DHA33

Dyes in History and Archaeology 33

Centre for Textile Conservation and Technical Art History

University of Glasgow

29 October - 01 November, 2014

ORAL PRESENTATIONS

Listed in programme order

Technical analysis of archaeological Andean painted textiles

Rebecca Summerour[1*], Jennifer Giaccai[2], Keats Webb[3], Chika Mori[2], Nicole Little[3]

[1]National Museum of the American Indian, Smithsonian Institution (NMAI)
[2]Freer Gallery of Art and Arthur M. Sackler Gallery, Smithsonian Institution (FSG)
[3]Museum Conservation Institute, Smithsonian Institution (MCI)

[1*]SummerourR@si.edu

This project investigates materials and manufacturing techniques used to create twenty-one archaeological painted Andean textiles in the collection of the National Museum of the American Indian, Smithsonian Institution (NMAI). The textiles are attributed to Peru but have minimal provenience. Research and consultations with Andean textile scholars helped identify the cultural attributions for most of the textiles as Chancay and Chimu Capac or Ancón. Characterization of the colorants in these textiles is revealing previously undocumented materials and artistic processes used by ancient Andean textile artists. The project is conducted as part of an Andrew W. Mellon Postgraduate Fellowship in Textile Conservation at the NMAI.

The textiles in the study are plain-woven cotton fabrics with colorants applied to one side. The colorants, which include pinks, reds, oranges, browns, blues, and black, appear to be paints that were applied in a paste form, distinguishing them from immersion dyes. The paints are embedded in the fibers on one side of the fabrics and most appear matte, suggesting they contain minimal or no binder. Some of the brown colors, most prominent as outlines in the Chancay-style fragments, appear thick and shiny in some areas. It is possible that these lines are a resist material used to prevent colorants from bleeding into adjacent design elements. Overall, the linear designs on the Chancay style fragments appear carefully applied, while colors on the Chimu Capac or Ancón style textiles are applied in a freer, looser style.

Building on previous work on similar textiles by other scholars, the materials and manufacturing techniques in four representative textiles are being identified and characterized by observation, documentation, and scientific analysis. Several analytical techniques are used to identify materials with emphasis on distinguishing between organic and inorganic colorants. Analysis is being completed in two stages. In the first round of analysis, non-invasive investigative techniques were emphasized in accordance with the NMAI's strict sampling policy. Non-invasive techniques included X-ray fluorescence, fiber optics reflectance, and Fourier transform infrared spectroscopies, as well as multispectral and hyperspectral imaging techniques, which were used to successfully characterize an insect-derived pink color, indigo in blues and black, and red iron earth pigments. Destructive analysis was executed on select yarn fragments. This included microscopic Fourier transform infrared spectroscopy (μ-FTIR), micro X-ray diffraction, and High performance liquid chromatography-diode array detector-mass spectrometry (HPLC-DAD-MS), which led to the identification of a probable gum accretion in one sample, and carminic and ellagic acids, components of cochineal and tannic dyes respectively, in two of the detached yarn fragments.

A second round of destructive analysis is planned for summer 2014, to identify materials that could not be characterized by non-invasive methods. Samples will be removed from the four representative textiles and analysis will include characterization of brown accretions, brown and reddish-brown colorants, and a black colorant that appears to contain an indigo component. Techniques will include polarizing light microscopy, μ-FTIR, and HPLC-DAD-MS.

Dyeing Practice and the Society: A Study of Historical Chinese Dyes of the Ming and Qing Dynasties (1368-1911) by Chemical Analysis and History of Art

Jing Han[1]*, Anita Quye[1]

[1]Centre for Textile Conservation and Technical Art History, History of Art, University of Glasgow, Glasgow G12 8QH

[1]*j.han.1@research.gla.ac.uk

In Imperial China, the colour of costume and textiles was an important symbol of status and much emphasis was placed on it. There is now increasing interest and research in historical Chinese costume and textiles to identify their dye sources. Through our research, we aim to improve understanding of the use of dyes in a wider context by studying further the practical regulations of dyeing and the influence of social factors. This research also aims to establish a methodology for the chemical identification analysis of historical Chinese dyes by Ultra Performance Liquid Chromatography (UPLC) with different detection methods.

The historical and archaeological dyes for our research are being collected from museums and archaeological institutes in both China and the UK. So far, 56 samples of various colour shades have been collected from 23 provenanced costumes and textiles belonging to the imperial family and officials of different ranks. Based on historical Chinese dyeing treatises from the 14th to 19th centuries, twelve common Chinese dyes and two mordants of historical significance have been selected and used to dye silk in the laboratory for analytical references.

Initial chemical analysis was carried out by UPLC with Photo Diode Array detection (UPLC-PDA) and UPLC-PDA-mass spectrometry. A database of the chemical composition of reference dyes has been created. The change of their chemical composition during ageing was being studied.

Historical samples are being analysed by UPLC-PDA in a semi-quantitative study of the dye sources. This enables relationships between different dyes and practical regulations for their use in the historical costumes and textiles to be studied, such as difference and communalities between the dyes used for yarns for patterns, and those used for fabrics for grounds and linings. The change in use of dyes over time and geographical areas will be discussed. Analytical results will also be compared systematically with historical dye recipes to investigate how closely theoretical procedure and practical use align. Meanwhile, the cultural meaning behind the use of dyes, such as the influence of the status of people and people’s preference of certain colours will be revealed.

New revolutionary chemical insights regarding the ancient purple dyeing process and Pliny's ultimate decipherment

Zvi C. Koren[1]*

[1]Director, The Edelstein Center for the Analysis of Ancient Artifacts, Department of Chemical Engineering, Shenkar College of Engineering, Design, and Art, Ramat-Gan, Israel

[1]*zvi@shenkar.ac.il
www.edelsteincenter.wordpress.com

This talk will be the first time that I will present my new recently published findings from my paper on the archaeological chemistry of the purple pigment [1].

Archaeological and chemical evidence associated with ancient dye vats used for purple dyeings have provided new scientific perceptions regarding the various stages of the process of dyeing with the pigments extracted from *Muricidae* mollusks. These steps were described two millennia ago by Pliny the Elder in his encyclopedic treatise on the natural history known during the Roman Period. In addition, a concise description of the dyeing of the related biblical bluish-purple *Tekhelet* dye was given three centuries later by the Talmud, which can also assist in understanding the composition of the related reddish-purple *Argaman* dyeing.

A critical re-analysis of Pliny's and the Talmud's writings, combined with the archaeological record and with modern laboratory experiments on all-natural dyeings, have provided new insights into the basic principles of chemistry associated with this ancient craft.

The major original findings from this current investigation will be discussed and should re-align our understanding of this process. The discoveries break new ground in the perceptions regarding the ancient purple dyeing process, and shatter some long-held notions in this area. In addition, though Pliny's description of the purple process has been questioned – and even disparaged – by some authors, this talk should completely validate – and vindicate – Pliny's account.

This talk will also discuss the HPLC dye analysis results on molluskan-purple pigments from historically important archaeological sources that shed light on the fashionable colors of kings and biblical priests.

REFERENCES

1. Koren Z. C. 2013. New Chemical Insights into the Ancient Molluskan Purple Dyeing Process. In: Armitage R. A., Burton J. H. (Eds.), *Archaeological Chemistry VIII*, ACS Symposium Series 1147, American Chemical Society: Washington DC; Chapter 3, pp. 43–67.

The Red Road of the Iberian Expansion, cochineal and the global dye trade: characterization of crimson textiles dyed with scale insects using UHPLC and multivariate statistical analysis

Ana Serrano[1,2*], Maarten van Bommel[2], João Lopes[3], Jessica Hallett[1]

[1] CHAM (Centre for Overseas History), Faculdade de Ciências Sociais e Humanas, Universidade Nova de Lisboa and Universidade dos Açores
[2]Cultural Heritage Agency of the Netherlands, Sector Research Movable Heritage
[3]Department of Pharmaceutics and Pharmaceutical Technology, Faculty of Pharmacy, University of Lisbon

[1,2*] ana.serrano@fcsh.unl.pt

An interdisciplinary project that connects both disciplines of History and Chemistry has been developed in order to attain accurate approaches on the impact of American cochineal as a red dyestuff in European and Asian textile production centres between the 16th and 18th centuries, in contrast to other locally-available red dye sources like kermes or Polish and Armenian cochineal insects.

Given the similar colorant composition of these red dye sources, a characterization study was performed on textile samples to assess possible modifications that can lead to a more accurate knowledge of their presence in historical textiles. Based on the work performed by Golikov [1,2], as well as other contemporary studies and historical recipes dated between the 15th and 18th centuries, several parameters for dyeing crimson were tested on silk and wool with American cochineal. Therefore, the influence of the pH, temperature, duration and the addition of ingredients such as soap, cream of tartar or turmeric were assessed. Then, the parameters that suited the best shades of crimson were selected to dye with kermes, Armerian and Polish cochineal.

Subsequently, the dyed samples were analyzed with ultrahigh pressure liquid chromatography coupled to a photodiode array detector (UHPLC-PDA) [3] and the chromatograms were analysed qualitatively and quantitatively with multivariate statistical data analysis methods [4]. The methodology developed demonstrated that it is possible to obtain consistent information about dyed samples and their composition, according to the experimental parameters and the textile substrate used. Along with the revision of historical sources for dyeing, this study has brought invaluable contributions to the study of cochineal and kermes insect sources used to dye historical textile samples, as well as to the historical evaluation of the incorporation of American cochineal into European and Asian dyeing traditions, from the 16th century onwards.

REFERENCES

1. Golikov, V., 2001, “The technology of silk dyeing by cochineal.II. The Experimental Investigation of the Influences of Type and Concentratins of Cations”, *Dyes in History and Archaeology*, *16/17*, 10–20.

2. Golikov, V., 2001, “The technology of silk dyeing by cochineal. III. The experimental investigation of the influences of pH, water quality, cream of tartar and oak galls,. *Dyes in History and Archaeology*, *16/17*, 21 – 33.

3. Serrano, A., Bommel, M. Van, Hallett, J., 2013, “Evaluation between ultrahigh pressure liquid chromatography and high-performance liquid chromatography analytical methods for characterizing natural dyestuffs”, Journal of Chromatography A, 1318, 102–111.

4. Serrano, A., Sousa, M. M., Hallett, J., Lopes, J. A., Oliveira, M. C., 2011, “Analysis of natural red dyes (cochineal) in textiles of historical importance using HPLC and multivariate data analysis”, *Analytical and Bioanalytical Chemistry*, 401, 735–743.

Polish cochineal - true or legend. Investigation of red dyes in Polish textiles from the collection of The National Museum in Warsaw

Ewa Orlińska-Mianowska[1]*, Monika Janisz[2], Elżbieta Rosłoniec[3], Katarzyna Lech[4]

[1] National Museum in Warsaw, Poland
[2] National Museum in Warsaw, Poland
[3] National Museum in Warsaw, Poland
[4] Warsaw University of Technology, Faculty of Chemistry

[1]*emianowska@mnw.art.pl

Polish cochineal (Porphyrophora polonica L.) had been using in Europe since antiquity until the end of the 16th century, when it was replaced by American cochineal - cheaper, more efficient and brilliant dye. So far, Polish cochineal was identified in many objects, particularly Italian and Spanish, but not Polish. Research of Polish cochineal in Poland has long tradition, however, a history of its use, economical and cultural significance in Poland are still not widely known. Since the 16th century Polish cochineal probably had been using locally in Poland.

We decided to check this hypothesis making studies on the group of objects from the collection of National Museum in Warsaw. We selected a group of textiles from the 16th to 19th century which might have been dyed by Polish cochineal. First results of analysis carried on Technical University of Warsaw confirmed our supposes. The fibre extracts have been examined by highperformance liquid chromatography coupled with spectrophotometric and tandem mass spectrometric detectors (HPLC–UV-Vis–ESI MS/MS). This system was proved to be especially useful for determination a variety of derivatives of the main colorant, carminic acid. Obtaind structural information have led to the identification of new compounds characteristic for Polish cochineal, which also have been present in the examined textiles.

Mjölon or ”Swedish sumac”
Arctostaphylos uva-ursi (L) as a dye source, and mordant

Margareta Bergstrand[1]*

[1]Primusgatan 67, Stockholm

[1]*Bergstrand.margareta@gmail.com

This paper presents a survey of literature and archive studies on the subject of Arctostaphylos uva-ursi (L) Sprengel used as a dye and tanning agent. It will also discuss the possible use of the plant as a mordant and an aid for other yellow dyes and give some examples of the practice of dyeing with mjölon.

Mjölon or bearberry is a small evergreen bush growing all over the country in Sweden mostly on sandy moors. Often it is confused with lingon (Vaccinum vitis–ida) but contrary to the delicious lingonberries, mjölon has a bland flour-like taste, which may explain its Swedish name, (mjöl = flour). However the branches and leaves of the plant have been used for a long time in Sweden as a medicinal plant, for tanning as well as a dye and mordant. Mjölon gives a yellow dye on its own or with alum mordant on wool. With an iron mordant it gives dull yellow, green, brown or grey colours and it has also been used for dyeing black. The dye has a fairly good light-fastness on wool.

According to some authors it has been used as a dye for wool since the Viking age. It has been mentioned in conjunction with the wall-hanging from Skog dated to 12th century [1] but in this case analytical results from the 1991 show that the yellow dye could derive from weld. Linnaeus describes mjölon in the journal of his journey to Lapland in 1730. [2] Some years later, on his journey to the island of Öland, Linnaeus finds the islanders using the plant as a dye and mordant source. [3] From the 18th and 19th centuries there are several accounts from dye-works as well as a few sample and recipe books from all parts of the country mentioning mjölon as a substitute for sumac (Rhus coraria). The dyers called it “smack” and used it for dyeing green and grey colours as well as for “Castor black”. The historian Carl Sahlin writes the history of the small dye-works owned by his family in Skåne in the south of Sweden, describing the practice of dyeing greys and blacks in the 1870´s.[4] In the 20th century Beda Larsson and Sandberg-Sisefsky, [1] among others, published mjölon recipes for craft dyers. A tradition of local dye recipes citing mjölon as a source for yellow and green colours ends with Lisa Johansson from Lapland in the 1960´s.[5] Now the practice of dyeing and tanning with mjölon is almost forgotten.

Mjölon was also widely used in the tanneries and sold to the cities by local farmers from all parts of the country. There are accounts of export of mjölon to Finland probably for the tanneries there. There is also evidence that mjölon was used for dyeing in Norway and Denmark. [6]

REFERENCES

1. Gösta Sandberg/JanSisefsky, Växtfärgning. 1967
2. Linnaeus, Flora Lapponica.1737
3. Carl von Linnés Öländska resa förrättad 1741
4. Carl Sahlin, Ett skånskt färgeri vid början av 1870-talet. 1928
5. Lisa Johansson, Gamla i Lappmarken kända växtfärgningsrecept. 1960
6. Birte Karin Fischer, Uld og Linnedfarvning i Danmark, 1720-1830. 1983

Colour fashions in Constantinople in the light of some unpublished archives of a Florentine Company (end of XVth century)

Ingrid Houssaye Michienzi[1], Dominique Cardon[2]*

[1]Ingrid Houssaye-Michienzi, University Paris Diderot - Paris 7, ANR ENPrESA
[2]Dominique Cardon, CIHAM/UMR 5648, CNRS, ISH, 14 av. Berthelot - 69363 Lyon Cédex 07, France

[1]ingridhoussaye@yahoo.fr
[2]*cardon.dominique@wanadoo.fr

The Archivio Salviati, upon which this communication is mostly based, is preserved in Pisa (Italy), at the *Scuola Normale Superiore*. This archive is the largest after that of Datini, a merchant in Prato. It contains thousands of account books and documents written from the 14th century until the 17th century, concerning textile production and international trade with many places in Europe and beyond.

This paper presents the first results of work in progress on the documents in this Archive that concern the history of dyeing. This is only one aspect of a vast interdisciplinary research programme on the study and publication of the Archive: the ANR (Agence Nationale de la Recherche, France)'s programme "ENPrESA".

The proposed paper is primarily based on the study of three account books written from Ottoman Constantinople at the end of the 15th century. On the *Giornale e Ricordi*, Giovanni di Marco Salviati wrote, in Tuscan language, the daily activities from 1491 to 1493. The information inside the journal is written again in two other registers, named *Debitori e Creditori*, which contain the accounts of people or merchandizes that corresponded to a debt or a credit. They are the only account books of Florentine people written within the Ottoman Empire that are known to be preserved in the archives of any country, so far.

Our study focuses on lists of bales of different types of woollen cloth sent to Constantinople, in which not only the length, but the colour of each piece of cloth is mentioned. This mass of information gives precious insights into the colour tastes of the Ottoman buyers at the time.
But the historical interest of these documents only appears in full light when compared with:

- similar lists included in the earlier account book of a Venetian merchant in Constantinople, Giacomo Badoer, just before the city fell to the Turk;
- a Venetian dyer's book contemporanean with the documents from the Salviati Archive, giving precise recipes for most of the colours mentioned in the lists;
- later documents from the French Archives, concerning the dyes and colours of the woollen-cloth specially produced for consumers in the Ottoman Empire, "the Levant", showing the long life of many colour names, giving recipes to obtain such colours, and illustrating them with dyed cloth-samples.

