiles using HPLC. As a result, it has been shown that the sum of decomposition products of berberine may be a clue to the indicator of degradation (1). Fluorescence life time measurement for cultural textiles was reported as an effective non-destructive way to analyse the deterioration state of silk (2). Here, we will report the deterioration state of silk cloths dyed with Amur cork tree, damaged by visible light.

After forced deterioration of silk cloths dyed with Amur cork tree was conducted for a predetermined time by using visible light, protoberberine alkaloids were extracted from each silk cloth and subjected to HPLC. As HPLC results, similar to the results of cultural textiles, the formation of degradation products from berberine, were observed. Also, as the irradiation time of visible light became longer, the amount of deterioration products increased.

Next the fluorescence lifetime of each silk cloth dyed with Amur cork tree and forced deteriorated were measured. Similar to the results of cultural textiles, the irradiation time of visible light became longer, the τ2 values decreased.

Analytical results of HPLC and of fluorescence lifetime were shown graphically (Fig 1). The relationship between the amount of deterioration products (X1+X2) and the τ2 values, in forced deterioration of silk cloths dyed with Amur cork tree was similar to that of cultural textiles. It was found that this deterioration process by visible light is one of the deterioration processes of cultural textiles dyed with Amur cork tree.

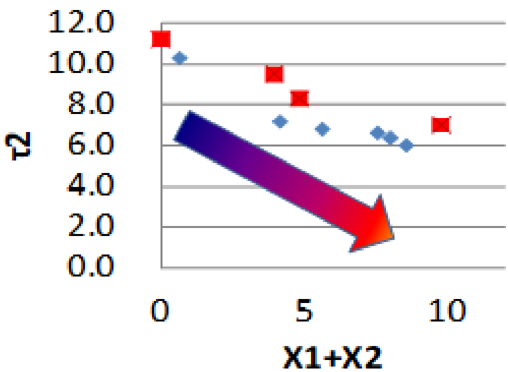

Figure 1. Relation of fluorescence life time (τ2) with the total amount of deterioration products from berberine (X1+X2). ■: cultural textile (modern, 18C,17C,14C) (2), ◆: forced deterioration silk cloth.

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(2) Y. Sasaki, R. Fukae, K. Sasaki 36th Meeting of Dyes in History and Archaeology, 2017, p.4.

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Pro-healthy activity of natural dyes. Tradition and contemporary research

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The Institute of Natural Fibers and Medicinal Plants from Poznan has been carrying out complex research connected with application of natural dyes on fabrics. Colours of nature, obtained from various plants has been used in dyeing linen fabrics. The last subject which is realized in Institute - Technology of designing innovative, functional and natural dyed textile product is financed by Ministry of Agriculture and Rural Development. The project is realised in 2017 - 2020. Comprehensive research on linen fabrics is conducted according to modern trends in looking for eco-products both comfortable and healthy. Natural sources of colour used in study of colours were: Weld, Tumeric Corepsis, French marigold, Dyer's Camomile, Dye's broom Madder, Logwood, Sappanwood, Gall oak, Myrobalan, Indigo, Cochineal.
The Institute has been carrying out studies on clothing influence on human organism. Additional feature of dyeing the fabrics with dyes of plant origin will increase their attractiveness, comfort of wearing, and will also have effect on human frame of mind. This time the studies were extended to test the dyed fabrics on people with different dermatoses. Natural plants as a source of colours represented crops of great economics importance. In recent years we have observed visible come back of the interest in natural raw - materials and techniques which had been often completely forgotten. The sudden revival of interest in natural dyes is not only for