Painters or shopkeepers: who made brazilwood lake pigments? (XIIIth-XVIth C.)

Anne Servais[1*]

[1]Anne Servais, Université Paris 1 Panthéon-Sorbonne, Paris, France

[1*]a_servais@hotmail.com

For the last decades, physicochemical analyses have improved so much that they now allow us to identify which organic dyestuffs artists applied in their works. Considering in particular red lake pigments, it is now possible to know if a painter used kermes/cochineal, madder, lac or brazilwood[1]. Recent analyses brought to light the presence of the latter in Italian[2], Dutch[3], German[4] and French[5] manuscript illuminations of the XIVth and XVth century, as well as in XVth century hand-colored prints. The great number of brazilwood lake recipes among medieval and Renaissance receptaries could lead to the conclusion that artists themselves (or their workshop) made those brazilwood pigments they used in their paintings.

This paper will investigate this matter further and wonder if we can totally rely on this one single type of source –receptaries- to assume that those brazilwood lakes were produced by the artists themselves. Using apothecary/grocer inventories as well as payment accounts for artists' materials we could retrace the production line or operational sequence and discover if painters bought the raw material (i.e. brazilwood logs, chips or dust) and transformed them themselves, why and how, or if they rather purchased ready-to-use pigments (i. e. brazilwood lakes), or if they preferred an intermediate state between the two.

During the Middle Ages and the Renaissance, dyestuffs and pigments were often sold by grocers and apothecaries who also retailed spices, medicines, candles, and sugar. Inventories were drawn up by a notary to assess the value of the shop for an inheritance or when the business was sold. They enumerate the commodities in stock, their form, their quantity and sometimes their price. They thus provide a lively and reliable snapshot of all the materials available to the artists of the time. Payment accounts were held by patrons who employed painters. They mention which materials were bought, their price, sometimes their form and quantity, the suppliers, and the work the material was aimed to. Unlike inventories that reveal which materials were offered for sale to painters, payment accounts disclose which commodities the artists actually purchased.

Confronting both kind of sources will enable us to grasp under which forms brazil were available on the market, if painters favoured one form of the dyestuff in particular and which one. We could then determine more precisely where the apothecary's work did end, and where the artist's began. We could then consider if those conclusions are congruent with what receptaries tell us. Finally, a comparison with other red lake pigments made of kermes/cochineal, madder and lac could be sketched in order to find out if the making and selling of brazilwood lake pigments are an exception among this category of pigment or if they correspond to a global pattern.

REFERENCES

1. Jo KIRBY and Raymond WHITE, "The Identification of Red Lake Pigment Dyestuffs and a Discussion of their Use", *National Gallery Technical Bulletin*, 17 (1996), p56-80.

2. Arie WALLERT, "Verzino and Roseta Colours in 15th Century Italian Manuscripts", *Maltechnik Restauro*, 92 (3), 1986, p52-68.

3. Arie WALLERT, "Early Netherlandish manuscript illumination: technical aspects of M̂illuminations in the Rime Bible ofM̂ Jacob van Maerlant", *Revista de Historia da Arte*, 2011, n°1 – série W <http://revistadehistoriadaarte.files.wordpress.com/2011/09/art13.pdf>

4. Robert FUCHS, Oliver HAHN und Doris OLTROGGE, "Die Arbeit im Werdener Skriptorium. Materialien und maltechnische Aspekte", in J. GERCHOW ed., *Das Jahrtausend der Mönche. Werden 799-1803*, exh. cat., Essen, 1999, p232-240.

5. Inès VILLELA-PETIT, "Palettes comparées : quelques réflexions sur les pigments employés par les enlumineurs parisiens au début du XVe siècle", *Quand la peinture était dans les livres, Mélanges en l'honneur de François Avril*, sous la direction de Mara HOFMANN et Caroline ZÖHL, Turnhout-Paris, 2007, p382-391 et p469-472.

Reading polychrome laces: Multispectral imaging techniques on historic textiles from the Collection of The Metropolitan Museum of Art

Chiara Romano[1*], Joanne Dyer[2], Nobuko Shibayama[3]

[1] Chiara Romano, Andrew W. Mellon Fellow 2012-2014, The Metropolitan Museum of Art
[2]Joanne Dyer, The British Museum
[3]Nobuko Shibayama, The Metropolitan Museum of Art

[1*]chiararomano.tessuti@gmail.com

In this study a combined methodology employing dye analysis and multispectral imaging techniques has been applied to identify and map natural dyes found in 16th, 17th and 19th century Italian polychrome laces from the collection of The Metropolitan Museum of Art. While historical textiles in general have gained more interest over the last decades, laces are still seriously understudied and their polychromatic aspect has not been analytically explored to date. The collection discussed is made up of over 100 pieces and represents a substantial body of material with which to make a significant contribution to the investigation of the techniques and materials used to create these early Italian polychrome laces.

Multispectral imaging techniques are increasingly being viewed as a powerful method with which to survey collections containing such large amounts of material, as they allow the visualization and spatial localization of materials under different wavelengths of illumination, using readily accessible, inexpensive technology. The resultant multispectral image sets often act as “maps” which highlight particular physical properties, allowing the objects to be viewed in a completely novel manner and emphasizing relationships between materials within the object, and often, between similar materials within a collection of related objects. These physical properties are frequently employed for the tentative identification of these materials. However analytical data to support these assignments is rarely provided in such cases. In addition, such assignments are often made on the basis of comparison between images which have not been acquired or processed according to standardized methodologies.

This study focuses on the digital documentation via such multispectral imaging techniques of the materials used in the historical textiles investigated and further analysis by HPLC-PDA of a number of red and yellow dyes chosen from a group of five laces from this collection. The aim is to begin to relate the physical properties observed from these images to the chemical identification of the materials by acknowledging the importance of standardization in the acquisition and post-processing of multispectral image sets and the collection of analytic data corresponding to the areas of study. Recent advances in the standardized acquisition and post-processing of multispectral images, as outlined by the protocols published as part of the CHARISMA project [1], are particularly useful in this regard, as they ensure that the images produced are not only consistent but adhere to a series of internationally established standards. This greatly facilitates reproducibility of the methodology by the user, but more importantly, enables these images to be compared with each other and exchanged by other conservation professionals adopting this systematic approach. The informed and impartial interpretation of the physical properties observed in such images across different laces from different periods provided by the visual correspondence between standardized images and analytical data would be a particularly powerful contribution to the visual vocabulary of these polychrome laces, enabling these to be read and understood in new ways.

REFERENCES

1. "Multispectral Imaging in Reflectance and Photo-induced Luminescence modes: A User Manual" J.Dyer, G. Verri and J. Cupitt, 2013, (Version 1.0) published online http://www.britishmuseum.org/pdf/charisma-multispectral-imaging-manual-2013.pdf

A Garland of Dyes: Dye Sources and the Stylistic Development of English Turkeywork Carpets

Jamie Mulherron[1], Lore G. Troalen[2], Rosie Upton[2,3] and Alison N. Hulme[3]

[1]National Museums Scotland, Department of Art and Design, Chambers Street Edinburgh, EH1 1JA, UK
[2]National Museums Scotland, Collections Services Department, 242 West Granton Road, Edinburgh, EH5 1JA, UK
[3]EaStCHEM School of Chemistry, University of Edinburgh, Kings Buildings, West Mains Road, Edinburgh, EH9 3JJ, UK

[1*]j.mulherron@nms.ac.uk

The production of indigenous hand-knotted carpets in England is an important but neglected area in world textiles. Turkeywork carpets were inspired by oriental carpets and were domestically made alternatives to them. Turkeywork often followed oriental design imitating and emulating patterns found on desirable and highly costly imported carpets - mainly from Turkey. But elements of European ornament were also used, there are clear parallels with, for example, English embroidery, and in some cases as in the NMS *Kinghorne Carpet* Oriental and Western patterns are found side by side. While on one hand the colour palette of English Turkeywork looked at oriental models on the other it was inflected by an English palette found in embroideries and English tapestries of the same date. Starting out essentially as a response to the demand for the oriental product, English carpet makers created a unique style and aesthetic drawing from English textiles and in particular developed a manner of rendering motifs and borders in a painterly almost pointillist technique which could be described as painting by knots - which necessitated numerous colours and gradations of the same colour.

Building upon dye analysis undertaken in 1992 on the *Kinghorne Carpet* [1], this project generates more comprehensive information on the dye sources used in the production of Turkeywork. As part of this study, dye analysis was undertaken using PDA-UHPLC analysis on two rare examples both held in Scottish collections: the *Kinghorne Carpet* at NMS and the *Chaloner Carpet* in the Burrell Collection, supplemented with the analysis of 7 other known Turkeywork carpets held in public and private collections, and findings taken from Turkeywork furniture upholstery found in NMS collections. A range of European natural dyes were identified, generating important new data for dye research and which helps us to understand better the aesthetic choices of Stuart and Elizabethan England and Scotland, the syncretism between textile techniques, and the dye pool used to create the colour world of this period.

REFERENCES

1. Quye, A. (1992), The analysis of dyes in the Strathmore table carpet (NMS, AR92/16, unpublished).

Fading colour of logwood as designer inspiration

Katarzyna Schmidt-Przewoźna Assoc. Prof. Dr.[1], Anna Brandys M.A.[2]

[1,2]Institute of Natural Fibres and Medicinal Plants,
Wojska Polskiego 71B, 60-630 Poznan, Poland

[1*] kasia@iwnirz.pl
[2*] anna.brandys@iwnirz.pl

Laboratory of Natural Dyeing *"Natural Art"* from the Institute of Natural Fibers and Medicinal Plants has been exploring and analyzing dyeing tree for uses wider than textile dyeing. The paper presents potential and future prospects of logwood.

Dyeing from natural sources is the oldest way of colouring textiles. The naturally dyed fabrics recently have attracted attention of both consumers and manufactures in fashion markets.

Logwood – called also *campeche* – has antibacterial, antiviral, antifungal and antioxidant properties. It is extensively used in Ayurvedic and homeopathic medicine in Asia and Africa. It is reported to contain various bio chemical compounds such as hematoxylin, small amounts of brazilein, hematein and large amounts of tannins.

The paper presents results of dyeing experiments conducted with the use of the above mentioned dyeing tree and also our own usage for modern fashion collection. After series of experiments on linen and cotton textile materials we find the best dyeing methods for logwood. Dye concentration, extraction and dyeing time are important to compare the colors obtained with this tree. The changes in hue and saturation were measured with the use of spectrophotometric methods. The paper shows results of this experiments.

The Laboratory of Natural Dyeing *"Natural Art"* uses natural organic dyestuffs to support production of new non-toxic, non carcinogenic textile products with natural antibacterial and antimicrobial properties. The dyes obtained from logwood comes from heartwood. Tree have an inspiring range of medicinal uses with potential antioxidant, anticancer and antifungal activities so textile products with logwood has also huge potential application of the compounds found in logwood tree in various fields of science economy.

Fig 1, 2. Logwood dress (and project) designed by
Laboratory of Natural Dyeing *"Natural Art"*

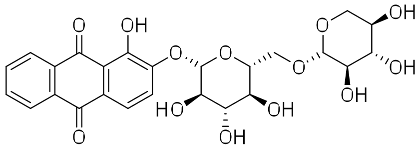
Extraction and Identification of Natural Dyes for Sustainable and Historical Applications

Lauren Ford,[1,2]* Richard S. Blackburn,[1] Christopher M. Rayner[2]

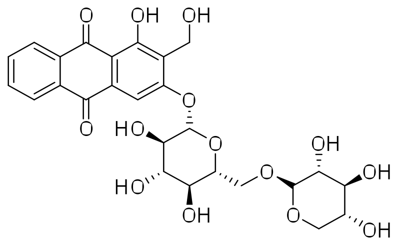
[1]Centre for Technical Textiles, University of Leeds, Leeds, LS2 9JT
[2]School of Chemistry, University of Leeds, Leeds, LS2 9JT

*cm10l2f@leeds.ac.uk

Natural dyes were used extensively throughout history for the dyeing of textiles [1]. One of the most commonly used dyes to create red colours was extracted from the roots of various madder species (*Rubia spp.*); the main compounds responsible for dyeing in madder are anthraquinone derivatives. By extracting different samples of ground madder it can be observed that plants grown in different geographical locations contain different ratios of these anthraquinone derivatives. This is most noticeable in the glycoside containing compounds, namely ruberythric acid (**1**) and lucidin primeveroside (**2**), which are the most abundant colorants in the dyestuff [2, 3]. Three types of madder were analysed: Iranian, Turkish and English madder.



1



2

Typically extraction of artefacts is conducted with mixtures of organic solvents with strong mineral acids to enable disruption of metal complexes formed with mordants and to suitable solvate the dye for separation from the fibre [3]. However, it has been previously highlighted that these methods remove important structural information from the dye molecules and mild, yet effective, extraction methods are required [4, 5]. Herein, madder extracts were analysed by HPLC-DAD and UV/Vis spectroscopy and significant differences in ratio of the anthraquinones and the nature of glycosylation were observed between different madder samples, demonstrating the importance of mild extraction techniques for the analysis of artefacts in order to preserve these glycosidic linkages. A novel, mild and highly effective extraction technique using glucose was developed, wherein extracted dyed samples displayed the same analytical profile of anthraquinones when compare to the original dyebath.

REFERENCES

1. Cardon, D., *Natural Dyes, sources, tradition, technology and science* ed. A. Publications. 2007, London: Archetype Publications Ltd
2. Henderson, R.L., C.M. Rayner, and R.S. Blackburn, *Isolation and extraction of lucidin primeveroside from Rubia tinctorum L. and crystal structure elucidation.* Phytochemistry, 2013.
3. Derksen, G., T. Beek, and H. Niederlander, *Analysis of anthraquinones in Rubia tinctorum L. by liquid chromatography coupled with diode-array UV and mass spectrometric detection.* Journal of Chromatography A, 2002. **978**: p. 119-127.
4. Zhang, X. and R. Laursen, *Development of Mild Extraction Methods for the Analysis of Natural Dyes in Textiles of Historical Interest Using LC-Diode Array Detector-MS.* Journal of Analytical Chemistry, 2005(77): p. 2022-2025.
5. Tiedemann, E.J. and Y. Yang, *Fiber-Safe Extraction of Red Mordant Dyes from Hair Fibers.* Journal of the American Institute for Conservation, 1995. **34**(3): p. 195-206.

To extract or not to extract: Strategies for the extraction of organic colorants from textile and paint samples

Maarten van Bommel[1*], Thibaut Devièse[2], Ioannis Karapanagiotis[3], Catherine Higgitt[2], Jo Kirby[4], Dimitrios Mantzouris[3], David Peggie[4], Art Ness Proaño Gaibor[1], Joanna Russell[2] and Ina Vanden Berghe[5]

[1]Cultural Heritage Agency of the Netherlands, Research department, P.O. Box 1600, 3800 BP, Amersfoort, (The Netherlands)
[2]British Museum, Department of Conservation and Scientific Research, Great Russell Street, London WC1B 3DG (UK)
[3]Ormylia Foundation Art Diagnosis Center, 63701 Ormylia, Chalkidiki (Greece)
[4]National Gallery, Scientific Department, Trafalgar Square, London, WC2N 5DN (UK)
[5]Koninklijk Instituut voor het Kunstpatrimonium–Institut royal du Patrimoine artistique, Jubelpark 1, B-1000 Brussels (Belgium)

[1]*M.van.Bommel@cultureelerfgoed.nl

Characterisation of organic colorants, i.e. dyestuffs and organic pigments, is considered to be key in the understanding of the creation process, the history, origin and dating of many cultural heritage objects such as textiles, paintings and furniture. Identification is currently mainly done using liquid chromatographic techniques. Since this requires that the colorants are brought into solution, an efficient extraction is crucial prior to the actual analysis. Many publications are available which describe different extraction methods for both dyes and organic pigments. At the 29th Dyes in History and Archaeology meeting in 2010 (Lisbon) a poster was presented which gave a review of these papers, and a freely accessible database was compiled afterwards in which these papers are summarised (research.ng-london.org.uk/scientific/colourant).

Based on the literature review, 17 different extraction methods were identified as most promising or commonly used for the extraction of dyes from textile and paint samples but many showed similarities. Following this overview a selection of extraction solvents was made, including hydrophobic solvents, such as DMF and DMSO, mild and strong acids (oxalic acid, citric acid, formic acid, hydrofluoric acid and hydrochloric acid) and complexing agents such as EDTA.

The present paper will give an outline of the collaborative work carried out within the framework of the European funded CHARISMA project. Within this research, the selected extraction methods were optimised and evaluated in the different laboratories involved. By using the same reference materials for extraction to perform a round robin experiment, and with the exchange of accurate information of how extraction procedures were carried out, the outcome of the extractions could be compared. The factors to be considered when selecting the most appropriate extraction method to use were discussed and evaluated, allowing us to present solid advice about the advantages and disadvantages of the different extraction procedures for textiles and paint or pigment samples. In addition, key elements in the optimisation will be discussed.

Financial support by the 7th Framework Programme of the European Union (CHARISMA Grant Agreement n. 228330) is gratefully acknowledged.

Scarlet, or Mock, or Not

Terry T. Schaeffer[1*], Laura Maccarelli[1], Diana C. Rambaldi[1]

[1]Schaeffer, Maccarelli, and Rambaldi: Conservation Center, Los Angeles County Museum of Art

[1]*terrys@lacma.org

"There is but this one shade of Scarlet in use…" wrote W.H. Worth in the 1840's in his personal dyeing manual, and then contradicted himself by providing several samples of different scarlet dyeings and by following these with recipes for mock scarlet. A cursory review of early to mid-19th century dye books indicates that cochineal was the red dye of choice for scarlet, although several other natural red dyes were used for mock scarlet. A variety of yellow dyes was commonly employed to increase the intensity of the color, including quercetin, annatto, and fustic. When conservators ask for dye information on "scarlet" textiles from this period and only a small fiber sample is available, HPLC is not an option. Therefore an alternative highly-sensitive analytical method is needed to provide information on the dyes present.

To increase dye identification capabilities, LACMA conservation scientists recently refined sample preparation procedures for Surface-Enhanced Raman Spectroscopy (SERS) of individual fiber samples (<0.5 cm total in length) and developed a modest library of red dye spectra using fibers from The Getty Conservation Institute's Schweppe reference collection of yarns (courtesy of GCI staff) as well as purified dyes. We are extending this project to include in our library yellow natural dyes and their components, again using Schweppe collection samples and compounds from chemical suppliers. We are also characterizing standard solutions of dye mixtures and fibers known to be dyed with more than one colorant. In some cases, HPLC is also used to support the interpretation of SERS spectra.

The SERS results on known mixtures of dyes prepared by varying the relative dye ratios and the pH reveal which dyes are likely to dominate the SERS spectrum in the presence of others, and how this depends on details of the preparation. The most abundant component need not provide the major contribution to the spectrum, as previously reported for mixtures of alizarin and purpurin [1]. For example, the contribution of some yellow dye compounds appears to be pH-dependent. Also, in many cases SERS spectra of madder-containing samples are dominated by bands due to pseudopurpurin, although that dye may not be the most abundant madder component present [2].

SERS results for "scarlet" and other red sample fibers from some late 18th and early 19th century museum objects will be presented, including a quilt with Turkey Red dyed patches. The results will show how SERS spectra may provide clues regarding the dyeing method.

REFERENCES

1. Z. Jurasekova, E. del Puerto, G. Bruno, J.V. García-Ramos, S. Sanchez-Cortes, C. Domingo, *J. Raman Spectrosc.* 2010; 41, 1455.
2. D. Rambaldi, F. Pozzi, N. Shibayama, M. Leona, and F. Preusser, 2014, submitted to *J. Raman Spectrosc.*

Dyer's Greenweed fingerprinting in historical textiles using UHPLC and MS-MS

Lore G. Troalen[1,2], Ashley S. Phillips[1,3], David A. Peggie[1,4], Perdita E. Barran[1,3], Alison N. Hulme[1]

[1]EaStCHEM School of Chemistry, University of Edinburgh, Kings Buildings, West Mains Road, Edinburgh, EH9 3JJ, UK
[2]National Museums Scotland, Collections Services Department, 242 West Granton Road, Edinburgh, EH5 1JA, UK
[3]School of Chemistry, John Garside Building, The University of Manchester, M13 9PL, UK
[4]National Gallery London, Scientific Department, Trafalgar Square, London WC2N DN, UK

[1*]l.troalen@nms.ac.uk

Polyphenolic components from *Genista* species have been well characterised because of their potential as anti-oxidants and as therapeutic leads; [1, 2] however, the identification of dyer's greenweed (*Genista tinctoria* L.) in historical textiles has been the subject of only limited studies. [3, 4] The flavones luteolin and apigenin, the isoflavone genistein, and the glycosides of these are known dye components of *Genista* species. [5] But genistein, and its glycosides, are also the main dye component found in many varieties of broom and gorse; notwithstanding, the dye source for historical textiles is usually ascribed to dyer's greenweed. [6] Whilst genistein is the principle component on which this attribution is made, [4] our studies of the dye extracts of historical samples show the presence of additional dye components that could enhance this identification. This paper presents a comprehensive study of the structure of these additional dye components using PDA-UHPLC and ESI-MS-MS techniques. Using this data, the analysis of modern and historical yarns will also be discussed, examining differences between the dye components adsorbed onto textiles, and relating variations in component ratios to dyeing processes such as over-dyeing, and to the effects of photo-degradation. [4, 7]

REFERENCES

1. Veitch, N.C. *Nat. Prod. Rep.* **2013**, *30*, 988-1027.
2. Sharma, V., Ramawat, K.G. In *Natural Products*; Ramawat, K.G., Mérillon, J.M., Ed.; Springer-Verlag Berlin Heidelberg: 2013, p 1849-1865.
3. Ferreira, E.S.B., University of Edinburgh, PhD Thesis, 2002.
4. Peggie, D.A., University of Edinburgh, PhD Thesis, 2006.
5. Ferreira, E.S.B., McNab, H., Hulme, A.N., Quye, A. *Chem. Soc. Rev.* **2004**, *33*, 329-336.
6. Cardon, D. *Le monde des teintures naturelles*; Belin Paris, 2003.
7. Troalen, L.G., University of Edinburgh, PhD Thesis, 2013.

Brazilwood lakes: towards the identification of a marker component

David Peggie[1*], Jo Kirby[1], Wim Genuit[2] and Julija Romanuka[2]

[1]National Gallery Scientific Department, Trafalgar Square, London. WC2N 5DN
[2]Shell Global Solutions International B.V. P.O. Box 38000, 1030 BN Amsterdam, The Netherlands

[1*]David.peggie@ng-london.org.uk

The use of brazilwood lakes in Renaissance paintings can be easily missed as the original red colour has almost always faded or degraded and the brownish colour observed during visual examination can be mistaken for other possible pigments (such as a yellow lake, for example). Although confirmation of the presence of a soluble redwood dyestuff is possible by HPLC analysis, this is usually by the detection of an unknown component, commonly referred to as 'Nowik C', rather than by the presence of brazilein, the main colouring component. This unknown component has been observed in samples from paintings including works by Raphael, Pietro da Cortona, Rembrandt and others.

The colour and properties of lake pigments and inks prepared using recipes derived from typical 15th- to 17th-century recipes were investigated by a series of experiments using both commercially available brazilin (the precursor of brazilein) and sappanwood (*Caesalpinia sappan* L.). This has revealed that brazilwood lakes have a marked susceptibility to alkaline conditions and that they are liable to deteriorate even without light exposure. The presence of the marker constituent (Nowik C) also seems to be favoured in samples prepared under alkaline conditions.

In collaboration with Shell, Amsterdam, investigations are currently on-going to identify this important marker component and it is hoped that by the time of the meeting, a structure can be proposed.

Iron gall dyestuffs – model study of degradation of textiles

Annalaura Restivo[1], Marialaura Dilillo[1], Ilaria Degano[1]*, Erika Ribechini[1], Maria Perla Colombini[1,2]

[1]Dipartimento di Chimica e Chimica Industriale, via Risorgimento 35, I-56126 Pisa (Italy)
[2]ICVBC-CNR, via Madonna del Piano 10, I-50019 Sesto Fiorentino (FI, Italy)

[1]*ilaria.degano@unipi.it

Iron gall inks are known to be responsible for the degradation of paper and parchment. The combined effect of the colouring material and the iron ions has been extensively studied in the last decade. Nonetheless, no systematic study about the degradation induced on textiles by iron gall dyes has been presented yet. We will present the results of a recently ended Italian project (VAT, “The Short Life of Tannins”) aimed at disclosing the role of tannins in the degradation of historical and archaeological textiles by means of a wide array of techniques. The results obtained by SEM morphological and EDX semi-quantitative analysis will be presented, showing a distinctive trend in the relative concentration of selected elements along the fibre section, under accelerated ageing. In parallel, the characterization of the oxidation state of the iron mordant was performed by means of synchrotron radiation based X-ray fluorescence.

Moreover, we identified several chemical parameters that may be used as early degradation warnings for preventive conservation of artefacts, or for the evaluation of the state of preservation of an artefact. Our survey includes the analysis of the amino acids constituting the core of the fibre by HPLC-MS, and focuses on the characterization of the lipid fraction that constitutes the external layer of the fibres by GC/MS. The degradation pathways followed by wool under the combined effect of the dyestuff and the mordant will be presented and discussed.

Mythic dyes or mythic colour? New insight into the use of purple dyes on codices

Maurizio Aceto[1,2]*, Aldo Arrais[1], Francesco Marsano[1], Angelo Agostino[3,4], Gaia Fenoglio[3,4], Monica Gulmini[3], Ambra Idone[3], Daniela Gastaldi[5], Pietro Baraldi[6], Cheryl Porter[7], Isabella Whitworth[8]

[1]Dipartimento di Scienze e Innovazione Tecnologica (DISIT), Università del Piemonte Orientale, viale Teresa Michel, 11 - 15121 Alessandria, Italy;
[2]Centro Interdisciplinare per lo Studio e la Conservazione dei Beni Culturali (CenISCo), Università del Piemonte Orientale, via Manzoni, 8 - 13100 Vercelli, Italy
[3]Dipartimento di Chimica, Università di Torino, via P. Giuria, 7 - 10125 Torino, Italy
[4]Nanostructured Interfaces and Surfaces Center of Excellence (NIS), via Giuria, 7 - 10125 Torino, Italy
[5]Dipartimento di Biotecnologie Molecolari e Scienze per la Salute, Università di Torino, via Nizza, 52 - 10126 Torino, Italy
[6]Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, via Campi, 183 - 41100 Modena, Italy
[7]Montefiascone Conservation Project, Montefiascone (VT)
[8]Indipendent scholar

[1*]maurizio.aceto@mfn.unipmn.it

Traditional knowledge concerning the use of Tyrian purple should probably be updated in the view of new analytical evidence. With particular respect to purple codices, i.e. the precious biblical texts written with noble metal inks on parchment dyed or painted with purple colorants, measurements carried out in the last years evidenced that this highly-renowned colourant has not, if ever, been used in their making. Non-invasive analysis has been performed in some cases [1-3] and in one case only invasive analysis has been used [4]; in all instances the use of lesser value dyes, such as folium and orchil, has been suggested. Recently, new insight has been given by micro-invasive analysis performed on a fragment of purple parchment taken from the *Codex Brixianus* (Brescia, Biblioteca Queriniana), a VI century purple codex produced in Gothic realm. It was possible to apply powerful analytical techniques, such as Surface Enhanced Raman Spectroscopy, MALDI-TOF-MS and HPLC-MS, to the analysis of extracts obtained from parchment. Historical reconstructions of dyes according to ancient recipes have been performed, allowing the preparation of dyed and painted standard samples. *Roccella tinctoria*, *Ochrolechia tartarea* and other lichen species were used to prepare orchil, while *Chrozophora tinctoria* fruits were used to prepare folium. A particular feature of these substrates, evidenced by XRF analysis, was the non-negligible content of bromine, possibly related, in the case of lichens, to their exposure to sea-spray. The results of micro-invasive analysis confirmed once more that Tyrian purple was not the dye used on purple codices and that both orchil and folium were used instead.

REFERENCES

1. M. Aceto, A. Agostino, G. Fenoglio, P. Baraldi, P. Zannini, C. Hofmann, E. Gamillscheg, *Spectrochim. Acta A* 95, 235 (2012).
2. M. Aceto, A. Idone, A. Agostino, G. Fenoglio, M. Gulmini, P. Baraldi, F. Crivello, *Spectrochim. Acta A* 117, 34 (2014).
3. M. Bicchieri, in *Codex Purpureus Rossanensis: storia, diagnostica e conservazione*, Roma, Accademia Nazionale dei Lincei (2014).
4. M. Thomas, F. Flieder, in M. Hours (Ed.), *La vie mystérieuse des chefs-d'oeuvres: la science au service de l'art*, Editions de la Réunion des Musées Nationaux, Paris, 1980, pp. 232-233.

A Multi-Disciplinary Approach to Analysis of Historical Red Lake Pigment Samples

Diane Kunzelman[1*], Ezio Buzzegoli[2], Mattia Patti[2], Claudia Marchese[2], Daniele Uldank[3], Ilaria Degano[3], Ilaria Bonaduce[3], Francesca Modugno[3], Margherita D'Ayala Valva[4], Francesca Rosi[5], Francesca Gabrieli[5], Austin Nevin[6], Sara Bellei[6]

[1]Opificio delle Pietre Dure di Firenze, Florence (Italy) [2] Università di Pisa, Dipartimento di Civiltà e Forme del Sapere, Pisa [3]Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Pisa [4]Scuola Normale Superiore di Pisa [5]Istituto di Scienze e Tecnologie Molecolari (CNR-ISTM), Perugia [6]Istituto di Fotonica e Nanotecnologie (CNR-IFN), Milan

[1*]diane.kunzelman@gmail.com

Extensive interdisciplinary investigation of a group of historical red lakes and colorants, generously placed at our disposal by the Lefranc&Bourgeois Archive in Le Mans (France) [1], has produced interesting results about their nature, significance, and relevance for non-invasive analysis of works of art. The materials were sampled for study as part of the research project *FUTURAHMA* (*From Futurism to Classicism (1910-1922). Research, Art History and Materials Analysis*) [2]. The project unites art historians, conservators and scientists from various Italian research institutes, forming the basis for a broad range of analytical approaches. These include the study of historical documents and developments, of techniques and materials, and their relationship to conservation.

Among the ample archival materials examined, attention focused on an apparently homogeneous group of lake pigments and components, conserved in powdered form in 20 original jars labelled with inscriptions and dates from 1890 to 1921. The materials therefore fell within our period of interest, and were of special relevance because of the primary importance of Lefranc in particular for the artists engaged in Divisionism. Sampling of the pigments was the premise for their physico-chemical characterisation by the various partners in the *FUTURAHMA* project.

To organise such a multi-analytical approach, the information gathered at Lefranc was first examined by comparing various written sources (labels, catalogues, promotional material), with results of non-invasive multispectral imaging of the 20 samples at various wavelengths (NIR, UV Fluorescence, Reflected UV, corresponding False Colour reconstructions). Comparison with similar imaging, done in the Lefranc archives on original hand-painted colour swatches contained in historical documents that reproduced their products in various media, and in laboratory records (often with additional information on names, numbering, formulation, methods of production), also contributed to the interpretation of data and the application of non-invasive imaging techniques to artworks which may not be sampled directly.

Chemical and physical investigations then followed, to accurately define the nature and composition of each of the 20 pigment samples, including the presence of trace components that might contribute to their classification. The survey comprised identification of the actual colouring material by High Performance Liquid Chromatography (using DAD and ESI-Q-ToF detectors), Raman spectroscopy, Fluorescence Lifetime Imaging and Fluorescence Spectroscopy; Fourier Transform Infrared and X-ray Fluorescence Spectroscopy were also applied to assess the presence of inorganic salts used in the pigment production. Representative examples are illustrated, including multispectral imaging of the entire set of samples and of comparable archival material, with reference to results from analysis. Focus has been placed in particular on discriminating among dyestuffs and lake pigments (often referred to by similar generic names, such as "Garance", "Laque", "Carmin", "Alizarine" etc.), and among their naturally derived and synthetic versions. In a period when many such variants or combinations are hypothetically possible, advances in methods for characterisation and analytical models for data interpretation, are particularly important, especially for conservation purposes due to different degrees of stability of the various materials.

REFERENCES

1. Lefranc-Colart, Le Mans (France), made sampling possible, and constantly aided and encouraged our initiative, for which we are particularly grateful.
2. Three-year (2013-2016) project promoted and financed by the Ministero dell'Istruzione, Università e Ricerca, Italy, within the *Futuro in ricerca 2012* program.

Correlation between colour, dye source(s) and fibres functionality– hazard or criteria for "gold embroideries" dating and provenance?

Ileana Cretu[1], Irina Petroviciu[2*], Ina Vanden Berghe[3], Jan Wouters[4], Mihai Lupu[1], Florin Albu[5], Andrei Medvedovici[6]

[1]National Museum of Art of Romania (MNAR), Bucharest, Romania
[2]National Museum of Romanian History (MNIR), Bucharest, Romania
[3]Royal Institute for Cultural Heritage (KIK/IRPA), Brussels, Belgium
[4]Conservation scientist – Consultant, Zwijndreecht, Belgium
[5]University of Bucharest, Faculty of Chemistry, Department of Analytical Chemistry, Romania
[6]Bioanalytical Laboratory, S.C. LaborMed Pharma S.A., Bucharest, Romania

[2*]petroviciu@yahoo.com; irinapetroviciu@mnir.ro

Religious embroideries worked in the Byzantine technique (14th-19th c.), also known as "gold embroideries", have been studied in terms of dye analysis, during the last 15 years, results being presented at earlier DHA meetings. Most of the analysis were performed by LC-DAD, as a joint research between Romanian institutions and the Royal Institute for Culture Heritage in Belgium (KIK/IRPA) [1] while some others by LC-DAD-MS, based on an analytical protocol developed in Romania [2]. These studies were focused on the identification of biological sources and their contribution to integrate religious embroideries, as well as other textiles from Romanian collections, in a European context. A closer look into the "gold embroideries" original manufacturing technique, based on the analysis of more than 175 samples from 35 textiles, raised several questions concerning the real function of the fibres sampled and studied. Investigation into 20 inscripted pieces, grouped over less than 100 years (15th c.), from the Putna Monastery collection suggested that the fibres could be grouped according to their functionality: support, metal embroidery, design contours and couching fibres.