textile dyeing but also for use in cosmetics, hair dye and food colouring and others products. There is big potential application of the compounds found in dyeing plants in various fields of science and economy. Natural dyes obtained from plants are being looked as an eco-solution and eco-friendly dyes with natural antibacterial and antimicrobial properties. Plant extracts contain tannins, flavonoids, saponins, essential oils, mucilage, vitamins and many other valuable nutritional substances. They have various properties e.g. medicinal, soothing, caring, and disinfecting. From this point of view they are well known for their health curing characterization. They protect skin against sun rays, whiten it and diminish discolourations, stimulate blood circulation in capillaries and are characterized with toning and astringent properties. Natural dyes are considered safe for people and also for the environment because of its non-toxic and biodegradable nature. In highly developed societies interest in fabrics from eco-friendly natural fibres is constantly growing. Their combination with colours obtained from plants increases their value. The plants contain compounds with cosmetic and medical properties, which positive effect has been known thousands years ago in Chinese and Indian medicine.

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(3) K. Schmidt, M. Zimniewska, M Pawlaczyk, Natural and Safe Dyeing of Curing Clothing Intendent for Patients with dermatoses, Postepy Fitoterapii, 2018 no 1. 286-293

French marigold as a source of yellow colour

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Tagetes species, commonly known as marigold, are grown as ornamental plants and thrive in varied agro-climates.

French Marigold *Tagetes patula* L. is an annual plant of the Asteraceae family, reaches a height of 20 - 30 cm. It is easy and efficient to grow. *Tagetes* L. is widely used as a potential source of biologically active products: carotenoids, which are used as food colours and dyes for fabrics, feed additives. They have anti-cancer, anti-inflammatory and antioxidant effects. They are used in the treatment of skin allergies and eczema. The infusion from the plant is used against rheumatism, cold and bronchitis. Leaf juice cures ear pain, leaves and flowers are used to treat eye diseases.

Cultivation of dyeing raw material was carried out on the experimental fields of INF&MP in Plewiska and Pętkowo as part of the Government Multiannual Program for 2017 - 2020.

The aim of the research was to obtain colouring extracts from the cultivated plants and dyeing on linen fabrics.

French marigold has been crushed and placed in Soxhlet Apparatus. Extraction was carried out using various solvents. The most optimal method was selected - extraction with methyl alcohol. The obtained flower extract was subjected to a compaction process on ROTAVAPOR® vacuum evaporator. The last step was to obtain a powdered colouring extract using a spray dryer BÜCHI Labortechnik AG.

Linen fabrics were subjected to three different dyeing processes: dried flowers, methanol paste from flowers and powdered colouring extract.

As a result of the experiments carried out the following colours were obtained: warm beige, sand, light yellow, yellow, copper, old gold. The next step of the Program will be the implementation of the dyeing technology for the production of fabrics and pro-healthy clothing collection.

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Yarns from the ashes: discovering and characterizing textiles in Pompeii

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Vesuvius eruption that destroyed Pompeii and the surrounding area in AD 79 represents one of the most important events in history, whose impact on both collective image and archaeology is outstanding. The cataclysm left behind an abundance of archaeological evidences; in fact, the archaeological remains constitute the most important source of knowledge we have about Ancient Romans daily customs and activities (1). Thus, their investigation allows to trace clear images of antiquity, not only in term of urban structure but also as material culture, exceptionally giving information about more perishable materials.

In this prospective, the set of textiles from the Parco Archeologico di Pompei e Museo Archeologico Nazionale di Napoli (MANN) constitute the major collection of roman textiles in Italy and represents an exceptional chance of deepening inside this class of materials in Roman society. These samples are characterized by a wide range of materials and weaving techniques as well as by different conservation conditions; they include dyed textiles, mineralized fabrics, gold threads (2).

A multidisciplinary research approach is fundamental to maximize the historical information achievable from these archaeological objects. In this work, the preliminary results from the characterization of some samples is presented; visual inspection through Optical and Scanning Electron Microscopies provides information on conservation conditions, morphology and origin of the fibre, while EDX, Fourier Transformed InfraRed and Raman spectroscopies are used to identify inorganic and organic components (3). Finally, HPLC is used to identify natural compounds used in ancient dye-baths (4-5). The combination of archaeological knowledge with scientific analysis results in an extensive collection of information on ancient Roman textile manufacturing, from dye-bath to gilding, and will add new tiles in Pompeii history reconstruction.

Figure 1. Examples of mineralized textiles from *MANN*

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P18

Natural dyeing - Use of natural dyes in natural fibres Operational Group

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The Natural dyeing - Use of natural dyes in natural fibres Operational Group (GO) aim is the production of dye plants for the extraction of natural dyes and their subsequent application in the dyeing of "campaniça" sheep wool, in order to enable the development of innovative products of added value that are eco-sustainable and the development of local and national economy.

Plant production will be implemented and the mode of cultivation will allow the selection of species that present the best cultivation and extraction results. Dye plants adaptation for extensive cultivation, and their economic valorisation is envisaged throughout the promotion of agricultural diversification to current and future producers of medicinal and aromatic plants in the country, by the incorporation of dyeing species.

Extraction process, concentration and preservation of the natural dyes and the pre-formulations for industrial application, will allow getting a set of dyes properly characterized.

Productivity, eco-sustainability and technical and economic feasibility of the extracted natural dyes from the selected plants will be accessed.

Dyeing and quality control process of the dyed products will be done together with the optimization of dye formulations for at least one stage of textile transformation - branch, yarn, fabric, knit or garment. Laboratory tests of dyeing will be carried out in a way to allow its application in automatic and industrial production environments. It will also be developed a portfolio of multifunctional yarns, 100% wool and naturally red, for the fabrication of planar textile structures, and also prototypes of various pieces made using the wool dyed with natural dyes. In order to ensure the obtainment of a product with quality to compete with the existing market, after dyeing, quality control tests will be carried out from where the reference values and allowable tolerance limits should be set. Characterization and treatment of wastewater resultant of this type of processes will be made with the goal of reducing the harmful effects that this industry usually entails, and in this way to ensure that the complete process can be considered eco-sustainable.
It is hopped at the end of GO different groups can benefit of the gathered knowledge and information.

Identification and characterization of natural yellow dye sources of Persian carpet using high pressure liquid chromatography-tandem mass spectrometry HPLC-MS

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The application of natural dyes in Persian textiles has a long history, which has been developed according to different cultures living in the geography of Iran during previous centuries. Following our previous literature review (1) we have focused on the identification and characterization of the natural yellow dye sources in Persian textiles; *Reseda luteola*, *Vitis vinifera*, *Eremostachys* sp., *Prangos ferulacea*, *Pistacia vera*, *Punica granatum linn.*, *Morus Alba* and *Anthemis L.*

The samples from the plants which are more common were collected from nature in province of Isfahan, one sample was bought from herbalist's shop in Tabriz and the rest were gathered from the few remained dyeing workshops in 70 km to Isfahan.

Textile samples were dyed with these plants, according to a recipe provided by Dominique Cardon. The extracts from the material sources and dyed textiles were analysed and characterized by HPLC_DAD-MS (2), with the aim of identifying markers which would be helpful in identifying dyes in Persian textiles. The results of our study, with an exception, showed that the principal aglycones can be compared to the previous studies (3-5) and proved the possible existence of these plants as sources of historic textiles.

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Identification of leuco-indigo by fluorescence spectrometric analysis

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In indigo reduction dyeing process, it is important to estimate the time of maximum conversion of indigo to leuco-indigo for optimum dyeing time. Conventionally, several methods such as oxidation-reduction potential (ORP) measurement, colour strength measurement by dyeing test, spectroscopic method, etc. were used (1,2). ORP for measuring leuco-indigo concentration is not clear, while dyeing test is time consuming and spectroscopic method is erratic due to the oxidation during manipulation.

In this study, we evaluate the level of indigo reduction by using fluorescence spectrometric analysis and investigate the efficacy for applying the online monitoring system of indigo reduction. The generation of leuco-indigo was confirmed by collecting the fluorescence emission at 500 nm using λ_{exc} = 400 nm, Fig 1.