The present study is intended to understand the possible connections between fibre colour, functionality and the biological source(s) used. Results obtained over 15 years are now re-organised by respecting the above-mentioned criteria. Most of the samples analysed represent the embroidery support, silk core of metalic threads and tassels. It should be considered that these categories are more appropiate for sampling during restoration. The clasification process allowed us to understand the "secrets" of the original working technique, by pointing to different uses of the same silk thread. For example, the face contour thread is green for the 15th century Romanian embroideries "made" at Putna Monastery [3]. Visual observation of similar contemporary objects with other origins (Greek, Serbians etc.) seem to have red contour while the Russian ones look black. May dye analysis bring arguments to support such hypothessis and transform them in criteria of dating or provenance?

The contribution will discuss the above-mentioned in more detail, based on case studies and will propose a general classification of the fibres functionality in gold embroideries, in corelation with colour and dye source. This should be considered as a start point in a possible identification of the original working technique, with consequences in provenance and dating. Such a task may be accomplished in a networking activity with similar research groups working on religious gold embroideries, from European and worldwide collections.

REFERENCES

1. Petroviciu, I. Cretu, I. Vanden Berghe, F. Albu, A. Medvedovici J. Wouters, *Analysis of dyes in 15th-17th century Byzantine embroideries from Putna Monastery, Romania*, in Dyes in History and Archaeology 24/25, in print
2. I. Petroviciu, F. Albu, A. Medvedovici, *LC/MS and LC/MS/MS based protocol for identification of dyes in historic textiles*, Microchemical Journal 95, 2010, 247-254
3. I. Cretu, M.Lupu, *The original technique: a new criteria to identify a liturgical embroidery?* Restitutio, Conservation-restoration bulletin (ed. by Dimitire Gusti National Village Museum) 7, 2013, 182-194.

Yellow silk for Buddha – Dye analysis on Tang dynasty textiles from the Famen temple near Xi'an, Shaanxi province, China

Regina Hofmann-de Keijzer[1]*, Regina Knaller[2], Maarten R. van Bommel[3], Ineke Joosten[3], Andreas G. Heiss[4], Helga Natschläger[5], Bernhard Pichler[1], Rudolf Erlach[1], Luc Megens[3] and Matthijs de Keijzer[3,1]

[1]University of Applied Arts Vienna, Department Archaeometry, Salzgries 14, 1013 Vienna, Austria
[2]Römisch-Germanisches Zentralmuseum, Mainz, Ernst-Ludwig-Platz 2, 55116 Mainz, Germany
[3]Cultural Heritage Agency of the Netherlands, Department Research Movable Heritage, Hobbemastraat 22, 1071 ZC Amsterdam, The Netherlands
[4]Vienna Institute for Archaeological Science, Althanstraße 14 - Geozentrum, 1090 Vienna, Austria
[5]Freelance sinologist, Vogelsanggasse 4/18, 1050 Vienna, Austria

[1]*regina.hofmann@uni-ak.ac.at

In 1987, Chinese archaeologists discovered a treasure in the chambers under the collapsed pagoda of the Famen temple, located 120 kilometres west of Xi'an in the Shaanxi Province of China. The objects of metal, jade, porcelain and silk represent gifts which were devoted to Buddha from the rulers of the Tang dynasty (618 - 907 AD). The gifts were donated prior to the sealing of the treasury in 874 AD and remained untouched until their excavation. In 2002, a conservation project on these Tang dynasty textile finds started initiated by the Shaanxi Provincial Institute of Archaeology in Xi'an and the Römisch-Germanisches Zentralmuseum in Mainz, fostered by the Chinese Ministry of Science and Technology, the Shaanxi Provincial Bureau of Cultural Relics and the German Ministry of Education and Research [1]. During this project a textile bundle with the inventory number T 68 was unfolded and it turned out that it consists of six garments: two trousers, one robe, one blouse and two skirts. Next to the conservation treatment the textile technology of these garments were studied.

The presentation discusses the results of an interdisciplinary project which was performed in 2013 in order to investigate the dyes of these garments. Ultra-high performance liquid chromatography coupled with photo-diode array detection was used for dye analysis [2]. Light microscopy served to study the homogeneity of the colours. Scanning electron microscopy with energy-dispersive X-ray analysis allowed a closer look to the structures of the threads and the identification of their chemical composition which might be a hint for the use of mordants. Textile dyeing in Ancient China was studied by the literature including historical Chinese sources [3]. Taking into account the distribution of plants based on the Flora of China [4], it will be discussed which dye plants might be possible sources for the detected dyes.

The detection of the yellow direct-dye berberine in all samples indicates that plants containing proto-berberine alkaloids were commonly used for silk dyeing in the Tang dynasty. The berberine-yellow was shaded with red from Sappan wood and with violet dyes from plants of the forget-me-not-family (Boraginanceae). The garments donated in honour of Buddha were made of shiny yellow silk which was decorated with silver ornaments and gold and silver threads.

REFERENCES

1. The results of this project will be published in a book about Famen textiles by the Römisch-Germanisches Museum, firstly in German, later in English and Chinese.
2. Ana Serrano, Maarten van Bommel, and Jessica Hallet: *Evaluation Between Ultrahigh Pressure Liquid Chromatography and High-Performance Liquid Chromatography Analytical Methods for Characterizing Natural Dyestuffs*. Journal of Chromatography A 1318, 2013, 102-111.
3. Chen Weiji: Zhongguo fangzhi kexue jishu shi (*History of Textile Technology in Ancient China*) Kexue Chubanshe. Beijing 1984 (in Chinese language).
4. Wu Zheng-yi and Ihsan A. Al-Shehbaz (Eds.): *Flora of China*. Beijing, St. Louis, 1994-2013.

A Coat of Many Colours: Dye Analysis of an Uzbek Coat

Victor J. Chen[1*], Gregory D. Smith[1], Amanda Holden[1], Niloo Paydar[1] and Kathleen Kiefer[2]

[1]Indianapolis Museum of Art, 4000 Michigan Road, Indianapolis, IN 46208, USA.
[2]Material Culture Conservation, LLC, 212 W 10th St, Suite B-240, Indianapolis, IN 46202, USA.

[1*]vchen@imamuseum.org

The Indianapolis Museum of Art has acquired an Uzbek man's silk embroidered coat believed to date from of the late 1800s to early 1900s. This type of coat is described in the textile literature as traditionally highly valued, usually individually made for special occasions [1]. Several Uzbek coats of almost identical design, with green and yellow vertical stripes decorated with two types of floral motifs variably in red, yellow and white, are known in other museums [2]. Because in the latter half of the 19th century, synthetic colorants began to be produced in Europe and were introduced into Central Asia, knowledge of dyes used on the IMA coat may help to shed light on its date. Samples of embroidery silk threads were collected, and extracted at 80°C, sequentially using 0.2 mM oxalic acid in MeOH-acetone-water, followed by pyridine-water, in order to maximize recovery of the color compounds. The two extracts from each sample were separately dried down, re-solubized in MeOH-water, combined, and then analyzed by LC-DAD-ESI-MS. The results showed that the sample from a yellow stripe contained some unidentified yellow compounds along with berberine, palmatine, and five other protoberberine alkaloids (PBA). A similar extract of common barberry bark (*Berberis vulgaris*) also contained these same seven PBAs. The sample from one of the red motifs gave Acid Red 88 (patent date 1877)[3], several other unidentified acid-sensitive red dyes that exhibited similar UV-vis spectra as Acid Red 88, and a trace amount of RhodamineB (1887). The turquoise thread from a green stripe yielded a trace of Rhodamine B, substantial amounts of Acid Green 16 (1899), Victoria Blue R (1892), Brilliant Green (1879), as well as several of their respective structural analogues of lower degrees of N-alkylation. Having excluded extraction artifacts, we surmise that these dye variants resulted from either age-related degradation, or the use of primitive synthetic methods in conjunction with impure chemical precursors, or both. The trace amounts of Rhodamine B could hypothetically serve as a dye brightener or be present as a contaminant in the dye bath. Taken together, our data are consistent with the IMA coat being a product of the early 20th century when natural and synthetic dyes were being used simultaneously.

Uzbek Coat, Indianapolis Museum of Art (2012.85)
Gift of David and Elizabeth Reisbord

REFERENCES

1. K.Fitz Gibbon and A.Hale "Uzbek embroidery in the nomadic tradition: the Jack and Aviva Robinson collection at the Minneapolis Institute of Arts" Minneapolis: Minneapolis Institute of Arts, USA, 2007, pp.129-162.
2. An example is in the Rickmers Collection (1894-1898) housed in Ethnologische Museum Berlin: www.smb-digital.de/eMuseum-plus (Identification number I B 2779).
3. Colour Index, volume 4, 3rd Ed., 1971.

David Smith: dyer and manufacturing chemist – man of transition

Susan Kay-Williams[1*]

[1]Dr Susan Kay-Williams – Royal School of Needlework

[1*]Susan.kay-williams@royal-needlework.org.uk

This paper is part of a broader investigation into the dye books, sample charts and other promotional and explanatory materials published as a result of the transition to synthetic dyes from the 1850s to 1910.

Undoubtedly many hundreds of dyers worked through the transition from the “natural” dyes of the pre-Perkin era to the aniline and other synthetic dyes post 1856, however very few dyers wrote and published across these periods. Yorkshireman David Smith did.

If one simply looks at how early the first commercial dye sample cards were produced (early 1870s) it would be possible to think that synthetic dyes had replaced the old style dyes completely within 20 years of Perkin’s discovery, but the work of David Smith shows this not to be the case, at least not in Yorkshire, and given that his earlier books went into second and third editions it is probably true of other places as well.

David Smith was a ‘practical dyer’ based in Halifax all his working life, his first book of recipes for dyeing, *Smith’s practical dyers’ guide* was published in the late 1840s, his second *The Dyer’s Instructor* in 1850 and his third *The English Dyer* in 1882. The *Dyer’s Instructor* was even translated into French.

This paper examines the contents of these books and how the recipes included changed over the 30+ year period, looking at the range of dyes and recipes he advocated at different times, based not only on the printed books but on his original notebooks*. Furthermore, Smith talks about the strength and fastness of his colours. While he was probably not thinking about their durability over 130 years, we can uniquely look at the longevity of some of the colours having referenced three copies of T*he English Dyer* to establish how well the colours have stayed true (to their printed names at least).

The paper also looks at Smith in the wider context, of what else was being published for dyers at the same time, based on original publications and samples from the UK, Germany and the USA.

*With thanks to the Bradford Textile Archive

German synthetic dyes go East and West, period 1860-1913

Matthijs de Keijzer[1]* and Regina Hofmann-de Keijzer[2]

[1]Cultural Heritage Agency of the Netherlands, Department Research Movable Heritage, Hobbemastraat 22, 1071 ZC Amsterdam, The Netherlands
[2]University of Applied Arts Vienna, Department Archaeometry, Salzgries 14, 1013 Vienna, Austria

[1]*m.de.keijzer@cultureelerfgoed.nl

The presentation discusses why Germany became the world leader in synthetic dyes and covered around 85% of the global demand before World War I. Attention will be given on the international German trade to the United States of America, Japan and China. Before 1890 German dyes were mainly exported to the European countries and to the United States but to a small extent to Asia. After 1890, the export shifted increasingly from Europe to Asia, because after 1900 India, China and Japan imported synthetic indigo as a substitute for the natural product in large quantities.
The fact that synthetic dyes quickly spread throughout the world was not only due to Germany's role as the major dye-producing country but also to their innovative marketing strategy. Develop-ment of a modern sales organization was possible, because representatives of the companies opened up new markets by travelling to European countries, Russia, the United States and later to Asia. Initially, partners in these foreign countries were export- and later trading companies. In the beginning the synthetic dyes were sold based on a commission or on profit-sharing. Other factors for a positive sales strategy were modern brand/product advertising, company-specific trademarks and awards for the dyes at (inter)national industrial exhibitions, especially at world exhibitions.
The next step for the German firms was to establish subsidiaries mainly to avoid tariff barriers. In Russia, they had to pay high tariffs for the final products, whereas intermediates and raw materials were subject to much lower duties. In France, subsidiaries were founded, because of their patent law. French patented products had to be produced there, otherwise the patents became invalid.
Principally, most of the synthetic dyes produced by the German firms were protected by company-owned patents, which led to high profits. Only in some cases conventions concerning price and quantity were useful. In the beginning of the 1880s, the Indigo Convention was arranged between BASF and Hoechst and the Alizarin Convention between BASF, Hoechst and Bayer, which had also an effect on the international trade.

<u>United States of America:</u> Already during the Civil War (1861-1865) France and England imported synthetic dyes. In the 1860s and 1870s still some national dye companies were erected. The American textile lobby was powerful and wanted dyes as cheaply as possible which meant that tariff barriers, in the period 1860-1883, were lowered. Especially the Tariff Act of July 1883 enabled massive inroads by the German and Swiss dye firms. Bayer was the most active dye company in the USA. During the outbreak of the war, in 1916, home based production was encouraged by the Revenue Act, which provided a protective barrier for foreign products. From that time on national dye firms were founded.

<u>Japan:</u> In the Meiji-era (1868-1912), Japan was entirely dependent on German imported synthetic dyes. The name of aniline dye appeared in Japanese import statistics since 1883. The colour blue was of special interest. The import of synthetic indigo appeared in 1902 and grew steadily. Some later, blue and black sulphide dyes were used for dyeing cheaper textiles. Circa 6.000 tons of synthetics were imported annually before 1914. From 1914 the Japanese textile industry suffered from a shortage of dyes, prices rose sharply and this was called the Dyestuff Famine.

<u>China:</u> The distribution of imported dyes in China could only be performed by merchant business, because for Europeans it was not easy to enter the country. The BASF was one of the companies with the longest presence in China and entered the market in 1885. At the turn of the 20th century synthetic indigo was the main selling product of the BASF. Henry Theodor Böttinger's visit in 1888/89 led to a boost of the Chinese business for Bayer. A 1907 report of this firm gives an insight which synthetics were exported: synthetic indigo, red substantive dyes, basic dyes for the mat industry and the cheap Ponceaus for the paper industry.

POSTER PRESENTATIONS

Listed in alphabetical order by author surname

Preliminary results from the characterisation of *folium*

Maurizio Aceto[1,2]*, Aldo Arrais[1], Francesco Marsano[1], Elisa Calà[1], Angelo Agostino[3,4], Gaia Fenoglio[3,4], Monica Gulmini[3], Ambra Idone[3], Luigi Menghini[5], Lidia Leporini[5], Nicola Di Matteo[5], Cheryl Porter[6].

[1]Dipartimento di Scienze e Innovazione Tecnologica (DISIT), Università del Piemonte Orientale, viale Teresa Michel, 11 - 15121 Alessandria, Italy;
[2]Centro Interdisciplinare per lo Studio e la Conservazione dei Beni Culturali (CenISCo), Università del Piemonte Orientale, via Manzoni, 8 - 13100 Vercelli, Italy
[3]Dipartimento di Chimica, Università di Torino, via P. Giuria, 7 - 10125 Torino, Italy
[4]Nanostructured Interfaces and Surfaces Center of Excellence (NIS), via Giuria, 7 - 10125 Torino, Italy
[5]Dipartimento di Farmacia, Università "G. d'Annunzio" di Chieti-Pescara, via dei Vestini, 31 - 66013 Chieti, Italy
[6]Montefiascone Conservation Project, Montefiascone (VT)

[1*]maurizio.aceto@mfn.unipmn.it

The term *folium* has been attributed since long times to the purple dye extracted from *Chrozophora tinctoria* (L.) A. Juss., the plant native to coastal Mediterranean countries known as turnsole. In the past there has been confusion concerning its real nature and in many instances similar names were given to lichen dyes and to dyes obtained from *Chrozophora* species. Literary citations are several [1-3] and the first recipes are dating to 11th century A.D.; it is possible that turnsole was already in use in Roman times and that it corresponded to the *Heliotropum tricoccum* cited by Pliny the Elder [4]. According to these sources, three hues could be obtained extracting the dye from *Chrozophora tinctoria*: a red at acid pH, a blue at alkaline pH and a purple at neutral pH.

The scientific knowledge on the composition of folium is at present relatively unsatisfying. Most of the available information can be circumscribed to the pioneering work by Guineau [5] who tentatively identified the dye in some 9th-11th century manuscripts by means of UV-visible diffuse reflectance spectrophotometry. In particular, the molecules responsible for purple/blue colour are unknown; it has been hypothesised a similarity with the molecules of orchil but without concrete scientific evidence.