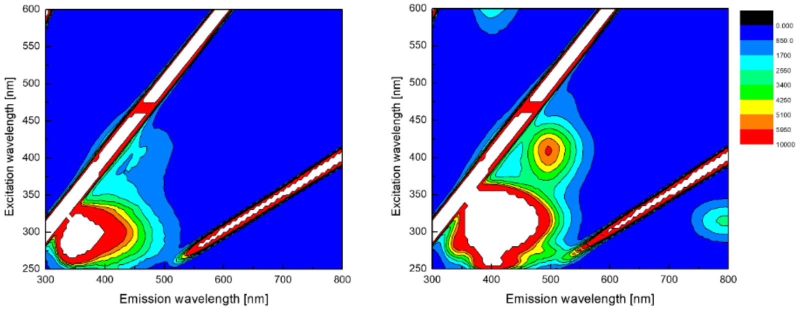

Figure 1. Total fluorescence spectra; (a) indigo and (b) leuco-indigo samples

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P21

Improvement of natural dyeing of leather

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Leather is believed to be the first material used since the first human race began wearing clothing. Therefore, it has been used as a material for clothing before any fibre, and it is the material with the longest history that continues to be used today for costume.

In Korean traditional costumes, the leather of cows, tigers, foxes, martens, otters, deer, roe deer, and shark skins was used. Although there is no record of pig leather in Korean costume history, it can be inferred that the leather was also used, considering that there are many women's hats made of pig hair (1). Pig leather is soft and lightweight, well ventilated and absorbs sweat easily. It is also cheaper than cowhide and sheep leather (2).

In this study, eco-friendly leather dyeing was examined using pig leather with onion skin colorants. In order to improve dye affinity, the leather was pretreated with sodium caseinate and its effect on dye uptake and colour was estimated. Mordanting effect was also examined in terms of dye uptake, colour variation, and colourfastness.

Pig leather pretreated with sodium caseinate showed relatively high dye affinity, resulting the increase of K/S value in natural dyeing with onion skin. Therefore, this study is expected to be used as basic data for the development of high quality natural dyeing products of pig leather.

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Enlightening the phenolic compounds present in iron-gall inks obtained through the use of historically accurate reconstructions

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The degradation of manuscripts catalysed by iron-gall inks is a major conservation issue and a serious threat to the world written heritage. These iron gall inks have been described as complexes of gallic acid or tannic acid, available in gall extracts, with iron ions (1).

To assess this hypothesis, we have prepared and studied medieval inks. The five historical recipes selected are the result of research on Iberian written sources of medieval techniques and contained three basic ingredients: Fe^{2+} obtained from an iron sulphate salt, a phenolic extract (tannins), and gum arabic (1,2). Different additives, such as other metal ions and pigments, and different extraction conditions were applied.

All the extracts and inks were prepared in fivefold and analysed by HPLC-ESI-MS and HPLC-DAD (3). HPLC-ESI-MS allowed the identification of the phenolic compounds present both in extracts and inks. HPLC-DAD allowed the quantification of these compounds.

The main goal of this work was to identify and quantify the major phenolic compounds present in the gall extracts and evaluate its variation by the addition of an iron sulphate salt and gum arabic when producing the iron-gall inks.

The analyses showed that the relative concentration of gallic acid and its glycosylated derivatives varies considerably with each recipe. In fact, in some cases, polygalloyl esters of glucose are present as major compounds.

These observations lead us to conclude that, so far, it seems that the chemical structures of the complexes present in iron gall inks are best described as mixtures of iron-polygalloyl and iron-gallate complexes, Fig 1.