In our study we have carried out an historical reconstruction of folium starting from fruits of *Chrozophora tinctoria* in order to try to elucidate its chemical composition and to increase the possibility of its identification on artworks. The different parts of the fruit, i.e. the internal seed and outer and inner cuticles, have been treated separately in order to obtain aqueous extracts; depending on the ripeness of fruits it is possible to extract a purple and a blue dye, but not a red one. Different techniques have been applied to extracts and to painted/dyed samples: SERS and FT-Raman spectroscopy, FT-IR, FORS, spectrofluorimetry and MALDI-TOF-MS. Preliminary results are presented, together with some possible identifications on early medieval manuscripts.

REFERENCES

1. C.S. Smith, J.G. Hawthorne, *Mappae Clavicula. A Little Key to the World of Medieval Techniques*, American Philosophical Society, Philadelphia (19749.
2. C.R. Dodwell, *Theophilus: the various arts*, Nelson, London, (1961).
3. F. Brunello, *De arte illuminandi*, Neri Pozza, Vicenza (1971).
4. Pliny the Elder, *Natural History, Book 9*, The Loeb Classical Library, Harvard University Press, Cambridge, Massachussets (1952).
5. B. Guineau, *Revue d'archéologie medieval* 26, 23 (1996).

Using LC-DAD-MS to investigate the biodegradation of cochineal and brazilwood chromophores with fungi isolated from an historical Arraiolos rug

Cristina Barrocas Dias[1-3*], Joana Junceiro[1], Ana Manhita[2,3], Rosário Martins[1,4], Ana Teresa Caldeira[1-3]

[1]Departamento de Química, Escola de Ciências e Tecnologia, Universidade de Évora, Rua Romão Ramalho, 59, 7000- 671 Évora
[2]Centro de Química de Évora, Rua Romão Ramalho, 59, 7000-671 Évora, Portugal
[3]Centro HERCULES, Largo Marquês do Marialva, 8, 7000-809 Évora
[4]Instituto de Ciências Agrárias e Ambientais Mediterrâneas, Universidade de Évora, Apartado 94, 7006-554 Évora, Portugal

[1-3*]cmbd@uevora.pt

Natural dyes were the only source of textile colour until the mid XIX century. Colour degradation of historical textiles is a well-known phenomenon among curators, being usually associated with the action of light. Biodegradation of dyes, degradation caused by the action of microorganisms (fungi or bacteria), has rarely been studied [1,2], and when done, is usually applied for the degradation of synthetic dyes present in the wastewaters of the dyeing industry [3].
In this work, we investigated the possible role of fungi isolated from historical Arraiolos Tapestries in the degradation of the chromophores of cochineal (*Dactylopius coccus*) and brazilwood (*Cesalpinia echinata*). Both red dyes have been previously identified in the production of the Arraiolos Tapestries [4].
The microorganisms were collected in the red wool embroidery areas of the Arraiolos rug using sterile cotton swabs and transported in a suspension of transport medium to the laboratory. In the laboratorythe cotton swabs were mechanically shaken for 1 h and inoculated under aseptic conditions in culture media specific for fungus growth. The cultures were incubated for 4 to 15 days at 28 ºC. The microbial isolates were stored at 4 ºC and periodically peaked. The characterisation of the microbial isolates was performed based on the observation of macroscopic and microscopic features, such as texture and colour of the colonies, hyphae morphology and reproductive structures. The following microorganisms were identified *Cladosporium* sp. (F1), *Aspergillus* sp. (F2), *Pennicillum* sp. (F3), and *Sporotrix* sp. (F4).
To study the influence of metabolic activity of microorganisms on the red dye chromophores, laboratorial cultures with high density of cells of individual pure cultures of isolated fungi were developed and inoculated in sterile aqueous solutions of the studied dye chromophores and on sterile alum mordanted wool dyed with similar cochineal and brazilwood dye baths.
The erlenmeyer with aqueous solutions of the dyes spiked with the individual fungus were left in the orbital shaker for 10 days at 28ºC. A 1 mL sample was taken right before the fungus inoculation, and after 5 and 10 days of incubation. These samples were used for LC-DAD-MS analysis in order to monitor the degradation of the cochineal and brazilwood chromophores [4].
Samples of the wool were collected before inoculation and after 48h, 6 and 10 days of fungal incubation. Colourimetry was done to evaluate the wool colour changes along the assay. Dye extraction and LC-DAD-MS analysis of the wool samples were performed to follow the chromophore degradation [4].
The results have shown that fungal contamination can have a profound impact in the colour of the textiles dyed with cochineal and brazilwood. The degradation of the chromophores is evident in the chromatograms and the degradation usually proceeds faster in the first days of the assay. As expected, chromophore degradation proceeds faster in solution. The chromatograms show that the microorganisms exude compounds into the media which can also contribute for the observed colour changes.

REFERENCES

1. O. Abdel-Kareem Annali di Chimica, 97 (2007) 527-539
2. B. Błyskal J. Cultural Heritage (2014) http://dx.doi.org/10.1016/j.culher.2014.01.008
3. G. McMullan et al., Appl Microbiol Biotechnol 56 (2001) 81–87
4. A. Manhita et al., J. Cultural Heritage (2013) http://dx.doi.org/10.1016/j.culher.2013.04.00

Alum production in late medieval time: A new Mediterranean approach

Didier Boisseuil[1*], Luisa Dallai[2]

[1]Didier Boisseuil, University of Tours, - Center for Renaissance Studies
[2]Luisa Dallai, University of Siena, Dep. of Historical Sciences and Cultural Resources

[1*]Didier.boisseuil@wanadoo.fr

Among the many commodities traded in the Western World at the end of the Middle Ages, alum seems to have been of great importance; the product was mainly useful for the european textile industry, then in full expansion, as well as in dressing leather and in metallurgical processes, and its trade was considered a monopoly of italian merchants (mainly Genoese) from the end of the XIIIth Century. Indeed, in chemical terms alum indicates a rather heterogeneous group of raw materials; among all, our study focuses on the so called "artificial alum production", and mainly on alunitic alum cycle.
Ongoing researches carried out in southern Tuscany and northern Latium, a productive district which became crucial by the half of the XVth century, are providing new interesting evidences on alum exploitation, both on a documentary and technical point of view. In southern Tuscany in particular, the archaeological excavation of the so called "Allumiera di Monteleo", carried out by the University of Siena, is providing new important information on adopted technologies; the project is highly multidisciplinary and allows the full integration of historical documents and archaeology for a more complete understanding of preserved material evidence.

Fig. Monteleo alum fournaces

Farther, these new evidences have to be put in a wider Mediterranean and European perspective, and this will be provided by a new European research network, the EMAE project, funded by the Ecole Francaise de Rome, CNRS and many national universities. The aim of this network is to better understand the methods of production, the circulation and the uses of the product in the Mediterranean basin (where it was produced) and the North Sea (where it was distributed).

REFERENCES

1. Didier Boisseuil « Production d'alun et monopole romain en Toscane méridionale (fin XV^{e} – début XVI^{e} siècles) », *Mélanges de l'École française de Rome - Moyen Âge* [En ligne], 126-1 | 2014, mis en ligne le 03 avril 2014, consulté le 14 avril 2014. URL : http://mefrm.revues.org/1879
2. Luisa Dallai, « L'allumiera di Monteleo nel territorio di Monterotondo Marittimo », *Mélanges de l'École française de Rome - Moyen Âge* [En ligne], 126-1 | 2014, mis en ligne le 03 avril 2014, consulté le 15 juin 2014. URL : http://mefrm.revues.org/1962

Formation and its printability specifications of natural indigo printing inks

Candan Cengiz[1*], Emine Torgan[2], M. Batuhan Kurt[1] and Recep Karadag[2,3]

[1]Department of Printing Technologies, Faculty of Applied Sciences, Marmara University, Goztepe- Istanbul/ Turkey
[2]Turkish Cultural Foundation, Cultural Heritage Preservation and Natural Dyes Laboratory Istanbul/ Turkey
[3]Laboratory of Natural Dyes, Faculty of Fine Arts, Marmara University, Kadikoy-Istanbul/ Turkey

[1*]candan@marmara.edu.tr

Natural organic dyes and natural organic lake pigments were used in the dyeing, printing, frescoes, etc. from prehistoric times to end of 19th century. Natural printing inks from obtained organic lake pigments have advantages since their production implies renewable resources causing minimum environmental pollution and has a low risk factor in relation to human health. Natural organic printing inks do not pollute the environment. They are neither toxic nor carcinogenic, and some also have antibacterial and antimicrobial properties. Most of the natural pigments are weak organic acids. The indigo plant (*Indigofera tinctoria* L.) is used to be for preparing inks. The natural pigments have been prepared from indigo (*Indigofera tinctoria* L.) plant dye qualitatively identified by using HPLC-DAD measurements.

After the preparation of printing inks with organic pigment of indigo *(Indigofera tinctoria* L.) plant dye and other organic compounds, with this ink were performed to print with various weight of paper and different printing pressure. It is used two different paper and both of them are used three different weightiness.

The identification of natural pigments and printing inks from produced in organic lake pigments and compounds are one of the most important targets aimed for in the scientific examination of paintings, textiles, illuminated manuscripts and printing materials. Thus, several analytical techniques have been used, for example RP-HPLC-DAD and SEM-EDX and brightness and color values of Indigo (*Indigofera tinctoria* L.) plant dye natural printing ink values were determined by CIE L*a*b* color space system.

In the study reported here, for the analysis and printing of natural printing properties of inks obtained from Indigo (*Indigofera tinctoria* L.) plant dye pigment an analytical method was developed. Identifying the color value, glossy, light fastness, surface energy and how much influence printing force of CIE Lab values. Finally, we believe that printing with prepared natural pigments and compounds inks can be an important advantage for environmental processes and food printing, child book printing and also etc.

REFERENCES

1. Develioglu O., Torgan, E. & Karadag, R., 2010, "Characterization of Colouring Matters by HPLC-DAD and Colour Measurements, Preparation of Lake Pigments with Ararat kermes (Porphyrophora hameli Brand)", *Jordan Journal of Chemistry Vol. 5 No.3, 2010, pp. 307-315.*
2. Develioglu O., Muhammed A., Fouad A., Torgan, E. & Karadag, R., 2012, "Chromatographic Analysis of Natural Pigments Produced from Datisca cannabina L. and Quercus infectoria Oliv. Plants and their Antimicrobial Activity", *J. Chem. Soc. Pak., Vol. 34, JN.Co.h4,em20.1S2oc.*
3. Karadag, R., Torgan, E. & Yurdun, T. 2010, "Formation and HPLC analysis of the natural lake pigment obtained from madder (*Rubia tinctorum* L.)", *Rewiews in Analytical Chemistry*, vol. 29, no. 1, pp. 1-12.
4. Wouters, J. & Verhecken, A. 1989b, "the scale insect dyes (Homoptera: coccoidea). Species recognition by HPLC and diode-array analysis of the dyestuffs", *Annales de la Societe Entomologique de Française*, vol. 25, no. 4, pp. 393-410.

Investigation of properties and printing forces of inks obtained from Dactylopius coccus Costa

Candan Cengiz[1*], M. Batuhan Kurt[1], Emine Torgan[2] and Recep Karadag[2,3]

[1]Department of Printing Technologies, Faculty of Applied Sciences, Marmara University, Goztepe-Istanbul/ Turkey
[2]Turkish Cultural Foundation, Cultural Heritage Preservation and Natural Dyes Laboratory, Istanbul/ Turkey
[3]Laboratory of Natural Dyes, Faculty of Fine Arts, Marmara University, Kadikoy-Istanbul/ Turkey.

[1*]candan@marmara.edu.tr

Since the ancient times, humans have made natural dyes by using some plant dyes, animals dyes and inorganic pigments. Humans have left their mark on their environment in the form of painted images, whether in the form of simple hands prints, works of fine art. The chemical method has been used to obtain these colours.

In this study, before cochineal lake pigments were obtained from (*Dactylopius coccus* Costa). After, the lake pigments were used to be for preparing inks. Colouring compounds of the inks were identified by HPLC-DAD. Then the preparation of printing inks with organic lake pigment of cochineal (*Dactylopius coccus* Costa), with this ink were performed to print with various weight of paper and different printing pressure. It is used two different paper and both of them are used three different weightiness.

The comparison of natural organic lake pigments and printing inks from produced in organic lake pigments and compounds are one of the most important targets aimed for in the scientific examination and printing materials. Thus, several analytical comparing techniques have been used, for example RP-HPLC-DAD, glossy, printing force, surface energy, light fastness properties, SEM-EDX and brightness and color values of cochineal insect (*Dactylopius* coccus Costa) natural printing ink values were determined by CIE L*a*b* color space system.

In the study reported here, for the analysis and printing of natural printing properties of inks obtained from cochineal (*Dactylopius* coccus Costa) pigment an analytical method was developed. Identifying the color value, glossy, light fastness, surface energy and how much influence printing force of CIE L*a*b* values. Finally, we believe that printing with prepared natural pigments and compounds inks can be an important advantage for environmental processes and food printing, child book printing and also etc.

REFERENCES

1. Develioglu O., Torgan, E. & Karadag, R., 2010, "Characterization of Colouring Matters by HPLC-DAD and Colour Measurements, Preparation of Lake Pigments with Ararat kermes (Porphyrophora hameli Brand)", *Jordan Journal of Chemistry Vol. 5 No.3, 2010, pp. 307-315.*
2. Develioglu O., Muhammed A., Fouad A., Torgan, E. & Karadag, R., 2012, "Chromatographic Analysis of Natural Pigments Produced from Datisca cannabina L. and Quercus infectoria Oliv. Plants and their Antimicrobial Activity", *J. Chem. Soc. Pak., Vol. 34, JN.Co.h4,em20.1S2oc.*
3. Romani, A., Zuccaccia, C. & Clementi, C. 2006, "An NMR and UV-visible spectroscopic study of the principal colored componenet of stil de grain lake", *Dyes and Pigments*, vol. 71, no. 3, pp. 218-223.

Material and microbiological characterization of the Évora Inquisition Banner

T. Ferreira[1]*, H. Mestre[1], A. Conde[2], P. Monteiro[3], A. Candeias[1,3], C. Dias[1], A.T. Caldeira[1]

[1]Departamento de Química, Escola de Ciência e Tecnologia, Centro de Química de Évora & Laboratório HERCULES, Universidade de Évora, Largo Marquês de Marialva, 8, 7000-809 Évora, Portugal
[2]Departamento de História, Escola de Ciências Sociais, CIDEHUS & Laboratório HERCULES, Universidade de Évora, Largo Marquês de Marialva, 8, 7000-809 Évora, Portugal
[3]Laboratório José de Figueiredo, Direção Geral do Património Cultural, Rua das Janelas Verdes, 1249-018 Lisboa, Portugal

[1]*tasf@uevora.pt

Évora was the first Portuguese city to receive the Inquisition in 1536, when the court of king D. João III was settled there. The first tribunals (Inquisitional Courts) were established in Lisbon, Évora, and Coimbra in 1541, and Évora celebrated its first public *act of faith* (*auto-de-fé*) in that year.

The Évora Inquisition Banner was produced for the *act of faith* that took place at the principal square of the city of Évora, in 14th May 1623, according to Túlio Espanca, a Portuguese historian from the 20th century [1]. After the extinction of religious orders in 1834, the Banner changed hands several times until it became into the possession of the Évora Museum (ME 171). It is considered an important item of the Portuguese cultural and religious heritage.

The Banner is nowadays in a very poor condition, due to the usage and to poor storage procedures during its troubled lifetime. Mechanical degradation is surely the responsible for it, but microbiological colonization has probably also contributed to it.

A two-faced medallion surrounded by a baroque frame occupies the central part of the artwork, with a golden strip finishing the top area and the inferior part being split into two triangular flaps. The obverse medallion face depicts the Inquisition coat of arms with a cross at the centre surrounded by a sword on the left and an olive tree on the right. The reverse face depicts the image of Pedro Arbués, who was the provincial inquisitor of Aragon, murdered in 1485, carrying a martyrdom palm.

Silk and metallic threads were sampled from different points of the embroidery work, representing the different metal thread typologies and coloured silk yarns. Sterile cotton swabs and sampled silk threads were used to investigate the microbiological contamination in the most degraded areas. Morphological evaluation of metal threads and silk fibres was carried out by optical microscopy and scanning electron microscopy (SEM). In order to determine the chemical composition of the metal threads and the mordants used in the silk yarn dyeing process analyses were carried out by energy dispersive X-ray spectrometry (EDS). Natural dyes used to dye the silk threads were identified by liquid chromatography with diode array and mass spectrometry detection (LC-DAD-MS) after chromophore extraction with EDTA/DMF. Microbiological analysis included isolation of fifteen bacterial and thirty five fungal strains from the collected samples.