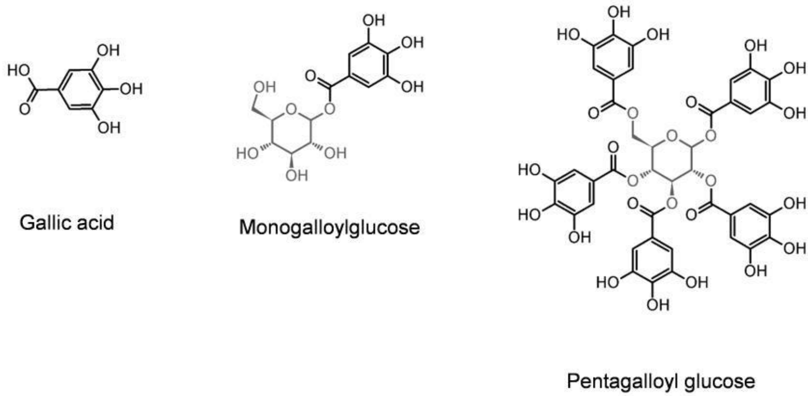

Figure 1. Molecular structures for gallic, monogalloylglucose and pentagalloylglucose, present in gall extracts

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P23

The rediscovery of the colouring elements in the highly degraded textile fragments from the princely grave from Poprad-Matejovce, Slovakia

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In 2006, a double-chambered chieftain's grave, dated to the early Migration Period (late 4th century AD), was discovered by construction work in Poprad-Matejovce, Slovakia. It was the start of a rescue excavation[1]. The whole grave was transported in 25 *in situ* blocks to Schloss Gottorf in Schlesswig, Germany, for examination and conservation.

Between 2008 till 2015, 15 *in situ* blocks have been opened revealing wooden furniture and construction parts of the inner and outer chambers. Nine of these *in situ* blocks, processed between 2013-2015 under the German Research Foundation's project "The chamber grave of Migration Period at Poprad, Slovakia – an interdisciplinary research project for

[1]Rescue excavation executed in collaboration between the IA SAS, the Sub-Tatran Museum in Poprad and the Foundation of the State Museums of Schleswig-Holstein at Schloss Gottorf in Schleswig.

evaluation of an extraordinary find”[2], revealed an assemblage of textiles and leather. Besides 85 pieces of well-preserved leather objects, many layers of often poorly preserved textiles were found, including textiles woven in tabby and twill, some tablet-woven pieces, sprang and many fragments of gold threads, which were consequently conserved by lyophilisation and restored where possible, Fig 1. The bad preservation of the textiles might be explained by previous contact with air as a result of an ancient robbery.
The presentation will focus on the identification of the dyes and mordants from one of the ‘best’ preserved textiles from the grave, a finely woven polychrome slit tapestry from which over 150 fragments were found. The organic dyes were identified with HPLC-DAD, while inorganic mordants were attested with SEM-EDX. Dye identification was heavily complicated by migration of organic substances from different objects in the grave as well as by the fact that due to the robbery, none of the finds were found on their primary location. The obtained results give clear evidence of the well-developed dyeing and weaving technology behind this masterpiece, requiring sophisticated technical skills to produce multiple colours, with a minimum of natural colouring elements and a well-considered use of sheep’s fleece.

Figure 1. Poprad chamber grave (from left to right): position of textile fragments (1) – large textile piece as found in the grave attached to wood (2) – unfolded and PEG 400 (10%) freeze dried (3) and after conservation (4)

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[2]Collaboration between the Centre for Baltic and Scandinavian Archaeology (ZBSA) in Schleswig, the Lower Saxony State Service for Cultural Heritage (NLD) in Hannover, KIK/IRPA and the Curt-Engelhorn-Centre for Archaeometry in Mannheim.