REFERENCES

1. T. Espanca, “Inventário Artístico de Portugal”, VII, Évora, 2 Vols. Lisboa: Academia Nacional de Belas-Artes (1966).

The purple pigment and dye used in Daskyleion in the Persian period

Alexandros Konstanta[1], Dimitrios Mantzouris[2], Ioannis Karapanagiotis[1,2*], Recep Karadag[3,4], Dimitrios Lampakis[1], Emine Torgan[4], Ali Akın Akyol[5] and Kaan Iren[6]

[1]University Ecclesiastical Academy of Thessaloniki, Dept of Management and Conservation of Ecclesiastical Cultural Heritage Objects, Thessaloniki, Greece
[2]Ormylia Foundation, Art Diagnosis Center, Ormylia, Greece
[3]Marmara University, Laboratory for Natural Dyes, Istanbul, Turkey
[4]Turkish Cultural Foundation, Cultural Heritage Preservation and Natural Dyes, Istanbul, Turkey
[5]Gazi University, Department of Conservation & Restoration of Cultural Properties, Ankara, Turkey
[6]Mugla University, Department of Archaeology, Mugla, Turkey

[1,2*]y.karapanagiotis@aeath.gr

Purple was used in abundance to decorate the impressive Korou tomb, which was excavated in the necropolis area of Daskyleion and dated in the second half of the 6th c. BC [1]. A multi-analytical study was carried out to investigate in detail two purple samples which were removed from (i) a painted/pigmented (P) area of the tomb and (ii) a textile (T), found within the monument. Microscopy (optical & SEM), elemental analysis (XRF & SEM-EDX) and molecular spectroscopy (micro-Raman & micro-FTIR) were used to investigate both, P and T, archaeological samples leading to the following results. High concentrations of Br were recorded in both samples; red ochre and calcium carbonate were identified in sample P; sample T was probably made of cotton.

Liquid chromatography (HPLC-DAD) was used to investigate the purple colourants and showed that both P and T samples, contain indigotin (IND), indirubin (INR), 6′-bromoindirubin (6′MBIR), 6-bromoindirubin (6MBIR), 6-bromoindigotin (6MBIR), 6,6′-dibromoindigotin (DBI) and 6,6′-dibromoindirubin (DBIR). These compounds are contained in *Hexaplex trunculus* and *Murex brandaris* sea snails [2,3] and some of them were identified also in *Thais haemastoma*, which is the third snail species used to produce true purple in the Mediterranean. The compositions of the two archaeological samples P and T, measured as integrated HPLC peak areas at 288nm, were found to be similar. Principal component analysis (PCA) was applied to identify the biological source of the purple pigment and dye used in P and T samples, according to our previously published method [2]. The PCA results suggested that the archaeological purple was most probably originated from *H. trunculus* species. The possibility that *H. trunculus* was blended with small amounts of *M. brandaris* and/or *T. haemastoma* during the preparation of P and T cannot be ruled out [4]. However, it is stressed that the semi-quantitative HPLC results collected for the archaeological samples are very similar with the composition of *H. trunculus* snails collected in the coastline of Thessaloniki (Macedonia, Greece) and analysed recently using HPLC.

ACKNOWLEDGEMENTS

This research has been co-financed by the European Union (European Social Fund - ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: ARCHIMEDES III. Investing in knowledge society through the European Social Fund.

REFERENCES

1. A.A. Akyol, E. Torgan, K. Iren and R. Karadag, *Organic lake pigment analysis of Daskyleion Koru tumulus in the Anatolian Persian period*, 32nd Annual DHA meeting, La Rochelle, France, October 3-4, 2013.
2. I. Karapanagiotis, D. Mantzouris, C. Cooksey, M.S. Mubarak and P. Tsiamyrtzis, *An Improved HPLC Method Coupled to PCA for the Identification of Tyrian Purple in Archaeological and Historical Samples,* Microchemical Journal 2013, 110, 70-80.
3. D. Mantzouris and I. Karapanagiotis, *Identification of Indirubin and Monobromoindirubins in Murex Brandaris,* Dyes and Pigments 2014, 104, 194-196.
4. Z. Koren, *New Chemical Insights into the Ancient Molluskan Purple Dyeing Process*, In “Archaeological Chemistry VIII”, Armitage, R.A. Burton, J.H. (eds), ACS Symposium Series, Vo. 1147, American Chemical Society, Washington, DC, 2013.

Silk Dyes and Mordants from the Medieval Waste Layer in Prague

David Kohout[1], Helena Březinová[2]
[1]David Kohout, Institute of Chemical Technology Prague
[2]Helena Březinová, Institute of Archeology of Academy of Science of the Czech Republic

[1]dawit.koho@seznam.cz

The archaeological investigation of the entrance shafts of collectors in Prague-New Town, conducted in 2004-2007, provided a large amount of medieval organic waste material. In addition to woollen fragments, the damp wetland environment also preserved silk fabrics in a wide range of shades. Liquid chromatography with mass spectrometry detection (HPLC-ESI-MS) was used to determine the original organic dye extracted from a small amount of collected fibres. One step extraction of dyes from silk threads (cca 0,5mg) using methanol: dichloromethane: formic acid (48:48:4).The central atom of the complex bond in mordant dyes was determined by mapping elements using a scanning electron microscope with an energy-dispersive detector. A synthesis of the acquired data produced an approximate determination of the original colour and the natural source of the dye. The current colour following conservation was measured spectrometrically in the visible radiation using the CIELAb colour coordinate system. The current and determined original colours were compared. Yellow was the most common colour on twenty-eight silk fragments of varying quality. Flavonoids dyes and their glycosylated aglycons were detected most frequently. Aluminium derived from alum was the main mordant determined in the study. Iron ions as the mordanting element were detected on darker silk fragments.

Pseudoindirubin: a marker for woad-dyed textiles?

Richard Laursen[1*] and Chika Mouri[2]

[1]Boston University
[2]Freer/Sackler Galleries of Art

[1*]laursen@bu.edu

During the analysis of some older indigo-dyed textile fibers from Iran and Central Asia, we observed, besides the usual indigotin and indirubin peaks, a third, earlier-eluting peak which we have called “pseudoindirubin” because its visible electronic spectrum contains two prominent peaks with maximal absorbances at about 560 nm (like indirubin) and at about 440 nm (like an anthraquinone, e.g. emodin). We have not obtained enough of this material to determine its color visually, but it is probably a shade of brown, based on its spectral characteristics. Subsequently we have observed “pseudoindirubin” in indigo from at least 5 specimens of woad (*Isatis tinctoria*) obtained from various sources, and in a plant from Peru, *Cybistax antisyphlitica*, but not—so far—in indigo from other plant sources (*Indigofera* spp., *Polygonum tinctorum* and *Strobilanthes cusia*).

We do not know yet the structure of “pseudoindirubin,” but do know that it has a molecular mass of 501 Da and, like indigotin and indirubin (both of which have molecular masses of 262 Da), is very insoluble in water; otherwise, it would not have persisted in textiles. We also sometimes see a second peak eluting just after “pseudoindirubin” that has a similar electronic spectrum. It may be a *cis-trans* isomer, as is seen for the indigos. “Pseudoindirubin” may be one of the components of the uncharacterized “indigo brown” materials described by Perkin and Everest (“The natural organic colouring matters,” Longmans, Green and Co., London, 1918, pp. 499-501), though “indigo brown” was found apparently in all species of indigo-producing plant.

Woad differs from the other common indigo-producing plants in that the primary precursor is isatan B, rather than indican. Therefore, the biosynthetic machinery of woad appears to be different from that in other plants and may be producing some unique compounds, such as “pseudoindirubin.” If this turns out to be the case, then the presence of “pseudoindirubin” may be useful for distinguishing between textiles dyed with woad indigo and those dyed with indigo from other plants. In any case, its presence should demonstrate that the textile was dyed with natural, rather than synthetic indigo. It should be pointed out, however, that just as the relative amounts of indigotin and indirubin can vary greatly—apparently depending on how the indigo was processed—the amount of “pseudoindirubin” may also depend on processing and may not be observed in all woad-dyed textiles.

Can the juniper be a good raw material as mordent and dyestuff?

M. Julia Martinez García[1*]

:

[1]Mª Julia Martínez García, TintArtEc, Natural dyes Center. University of Valencia, Spain.

[1*]m.julia.martinez@uv.es

Juniper is a shrub present in the Mediterranean forest. It has fruits as small grains with medicinal and tonic properties. The juniper plant is not a classic raw material for dyes. Nevertheless, this shrub has some dyes substances. Some parts of the plant have a high tannin and flavonoid content, principally quercetin. Flavonoids are the most important yellow dye, obtained from many plant sources. They are soluble in water [1]. Quercetin is used for dye of yellow and red, for example is present in the *Rhamnus* spp. and onion peels [2]. For this reason, we would like suggesting the possibility to use certain parts some species *Juniperus* shrubs as mordants and natural dyes.

Traditionally, Spanish people made with juniper a tincture, a infusing the berries with water [3]. The classical authors as Pliny and Dioscorides explained about the properties of juniper. Particularly, Dioscorides lauded his styptic virtues. A coin with representation of juniper was found in archaeological context from workshop making purple dye. We have some data about his use in Antiquity as dye raw material: specie of juniper, *Juniperus phoenicea* L., was use as dyestuff raw material in Egypt. Appears in the texts cited as "juniper fresh", and was used to dye a strip of linen used in the temple of Dendera, in Upper Egypt. Moreover, the Egyptians prepared a light brown dye with chromium sulphate, alum and juniper berries [4].

Considering the commentaries of classics authors and the Ancient Egyptians texts, we will make the experimentation with the berries, bark and branches of *Juniperus oxicedrus* L and *Juniperus phoenicia* L. for demonstrate his properties as mordant and solid dyestuff for different textiles raw materials as wool, cotton, linen and silk.

REFERENCES

1. Cardon (2007); D. Cardon, *Natural Dyes Sources, Tradition, Technology and Science*, Antique Collectors Club Ltd, London, 678.
2. Cardon (2007); D. Cardon, *Natural Dyes*, *Tradition, Technology and Science*, Antique Collectors Club Ltd, London, 681-682.
3. Font i Quer (2005); Pio Font i Quer, *Plantas medicinales, El Dioscórides renovado*, Península, Barcelona, 83.
4. Manniche (2006); L. Manniche, *An Ancient Egyptian Herbal*, The British Museum Press, 118.

Reconstructing medieval lake pigments from "The book on how to make colours"

Maria João Melo[1*], Rita Castro[1], Tatiana Vitorino[1]

[1]Department of Conservation and Restoration & REQUIMTE-CQFB, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Campus da Caparica, 2829-516 Caparica, Portugal

[1*]mjm@fct.unl.pt

Figure 1: "The book on how to make colours", MS Parma 1959, courtesy of L. U. Afonso.

In this poster we will present and discuss the recipes for producing lake pigments available from "The book on how to make colours", the oldest Portuguese illuminators' manual and the only Judeo-Portuguese text on the art of manuscript illumination, Figure 1. "The manuscript once belonged to the collection of Giovanni Bernardo De Rossi (1742-1831) and is now at Parma's Bibliotheca Palatina under the signature MS 1959." [1].

This 15th c. medieval treatise describes the main steps and ingredients for producing lake pigments based on lac dye and brazilwood [2-3]. More than one recipe is included for each of the dyes, enabling to obtain different shades of red/pink/carmine colours [4, 5].

The challenges of reproducing with historic accuracy a medieval pigment in the laboratory will be addressed, with a particular focus on the final colour and the molecular composition. Would an artist be better prepared than a scientist to reproduce these medieval recipes?

REFERENCES

1. L. U. Afonso, *New developments in the study of O livro de como se fazem as cores das tintas*. In: Afonso LU, editor. The Materials of the Image. Lisboa: Campo da Comunicação; 2010, p. 3-27
2. D. L. Strolovitch, *O libro de komo se fazen as cores das tintas todas* (Transliteration). In: Afonso LU, editor. The Materials of the Image. Lisboa: Campo da Comunicação; 2010, p. 213-223.
3. http://www.dcr.fct.unl.pt/arquivo-digital/luminura-medieval
4. -M. J. Melo, V. Otero, T. Vitorino, R. Araújo, V. S. F. Muralha, Ana Lemos and Marcello Picollo, "Three Books of Hours from the 15th century: a multi-analytical and interdisciplinary approach", *App Spec.*, 68 (2014) 434-444
5. -R. Castro, J. A. Lopes, F. Pozzi, M. Leona and Maria João Melo, "Combining SERS and microspectrofluorimetry with historically accurate reconstructions for the characterization of lac dye paints in medieval manuscript illuminations", *submitted*

Preparing the next generation of the DHA meetings

Roxany Moustarda[1*], Ioannis Karapanagiotis[2]

[1]First Primary School of Trilofos, Thessaloniki, Greece
[2]University Ecclesiastical Academy of Thessaloniki, Dept of Management and Conservation of Ecclesiastical Cultural Heritage Objects, Thessaloniki, Greece

[1*]roxamousta@yahoo.gr

How can we attract children's attention to ancient dyes? It is extremely easy! The books of history distributed in the primary schools in Greece, are full of photographs of ancient painted and dyed objects that provide the basis and motivation to initiate a discussion among young students about the colouring materials used in antiquity. For instance, several coloured objects and paintings of the Cycladic and Minoan civilization, including the famous paintings of Thera, where molluscan purple was used [1,2], are included and described in the book of history of the 3rd grade of primary education in Greece. Remarkably, the origin of the colours, which are shown in the photographs of the archaeological objects, is not even mentioned. However, this is the very first, spontaneous question of the children: what were the materials used in the ancient Minoan art? Apparently, this is a typical question for people participating in the DHA meetings. Consequently, it is extremely easy to attract children's attention to the topic of the DHA meetings.

Then the next question that comes up is related to the educational program that has to be set up: how can we organize a class on ancient dyes in a primary school? More important, what will be the benefits for the schoolchildren? Is it only the extra knowledge that they will gain in their history class? These were the questions that were imposed at the beginning of a project which was implemented in the 1st Primary School of Trilofos, Greece, aimed at teaching and revealing the beauty of ancient dyes to children at the age of eight (3rd grade). The project was organized in four educational levels: (i) an introduction on ancient, natural dyes was presented by the teacher. In the 4 hour powerpoint presentation dyestuff sources (plants, insects, mollusks) were described; and yes, photographs were included, which attracted the attention of the children. Furthermore, photographs of selected historical objects which were previously subjected to dyestuff analysis were shown in the presentation, bridging thus natural dyestuff sources with the class of history. (ii) In a second level, dyeing of wool will be demonstrated in the laboratory showing and explaining the various treatment steps. Dyes of plant origin, such as madder (red), weld (yellow) and indigo (blue) will be used for the dyeing processes. The natural origin of ancient dyes will be stressed, implying that these materials do not have any harmful effect on the environment or human health. We decided to rule out the use of small animals (insects and mollusks) for the dyeing experiments. Ethical issues related to the treatment of small animals are of great importance, especially when the participants are students at the age of eight. In fact, we suggest that the DHA community has to address this critical point, probably in cooperation with biologists and other scientific societies. (iii) Groups of students, working in a cooperative basis, will repeat the dyeing processes. (iv) Finally, these working groups will describe and present their own results to the whole class.

REFERENCES

1. I. Karapanagiotis, S. Sotiropoulou, E. Chryssikopoulou, P. Magiatis, K.S. Andrikopoulos and Y. Chryssoulakis, *Investigation of Tyrian Purple occurring in historical Wall Paintings of Thera,* 23rd Annual DHA meeting, 2004.
2. I. Karapanagiotis, D. Mantzouris, C. Cooksey, M.S. Mubarak and P. Tsiamyrtzis, *An Improved HPLC Method Coupled to PCA for the Identification of Tyrian Purple in Archaeological and Historical Samples,* Microchemical Journal 2013, **110**, 70-80.

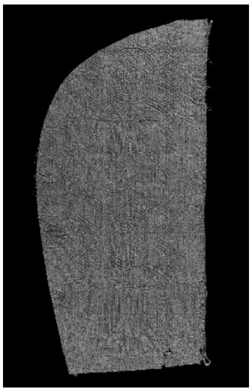
Dye Sources and Technical Analysis of the 13th and 14th Century Parrots in Roundels Silks

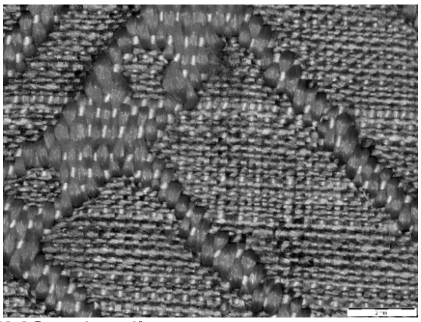
Jamie Mulherron[1], Lore G. Troalen[2], Rosie Upton[2,3] Miriam McLeod[2] and Alison N. Hulme[3]

[1]National Museums Scotland, Department of Art and Design, Chambers Street Edinburgh, EH1 1JA, UK
[2]National Museums Scotland, Collections Services Department, 242 West Granton Road, Edinburgh, EH5 1JA, UK
[3]EaStCHEM School of Chemistry, University of Edinburgh, Kings Buildings, West Mains Road, Edinburgh, EH9 3JJ, UK

[1*]j.mulherron@nms.ac.uk

This poster will present an investigation into the dye sources, material construction, and metal thread analysis of a group of highly significant late 13th century woven silks with the motif of two parrot-like birds in a roundel. Although in the vein of Byzantine-Islamic woven silks these are considered among the earliest examples of high quality 'European' silk weaving and have variously been attributed to Sicily, Lucca in Tuscany and even Spain. The type was eagerly sought out by collectors and museums in the late 19th and early 20th centuries yet their origins and in some cases authenticity remain uncertain. NMS holds an outstanding fragment example of the type which probably comes from the same chasuble as another piece in the Metropolitan Museum. We have also been fortunate to sample a further rare example in a private collection. Dye analysis will concentrate on the identification of the red and green dye sources particularly looking at the use of cochineal - and its origins - in early European silks. Our combined approach of dye analysis, weaving technique and thread analysis will contribute major new information which will help better understand these beautiful and rare examples of early European silk weaving.


NMS


NMS - detail


Private Collection

REFERENCES

1. David Jacoby, 'Silk Economics and Cross-Cultural Artistic Interaction: Byzantium, the Muslim World, and the Christian West', *Dumbarton Oaks Papers* 58 (2004), pp. 197-240
2. Anna Muthesius, *Byzantine Silk Weaving AD 400 to AD 1200*, Vienna, 1997
3. Anna Muthesius, *Studies in Byzantine and Islamic Silk Weaving*, London, 1995

Sensitivity of the red and blue dyes to the Bookkeeper preparation

Anna Nowicka[1*]

[1]Academy of Fine Arts in Warsaw, ul. Krakowskie Przedmieście 5, 00-068 Warsaw

[1*]ananow@wp.pl

The research described below is a part of a project. The project, carried on at the Faculty of Conservation and Restoration of Works of Art at the Academy of Fine Arts in Warsaw since December 2011, is financed from the resources of the National Science Centre, awarded on ground of decision number DEC-2011/01/N/HS2/02308.

It is beyond any doubt that maintaining pH of the cellulose material at a proper level (i.e. higher than 7) prolongs its durability. Deacidification of paper is a standard procedure, but deacidification of painting supports (e.g. linen supports) would also be desirable. Slowing down the degradation of cellulose would probably help to avoid such radical operations as lining the original canvas in the future.

A great problem is that of the influence of the deacidificating preparation on the colourful layers laying on the paper being deacidificated. First of all, the durability of the oil binder sensitive to the alkali is uncertain. The other problem is the stability of the pigments that change their properties in the alkaline environment, in which the deacidification process is carried out.

The subjects of the research were, among others, two red dyes - cochineal and alizarin crimson and one blue - indigo (produced by Kremer), which were used to prepare oil paint. The paint was prepared on one's own and put on the ground made of Whatman blotting paper (3) to prepare paintings for the tests. A waterless preparation Bookkeeper, containing magnesium oxide suspended in fast-evaporating and low-reactive organic solvent (perfluoroheptan), was chosen for deacidification. The research did not show any harmful effects on the oil layers containing the abovementioned organic dyes.

The samples were aged under the UV light (in a Suntest chamber) and in the environmental test chamber, while being exposed it to the elevated temperature and high humidity. The following comparative studies (of deacidificated and reference samples) were carried out:

-examination of colour changes with a spectrophotometer;
-examination of pH of the ground at various stages;
-SEM imaging and SEM-EDS analysis;
-HPLC analysis.

REFERENCES

1. A.-L. Dupont, J. Tẻtreault, *Cellulose degradation in an acetic acid environment*, "Studies in conservation", Vol.46, No.3, 2000.
2. N. Eastaugh, V. Walsh, T. Chaplin, R. Sissall, *Pigment Compendium*, Routledge, 2008.
3. E. West Fitzhugh, *Artists' Pigments, A Handbook of Their History and Characteristics,* vol.3, Washington-New York-Oxford , 1997.
4. H. Schweppe, *Handbuch der Naturfarbstoffe*, Hamburg 1993.
5. S. Zumbűhl, Nadim C. Scherrer, *Aktive Passivierung der Degradation cellulotischer Strukturgefüge - Untersuchungen zur „Ensäuerung" textiler Gemäldebildträger,* „Zeitschrift fűr Kunsttechnologie und Konservierung" 2003, 17 Jahrgang, Heft 2, s. 387-396.
6. S. Zumbühl, S. Wuelfert, *Chemical aspects of the Bookkeeper deacidification of cellulosic materials: the influence of surfactants,* "Studies in conservation", Vol.46, No.3, 2001, s. 169-180.

Dye analysis contributes to the interpretation of the object's history: investigating upholstery of the 1841 horse-drawn railway carriage 'Hannibal' at the Technisches Museum Wien

Luba Dovgan Nurse[1*], Valentina Ljubic-Tobisch[2], Chris Clouter[2], Maarten R. van Bommel[3], Alisa Selviasiuk[3], Matthijs de Keijzer[3], Regina Hofmann-de Keijzer[4]

[1]Freelance textile conservator, UK.
[2]Technical Museum Vienna, Austria.
[3]Cultural Heritage Agency of the Netherlands.
[4]University of Applied Arts Vienna, Austria.

[1*]ldnconservation@gmail.com

This poster discusses the investigation of the upholstery of a horse-drawn railway carriage known as Hannibal (built around 1841 and used until 1872), part of the collection of the Technical Museum Vienna, Austria, that has been recently conserved to prepare it for re-display in the permanent galleries. Hannibal has been part of the museum's collection since the late 1870s and has undergone many undocumented restoration campaigns and alterations that made the identification of the components and layers of upholstery challenging. Conservation investigation identified that the upholstery of the passenger coach was not original but a replacement, made from recycled materials, while the upholstery of the fixed exterior hoods (driver's and rear passenger seats) retained some of the original passementerie concealed under multiple layers of re-upholstery. To establish the chronology of the upholstery layers in order to determine the significance of the earlier interventions in the context of the carriage's history and to determine their stability during display, dyes were analysed by UHPLC-PDA at the Cultural Agency of the Netherlands and interpreted in collaboration with the University of Applied Arts Vienna. Analysis of the dyestuffs helped to understand the significance of alterations and restorations in the context of the museum's earlier practices.

Anatolian hand-woven Boyabat scarf's technical and asesthetical properties

D.Gizem Özkan[1*], Halide Sarıoğlu[2]

[1]D. Gizem Özkan, Ph.D. Student, Gazi University
[2]Halide Sarıoğlu, Prof.Dr., Gazi University

[1*]gizem_ozkan@yahoo.com

Most common traditional Turkish handcrafts have been hand-woven fabrics which have lost its significance nowadays. The original samples of hand-woven fabrics tend to fade away. For this reason, it is very important and necessary to introduce, search and document this cultural heritage. In this poster, it is intended to introduce the shuttle hand-weaving type of fabric called "Boyabat Scarfs".

Boyabat district is situated in the province of Sinop in the Black Sea region of Turkey. Boyabat is a district with a population of about 44.000. It is believed that the establishment of this district was in 600 BC and its former name was Germanikopolis. Boyabat was ruled by Kaskians, Hittite, Paphlagonians, Lydians, Persians, Macedonians, Romans, Byzantines, Seljuks and Ottomans successively [1]. Boyabat scarfs are fine woven cotton fabrics about 1 m^2 in size and has burgundy colored stripes on the edges and decorated with motifs in the middle with colored yarns. In the region, weaving the scarf was learned and inherited from the elders and also it was an occupation that was considered as an additional income to the family [2, 3]. In 2010 by the initiative of the Boyabat Mayor, scarfs were trademarked as the geographical indication by the Turkish Patent Institute and is still being protected [4]. While weaving the scarf, simple type of high handlooms are used. All parts of these handlooms are made from pine wood. The texture of the scarf is plain weave and cotton yarns are used on the ground and in the motifs. As in all traditional products, the motifs and colors used in the scarf are unique to the region. It is clear that while designing and entitling the patterns; historical, social and political events influenced the people of the region [2].

In this poster presentation, technical features such as materials and weaving type and aesthetical features such as color, pattern and composition detected from an original scarf sample will be introduced. Also age, type of yarn, dyes and texture analysis of an original sample of scarf (reflecting the traditional features) will be included.

REFERENCES

1. "Boyabat Governorship Historical and Demographic Information" May 2014. http://www.boyabat.gov.tr/btarih.html
2. Sarıoğlu,H. (1994). A research on Eflani and Boyabat Scarf Weaving, Ph.D. Thesis, Ankara
3. Yayla,S. (1976). Women headscarfs in Boyabat Yaylacılı Village, Halkbilim, 3, 15, 4
4. "Turkish Patent Institute Registered Geographical Indications" May 2014. http://www.tpe.gov.tr/portal/default2.jsp?sayfa=431

Optical and spectroscopic techniques in the identification of historic pigments and dyes

Marta Pilarska[1*], Jarosław Rogóż[1], Paweł Szroeder[2], Elżbieta Basiul[1], Teresa Kurkiewicz[1], Adam Cupa[1]

[1]Institute for the Study, Restoration and Conservation of Culture Heritage, Faculty of Fine Arts, Nicolaus Copernicus University, ul. Sienkiewicza 30/32, 87-100 Toruń, Poland
[2]Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, ul. Grudziądzka 5/7, 87-100 Toruń, Poland

[1*]pilarska.marta@gmail.com

Identification of pigments and dyes is crucial when solving the problems of conservation and restoration of various kinds of artworks: paintings, polychrome objects or illuminated manuscripts. In this paper a new approach for fast pigment and dyes identification is proposed, in which such optical methods as near-infrared (NIR) reflectography and the false-colour infrared imaging are combined with elemental analyses and molecular spectroscopy.

The NIR reflectography and false-colour infrared (NIR, red and green channels) images are compared to the photographs recorded in three channels of visible light (red, green and blue channels) resulting in preliminary conclusions concerning the pigments used in the particular artwork and their distribution. Results of these optical examinations are used to determine the position of sampling for further studies. The cross sections of the collected samples are subjected to the laboratory tests, which include optical microscopy, elemental analyses by SEM-EDX, and analyses of molecular composition by µATR-FTIR and micro-Raman spectroscopy. Laboratory tests aims at verification of the non-invasive examinations.

We will present results of case studies performed on the 17th century wax sculpture of Our Lady of the Bowed Head (from the collection of National Museum in Poznań, Poland. In polychrome of this object a mixture of Prussian blue and indigo was discovered. Another example to be presented is the Codex Aureus Gnesnesis from Gniezno (Poland), dating back to the 11th century. On illuminated pages of the investigated manuscript verdigris and copper resinate were found.

We show that the combination of optical and spectroscopic techniques can be also used for fast and effective identification of synthetic dyes used in historic inks. Such 19th century synthetic dyes as: nigrosine, methylene blue, crystal violet (gentian violet), malachite green, magenta, indigo carmine or sudan black, can be detected.

The presented approach is a starting point for the elaboration of fast, precise, and cost effective protocol for identification of pigments and dyes in artworks of many kinds.

All in the mix at the 19th C Blantyre dyeworks: synthetic violets and coloured pigments

Anita Quye[1]*, Julie Wertz[1], Maarten van Bommel[2], Ineke Joosten [2] and Karen Carruthers[3]

[1]Centre for Textile Conservation and Technical Art History, History of Art,
University of Glasgow, G12 8QH
[2]Rijksdienst voor het Cultureel Erfgoed (State Service for Cultural Heritage),
Amsterdam, The Netherlands
[3] David Livingston Centre, National Trust for Scotland, Blantyre

[1]* anita.quye@glasgow.ac.uk

In the collections of the National Trust for Scotland's (NTS) David Livingstone Centre, Blantyre, is a vial of coloured solid particulate material, described in the collection record as:

"Glass tube of dye, found by plot holders on the site of the old Dye Works" (Object 384)

It has no strong provenance for where or when it was found, but it is speculated to relate to the dye works and textile mills that operated in this part of Blantyre from 1794 until 1904, mainly by the Menteith family. Like other Scottish textile producers around Glasgow of that era, these works produced Turkey red cloth. Hence it has long been expected that the vial contents relate to the Turkey red processes undertaken there. The NTS asked the CTCTAH to analyse the contents to understand the artefact's significance and legitimacy of its association with Blantyre's past dye and textile works.

Initial low-power light microscopy revealed the hard granular contents as an inhomogeneous mixture of yellow, red-brown, purple-red and white particulates that looked more inorganic than organic. Infrared microspectroscopy of one white particle indicated a carbonate, but gave no result for a purple particle which was thought to be an organic colorant. With the new dye analysis facility at the CTCTAH under development at the time, the analytical investigation continued in collaboration with the State Service for Cultural Heritage (RCE).

Ultra performance liquid chromatography with photo diode array detection (UPLC-PDA) revealed an early synthetic dye, either Methyl Violet, a pararosaniline basic dye in commercial production from 1866, or partially photo-degraded Crystal Violet, a related dye available from 1883. There was no detectable evidence for natural madder or synthetic alizarin which were widely used in nineteenth century Europe for Turkey red textiles.

Particulates that might be calcium carbonate and quartz were identified by scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDS), also at the RCE. Yellow and red-brown particles in the mix were composed of iron oxides and iron hydroxides. These might be coloured pigments. Further analysis by x-ray diffraction (XRD) at National Museums Scotland is planned to identify the minerals to shed light on any relevance to textile dyeing and printing.

To date the vial does appear to be connected to textile dyes, maybe indicating dyeing and printing activity for Turkey red cloth or other textiles, but not the Turkey red dyeing process itself. With the significance of the vial now revealed, conservation considerations for display and access are important because both of the possible synthetic dyes are light-sensitive.

It is remarkable that this fragile vial seems to have survived on exposed ground for some years, and fascinating that it might provide us with primary source evidence of past Scottish textile production. Understanding what the mixture represents requires more investigation into the dyed textile activities of nineteenth century Scotland, through the likes of the research network ReCREATE http://www.gla.ac.uk/recreate/.

Colourful textiles from a naturally-mummified medieval body from Sudan

Joanna Russell[1]*, Marei Hacke[1], Thibaut Devièse and Catherine Higgitt[1]

[1]British Museum, Department of Conservation and Scientific Research, Great Russell Street, London WC1B 3DG (UK)

[1]*jrussell@thebritishmuseum.ac.uk

Textiles with exceptionally well-preserved colours were found associated with a naturally-mummified medieval body found in the Fourth Cataract region of the Nile in Sudan. The richness of the textiles, together with the position of the burial under the wall of a Christian church, suggest that this may have been a high status individual. Three textiles surrounded the body, two of which display a variety of bright colours, in addition to a blue-dyed animal skin, possibly worn as a cloak. The textiles were investigated as part of a larger project to examine and conserve a large group of bodies from this area of Sudan, as part of the Merowe Dam Archaeological Salvage Project.

Nine samples of fibre, displaying a range of colours and fibre types, were taken from the garments and subjected to analysis for fibre and dye identification. Eight of these were taken from the two brightly coloured textiles associated with the body, and one sample was taken from the blue-dyed animal fleece. The samples were examined using a light microscope and variable pressure scanning electron microscope (VP-SEM). Fourier transform infrared spectroscopy (FTIR) and high performance liquid chromatography (HPLC) were used to identify the dyes present. One of the textiles, believed to be wool from visual examination, displayed a wide range of colours, with anthraquinone (red), flavonoid (yellow), indigoid (blue) and tannin-based (brown) dyes being identified by HPLC. The second textile, identified as degummed *Bombyx mori* silk by VP-SEM examination, was woven from red, blue and white weft threads over mainly blue warp threads to create a colourful patterned textile. An indigoid and an anthraquinone red dye were identified using HPLC. An indigoid dye was also found on the dyed animal skin.

Fading colour of logwood as designer inspiration

Katarzyna Schmidt-Przewoźna Assoc. Prof. Dr.[1], Anna Brandys M.A.[1]

[1]Institute of Natural Fibres and Medicinal Plants,
Wojska Polskiego 71B, 60-630 Poznan, Poland

[1*] kasia@iwnirz.pl, [2*] anna.brandys@iwnirz.pl

Laboratory of Natural Dyeing *"Natural Art"* from the Institute of Natural Fibers and Medicinal Plants has been exploring and analyzing dyeing tree for uses wider than textile dyeing. The paper presents potential and future prospects of logwood.

Dyeing from natural sources is the oldest way of colouring textiles. The naturally dyed fabrics recently have attracted attention of both consumers and manufactures in fashion markets.

Logwood – called also *campeche* – has antibacterial, antiviral, antifungal and antioxidant properties. It is extensively used in Ayurvedic and homeopathic medicine in Asia and Africa. It is reported to contain various bio chemical compounds such as hematoxylin, small amounts of brazilein, hematein and large amounts of tannins.

The paper presents results of dyeing experiments conducted with the use of the above mentioned dyeing tree and also our own usage for modern fashion collection. After series of experiments on linen and cotton textile materials we find the best dyeing methods for logwood. Dye concentration, extraction and dyeing time are important to compare the colors obtained with this tree. The changes in hue and saturation were measured with the use of spectrophotometric methods. The paper shows results of this experiments.