P24

An investigation of the photostability of 19th c. artist's cochineal lake pigments: light aging vs microfading spectrometry

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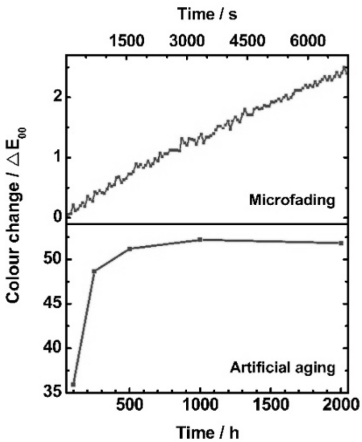
Cochineal lake pigments are based on metal complexes of carminic acid (1). Light-sensitive and prone to fading, their use has resulted in undesirable changes to artworks (2). Their commercial manufacture was studied through the 19th c. archive database of Winsor & Newton (W&N), an important colourmen committed to produce high-quality products (3). This unique opportunity has allowed to make reconstructions with as much historical accuracy as possible of W&N's Carmine, Crimson, Scarlet and Purple Lakes (4). The reconstructed lakes correlated well with historic samples which validates them as accurate references. Gum-arabic and poly(vinylacetate) paints prepared with pigment reconstructions and historic samples were subjected to light aging for 2000 hours with a high-intensity xenon light source (λ_{irr}>320 nm). The visual and molecular changes were followed through a multi-analytical approach including colorimetry and Vis-NIR reflectance hyperspectral imaging. The kinetics of colour change was different for the Carmine, Crimson, Scarlet and Purple Lakes and the degradation was more evident in the poly(vinylacetate)

paints. Gum-arabic has higher absorption at λ_{irr}>320 nm which may act as protection from colour change. Microfading spectrometry was also used as an *in situ* method to investigate the light-sensitivity of the same references in a relatively short period of time. Microfading spectrometry combines visible reflectance spectroscopy and accelerated light aging and has been used in cultural heritage institutions for determining the photostability of artists' materials (5). A high-intensity solid state plasma light source was used to irradiate a 0.5 mm spot in the paints during 0.5 to 2 hours. This work presents a comparison between the data obtained with the artificial light aging apparatus and the microfading tester. The relative photostability of the Carmine, Crimson, Scarlet and Purple paints was found to be different with the two aging methods. The advantages of the application of each method towards the study of the photostability of artists' materials, as well as the representativeness of the data obtained will be discussed.



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P25

The revival of the ancient technique of printing with mordants and dyeing in bi-colourants to achieve contemporary poly-chromic designs

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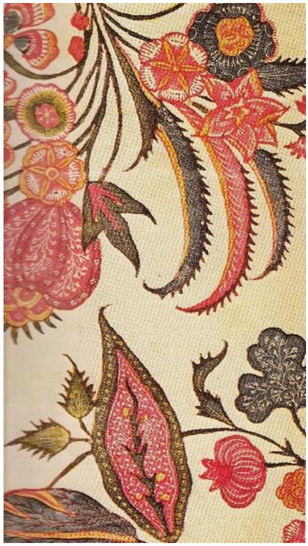
This paper explores the creation of a range of sustainable patterned fabrics by employing various Bio-colorants (natural dyes) in combination with a range of mordants that have a lesser impact upon the environment to create a poly-chromatic design within single dyeing process.
Practice based research was undertaken into dyeing and printing with Madder, Logwood, Weld and Woad or Indigo in combination with a selection of mordants Alum, Copper Acetate, Iron Acetate and Tannins onto a range of fabric bases which includes the new regenerated fibres alongside traditional natural ones as a sustainable option (1, 2).
Mordants that have been used from ancient times produce a pattern during the dyeing process. By looking at these historical (3, 4) and traditional applications (5) from across the globe, it was hoped that a more sustainable method of patterning either through printed (screen and block), stencilled or hand-painted techniques could be designed.
According to Robinson (6): Pliny the Elder (AD 23-79), writing of the ancient Egyptians, stated that, ‘Garments are painted in Egypt in a wonderful manner, the white clothes being first coated, not with colours but with drugs which absorb the colours. Although the dyeing liquid is one colour, the garment is dyed several colours according to the different properties of the drugs which have been applied to the different parts: nor

can this be washed out' It is thought that this passage was describing madder dye alongside as the various mordants – alum, iron salts and copper salts as they were known at that time (7).