The Laboratory of Natural Dyeing *"Natural Art"* uses natural organic dyestuffs to support production of new non-toxic, non carcinogenic textile products with natural antibacterial and antimicrobial properties. The dyes obtained from logwood comes from heartwood. Tree have an inspiring range of medicinal uses with potential antioxidant, anticancer and antifungal activities so textile products with logwood has also huge potential application of the compounds found in logwood tree in various fields of science economy.

Identifying fuchsine visually in dress and textile collections

Anita Quye[1], Eve-Anne Scholler[1*], Sabine Wieber[1]

[1]History of Art, University of Glasgow
8 University Gardens, Glasgow G12 8QH

[1*]e.scholler.1@research.gla.ac.uk

The discovery and subsequent industrialisation of aniline dyes in the second half of the nineteenth century revolutionised the European chemical industry and its approach to dyeing. Mauve was the first aniline dye to be available on the market, but fuchsine – or magenta as it was often called in Great Britain – was usually considered to be the most significant aniline dye. It was first patented by François-Emmanuel Verguin in Lyon in 1858 and soon produced by Renard Frères and several other manufacturers in France, Great Britain, Germany and Switzerland. [1] Fuchsine's chemical and economic impact has been extensively studied in both contemporary and recent sources. However, its cultural impact, always assumed to be important, has been little investigated. [2] This lack of research might be partially explained by the difficulty of recognising its presence in written, visual and material sources.

This research has sought to enable the cultural study of fuchsine by establishing a methodology to identify it. This particular methodology is constituted of three main stages, each focusing on a different type of source. The first stage uses contemporary dyeing manuals and dictionaries to clarify and explain the complex terminology of the dye. Fuchsine was given a great variety of names, such as aniline red, Magenta, rosaniline or Solferino which all have slightly different connotations and usages. Understanding the historical and geographical context of each of these names helps to detect and interpret fuchsine in written sources, including captions of textile samples. Textile samples from dyeing manuals are the focus of the second stage which explores the multiplicity of appearances which fuchsine can take on textile, depending on the fibre, concentration, purity and manufacturer. The most representative appearances of fuchsine on silk, wool and cotton, identified in the second stage, are used as references in the third stage in order to identify likely examples of fuchsine in dress and textile collections.

This multidisciplinary research demonstrates how scientific literature can be of great use to the study of colour and dyes in dress and textile histories. Using this methodology systematically and on a large scale would facilitate the detection and interpretation of fuchsine-dyed textiles in collections. Although the focus of this particular study has been put on one dye, this methodology has potential beyond the scope of fuchsine and could be applied to other synthetic dyes and, with some adaptation, to natural dyes as well.

REFERENCES

1. Travis, Anthony S. *The Rainbow Makers: The Origins of the Synthetic Dyestuffs Industry in Western Europe*. Bethlehem: Lehigh University Press ; London: Associated University Presses, 1993, 31 and 67.
2. Breward, Christopher. *The Culture of Fashion: A New History of Fashionable Dress*. Manchester: Manchester University Press, 1995, 161.

Alternative Bioprocess of Indigo Reduction Dyeing using Freeze-dried Bacteria Strains from Traditional Indigo Vat

Younsook Shin[1*], Kyunghee Son[1], Eun Sil Choi[2], Dong-Il Yoo[3]

[1]Dept. of Clothing and Textiles
[2]Dept. of Biological Science
[3]Dept. of Polymer and Textile System Engineering, Chonnam National University, Gwangju, South Korea

[1*]yshin@jnu.ac.kr

Indigo-blue is one of the oldest natural dyes for blue color and is traditionally produced from indican by innate enzyme in indigo plant. Today, indigo is one of most important vat dyes in textile industry used extensively for dyeing cotton yarn in the manufacture of denims and blue jeans. Indigo is insoluble and, therefore, for commercial dyeing, it is converted to the colorless and soluble leuco-form by chemical reduction using sodium dithionite, which generates environment-polluting, highly alkaline effluents, in addition to by-products containing sulfur [1]. It is a challenging task to develop cleaner processes for indigo dyeing due to the global trend of sustainability and the environmental concerns.

In the previous study, we identified the bacterial population or community resident in indigo vat traditionally used in Korea. 16S rRNA sequences-based meta-genomic approach paved a way for the understanding and interpreting the bacterial community related to natural indigo fermentation. These results used as a basis for developing the bioprocess of indigo reduction by mimicking fermentation method [2].Four bacterial strains were isolated based on this community analysis and their reducing activity was investigated. An eco-friendly bioprocess of indigo reduction using isolated bacteria with indigo reducing activity was developed by optimizing cultivation of bacteria and applying them for indigo reduction dyeing.

In this study, we prepared dried bacterial cultures by lyophilization for making better uses, storage and transport [3]. Dried bacterial cultures can be used directly for indigo fermentation dyeing. Survival rate of bacteria after lyophilization was estimated depending on storage time. Also, indigo reducing activity of the dried bacterial culture was compared to fresh bacterial culture through dyeing tests.

ACKNOWLEDGEMENTS
This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2014022302).

REFERENCES

1. M. Bozic, V. Kokol, Ecological alternatives to the reduction and oxidation processes in dyeing with vat and sulphur dyes, *Dyes and Pigments* 76 (2008) 299-309.
2. S. K. Nicholson, P. John, The mechanism of bacterial indigo reduction, *Appl Microbiol Biotechnol* 68 (2005) 117–123.
3. S. Koch, E. Eugster-Meier, G. Oberson, L. Meile, C. Lacroix, Effects of strains and growth conditions on autolytic activity and survival to freezing and lyophilization of bactobacillus delbrueckii ssp.lactis isolated from cheese, *International Dairy Journal* 18 (2008) 187–196.

Reproduction and Evaluation of Traditional Black Dyes of Korea

Younsook Shin[1*], Kyunghee Son[1], Jun Yan[1], Dong-Il Yoo[2]

[1]Dept. of Clothing and Textiles
[2]Dept. of Polymer and Textile System Engineering, Chonnam National University, Gwangju, South Korea

[1*]yshin@jnu.ac.kr

In textile Industry growing interest to develop sustainable and renewable natural colorants is a global trend to adapt for modern fashion. Black is the most frequently used color and one of the most important colors for trendy consumers today. According to oriental concept of Yin and Yang, black is symbolized as water, foundation of living things, and North [1]. Until 19th Centry from Goguryoe and Yi Dynasty in the Korean Peninsula, natural black dyes has been used for leather shoes, hat, belts and hair accessories as well as official outfits, ceremonial cloths for children, mourning cloths, clerical robes, papers, etc [2].

Traditionally, black color was obtained by using chestnut, oak, gallnut, persimmon, alder, pomegranate rinds, sumac, amur maple, charcoal from pine tree and azalea, Chinese ink, etc. Iron mordant was essential component for obtaining black color [3, 4]. In addition, combination dyeing with indigo/madder was also a way of obtaining black color.

In this study, we applied traditional processes to obtain natural black color. The characteristics of natural black color obtained were investigated by evaluating color quality and color fastness.

ACKNOWLEDGEMENTS
This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MOE) for the BK21 plus project in 2014 (No S13HR15D0801).

REFERENCES
1. D. Cardon, Natural Dyes: Source, Tradition, Technology and Science, Archetype Publication, 2007
2. J. N. Lee, Natural Dyeing, HyunAm-Sa, 2005
3. T. H. Choi, S. I. Yoo, S. H. Lee, H. W. Jeong, E. J. Y, Natural Dyeing of Hanji with Alnus japonica Fruit Extracts, Wood Engineering, 37 (2009), 415-416.
4. B. H. Son, J. H. Chang, Dyeing Properties of Silk Fabric with Alnus firma Fruit Extracts, *Korean J. of Home Economics*, 40 (2002), 109-118.
5. H. S. Cha, Y. S. Jung, D. G. Bae, Natural Dyeing with aqueous Extracts of Black bean seed coat, *Current Research on Agriculture and Life Science*, 30 (2012), 76-81.

Textile Dyeing with Aqueous Extracts from Cone of *Metasequoia*

Jun Yan[1], Dong-Il Yoo[2], Younsook Shin[1*]

[1]Dept. of Clothing and Textiles
[2]Dept. of Polymer and Textile System Engineering, Chonnam National University, Gwangju, South Korea

[1*]yshin@jnu.ac.kr

In recent years, the awareness of need for sustainable development is growing stronger due to the depletion of natural resources. An increasing number of research and development efforts have been focused on the conversion of waste, biomass and various residues into energy, fuels and other useful materials. The growing interest in the substitution of synthetic dyes by natural ones has stimulated to search new raw materials because textile dyeing industry is one of the most polluted the environment with wastewater [1].

Natural wastes are often parts of plants/vegetables not used in the production process or by-products, whose quantity is very large and so, disposal is a cost for the manufacturers. Forestry waste, such as saw dust, leaf, cone etc., has been interested in the recovery and reuse for converting to valuable materials and energy. In many cases these by-products may contain high value species with bioactive properties. And they can reuse in other fields such as pharmaceutical, food, cosmetic and textile [2-4]. We explored to utilize the cone *of Metasequoia glyptostroboides* as new raw resource of natural colorants. *Metasequoia glyptostroboides* is a fast growing tree genus in the conifer family *Cupressaceae*. *Metasequoia glyptostroboides* is propagated and distributed in many parts of the Asia and North America as well as in Europe. They are popular for roadside trees.

The purpose of this study was to investigate the dyeing properties of extracts from cone of *Metasequoia* for exploring as a new dye resource materials. Dyeing properties of *Metasequoia* cone extracts were studied by investigating the characteristics of colorant, effect of mordant on color change, and color fastness.

ACKNOWLEDGEMENTS

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MOE) for the BK21 plus project in 2014 (No S13HR15D0801).

REFERENCES

1. D. Cardon, Natural Dyes: Source, Tradition, Technology and Science, Archetype Publication, 2007.
2. J. A. Nzihou, Waste Biomass Valorization, 1, (2010), 3-4.
3. S. Rodrıguez Couto, E. Rosales, M. Gundın, M. A. Sanroman, Exploitation of a waste from the brewing industry for laccase production by two *Trametes* species, *Journal of Food Engineering* 64 (2004) 423–428.
4. W.Peschel, F. Sa´nchez-Rabaneda, W. Diekmann, A. Plescher, I. Gartzı´a, D. Jime´nez, R. Lamuela-Ravento´s, S. Buxaderas, C. Codina, An industrial approach in the search of natural antioxidants from vegetable and fruit wastes*, Food Chemistry* 97 (2006) 137–150.

A Versatile Tradition:
Textile dyeing for book conservation, using the Daubeny Library board slotting project as an exemplar

Victoria Stevens, ACR[1*]

[1]Oxford Conservation Consortium

[1*]victoria.stevens@magd.ox.ac.uk

Dyed textiles have been used extensively throughout the history of book binding for lining, protecting and covering. Their importance for book production reached its apotheosis through the development of dyed starch-filled buckram cloth for case bindings in the early decades of the nineteenth century. Through the study of various dye and filling systems for textiles in historic book manufacture combined with an investigation of techniques used in modern textile conservation, their use in present book conservation practice has been informed and advocated. More specifically, this process has identified custom-dyed textiles as a very suitable component in the recently developed method of board reattachment knows as board slotting.

Using the on-going treatment through board slotting of a severely damaged collection of early to mid nineteenth century hollow backed bindings in the Daubeny Library, Magdalen College, Oxford as an exemplar, this poster aims to highlight both the historic and current use of dyed textiles in book binding and conservation. It will explore the dye systems previously used in industrial book production and demonstrate how the tradition of dyed textile use has been modified for small-scale treatment methods and practice in current book conservation. Furthermore, it will detail the inter-disciplinary co-operation that informed the choice of dye system for the project as well as the refining of the dye method and cloth preparation through collaboration between book conservators. The importance of the dye system to the success of the binding and conservation process will be emphasised throughout.

Dyes and possible mordants in miscellaneous Finnish archaeological textiles

Krista Vajanto[1], Maarten van Bommel[2]

[1]Department of Philosophy, History, Culture and Art Studies, Archaeology, P.O. Box 59, 00014, University of Helsinki, Finland
[2]Cultural Heritage Agency of the Netherlands, P.O. Box 1600, 3800 BP, Amersfoort, the Netherlands

[1]krista@vajanto.net
[2]m.van.bommel@cultureelerfgoed.nl

Our presentation discusses Late Iron Age (ca 1000 AD) Early Modern (ca 1600 AD) archaeological dyed woollen textile fragments found in Finland from inhumation burials. The aim is to shed light on the dyestuffs and mordants.

The UHPLC and HPLC analyses were done in the Cultural Heritage Agency of the Netherlands. The analysis detected indigoid compounds, alizarin and purpurin and several unidentified red-orange components, presumably anthraquinones. Interestingly, same unknown red-orange dyestuffs were found both in the Iron Age and in the Early Modern material. The unidentified dyestuffs possibly refer to the use of an unknown local dye resource.

The SEM-EDX analyses were done in the Nano-Microscopy Center of Aalto University in Finland and performed with JEOL JSM 7500 F apparatus using carbon coated samples. The SEM-EDX analysis detected elements that are typical to wool itself (C, O and S) in all of the samples. Found metal elements (Fe, Cu) might refer to use of iron and copper as mordants. However, these and other metals elements (As, Ag) might be also contamination from burial offerings.

In addition, possible alum (Al, K) was found from some samples. Predominant in the Iron Age samples was a different element spectrum, which contained aluminium and silicon (Al, Si). According to reference samples this might indicate the use of clubmoss (*Lycopodium*) as mordant. Due to certain lighter elements (Na, Cl, Mg, K), the indigoid textiles were possibly dyed in urine vat and using wood ash lye. These same elements were found in the reference samples. However, there might be also other possibilities to explain these element findings, like contamination from the burial environment and mineralisation of the fibres.

Creation and analysis of synthetic alizarin and replicating Turkey red

Julie H. Wertz[1]*, Anita Quye[1], David France[2], Lesley Richmond[3]

[1]Centre for Textile Conservation and Technical Art History, History of Art,
University of Glasgow, G12 8QH
[2]School of Chemistry, University of Glasgow, G12 8QQ
[3]Scottish Business Archive, Archive Services, University of Glasgow, G11 6PE

[1]*j.wertz.1@research.gla.ac.uk

The synthesis of alizarin was a landmark event in the development of synthetic textile dyes as the first naturally occurring colourant to be replicated in the lab.[1] At the time alizarin was first commercially produced, 1869, there was a fair understanding of its structure and tinctorial properties.[2] Dyers and chemists soon learned, however, that other hydroxyanthraquinones were forming during the synthesis and the product was not pure alizarin. Compounds like anthrapurpurin and flavopurpurin, which are not present in madder-extracted dye, were forming.[3] While there is a solid body of work investigating the components of madder dyes, very little analysis has been done on synthetic alizarin or work on replicating historical production methods.[4] Commercial alizarin today is of high (97% and above) purity, but historically would have varied greatly.[5]

This project aims to synthesize alizarin following historical processes to obtain a product similar to one that would have been used to dye textiles of the era. The goal is to be able to identify which components are present in order to better understand the chemical composition of historical textiles. Initial analysis on the alizarin and madder extract will be carried out using Ultra Performance Liquid Chromatography with Photo Diode Array detection (UPLC-PDA), allowing for better results with minimal sample. This work will allow us to understand how best to preserve these artefacts, especially if they contain light-sensitive components as part of the alizarin makeup. It also has the potential to indicate whether a textile is dyed naturally or synthetically.

The focus for the study is the Turkey red textile dyeing process, which was a major industry in Scotland for around 150 years. In addition to synthesizing and investigating the chemistry of synthetic alizarin, the overall project aims to re-create and analyze samples of Turkey red. Successful replication of Turkey red oil has already been achieved, as well as insight into the chemistry of applying oil onto the fabric. Current work involves the synthesis of alizarin, which after analysis will be applied to the oiled textiles in order to produce samples for analysis prior to examining historical artefacts.

Our research is a cross-disciplinary endeavour between the Centre for Textile Conservation and Technical Art History and the School of Chemistry at the University of Glasgow, with cooperation from the University's Scottish Business Archive.

REFERENCES

1. Anthony S Travis, *The Rainbow Makers*, (Cranbury, NJ: Associated University Presses, Inc., 1993).
2. Alan T Dronsfield, Trevor Brown, and Christopher J Cooksey, "Synthetic Alizarin- the Dye That Changed History," ed. Jo Kirby, (presented at the Dyes in History and Archaeology 16, Lyons, 1997), 34–38.
3. Joseph Dépierre, *Traité de la teinture et de l'impression des matières colorantes artificielles. 2[me] partie, l'Alizarine artificielle et ses dérivés*, vol. 2, (Paris: Baudry et Cie, 1892).
4. Goverdina C H Derksen, "Red, Redder, Madder: Analysis and Isolation of Anthraquinones From Madder Roots (Rubia Tinctorum)," ed. Aede de Groot, Anthony Capelle, and Teris A van Beek, (Wageningen Universiteit, n.d.).
5. Edmund Knecht, Christopher Rawson, and Richard Loewenthal, *A Manual of Dyeing*, (London: Charles Giffin & Company, Limited, 1893).