Since this ancient time, the application of natural dyes evolved over the centuries into an advanced form of dyeing as this was only form of permanently colouring fabrics until the advent of synthetic dyes by Perkins in 1856. The 'Art of Dyeing' became a highly secretive and protected practice with the formation of Dyers Guilds from the 14^{th} c. The technique of the application of different mordants to create more than one colour evolved within the Far East employed initially to produce the 'Indienne mania' (Chintz) madder dyed calicos of the 17^{th} c. and 18^{th} c. and later with the development of 'Turkey Red' prints, the secrete of which remained undisclosed until the late 18^{th} c. (7).



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P26

Solar patterning: the employment of fast and fugitive colorants via the historical: anthotype, cyanotype and leuco-vat: solar dye patterning processes

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This paper discusses on-going research into natural dyes, mineral dyes (Lake pigments or raised colours) and leuco-vat dyes (Inko and SolarFast) with the potential to create a sustainable method of patterning fabric that employs the light sensitivity and fastness properties (fast or fugitive) of historic colorants in creating a permanent (photographic) image in colour upon natural or manufactured fibre bases. The aim of which, was to understand the success or failure of these types of photographic processes known today under the heading of 'Alternative photography' and consider the question: Could this kind of photographic image making be applied as a future, sustainable method of design generation, colouration and patterning of fabric for fashion and interiors? The objective was creating an alternative surface design process that relies upon light and natural colouring substances/dyes as the main patterning and processing medium.
As an eco-form of patterning that uses light as the main catalyst for cloth decoration, the use of historical cyanotypes is well known and the revival of light sensitive vat dyestuffs is well documented and commercially successful but, the application of natural dyes as Anthotypes is still at investigatory.

Instigated by the output of collaborative research between two different disciplines: Textile surface print design and early colouration methods; that since the 1840's has been applied as explorative photographic imaging processes (1). The research initially considered the relationships between natural plant extracts & 'Anthotypes' (2) and 'Prussian blue' & 'Cyanotypes' or 'Blue prints' (3) under different application techniques and light exposure sources.

The main aim of the research was to combine creative design practice with the historical context through research in understanding the reasons: Why and How Cyanotypes and Anthotypes work? Their correlation with sunlight, ultraviolet and infrared light in relation to quality and colour of images; in combination with the fastness properties of natural dyes/substances employed within the process. Analysis could be made into which colorants are the most successful and reliable for future use.

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P27

The expansion of colour space in hair dyeing by using mordant technique

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Natural colorants are attracting as the substitute of synthetic colouring materials for hair dyeing. It is because natural colorants are lower toxic and more eco-friendly than synthetic ones. Metallic mordant technique has been applied to widen the colour space of dyed samples (1,2). In view of similarity in morphological and chemical structure, wool was adopted as the reference material for human hair to evaluate the colour properties of hair dyeing. The colour properties of the dyed samples were evaluated by using CIE L*a*b* and Munsell colour systems. In previous work, we got wider colour space by using metallic mordant (3). We compared and evaluated the colour space of the dyed samples obtained by using metallic mordant and those obtained by using simple mixture of natural colorants.

We selected natural colorants such as sappan wood, amur cork tree, gardenia fruit blue, logwood to obtain red, yellow, blue, and brown shades. Natural colorants were dyed onto wool and human hair at some given condition. Human hair dyeing onto bleached sample was applied as follows; coated with the mixed paste, wrapped in aluminium foil, and then kept in an oven at 40℃ for 30min. Dyed hair samples were analysed by UV-Vis spectroscopy, colourfastness to light and washing. The addition of an alum or ferrous mordant was effective to expand the colour space of hair and to increase the colourfastness to washing and light. For the hair dyeing by using Fe mordant, darker shade colour of smaller a* and b* values and higher colourfastness were obtained.

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