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CONTENTS

SOCIAL PROGRAMME

Wednesday, 5 October

Welcoming reception

Gipsoteca of the Università di Pisa

Thursday, 6 October

Registration and main conference at the Auditorium of the

Polo Didattico delle Piagge

(Università di Pisa)

Via Giacomo Matteotti, 3, Pisa

Conference dinner

(*Prior registration required)*

Friday, 7 October

Main conference at the Auditorium of the Polo Piagge

(Università di Pisa)

Via Giacomo Matteotti, 3, Pisa

Saturday, 8 October

Visit to the Museo del Tessuto and Duomo di Prato (Prato, Italy)

(Departure from the conference venue - expected return, 18:00).

Prior registration required

MAIN CONFERENCE PROGRAMME

Auditorium of the Polo Piagge, Università di Pisa
Via Giacomo Matteotti, 3, Pisa, Italy

Thursday, 6 October

09:00	Registration and refreshments, placement of posters
09:30	Opening addresses
Session 1	Chair: Maria Perla Colombini
10:00-10:20	**Ingrid Houssaye-Michienzi**, Dominique Cardon, *Red dyes in the florentine dye company "Francesco di Giuliano Salviati e Comp., tintori d'arte maggiore", 1483-1498*
10:20-10:40	**David Kohout**, Helena Březinová, Josef Chudoba, Ivan Víden, *Textiles from medieval waste layers in New Town Prague– Identification of organic dyes*
10:40	Questions
10:50-11:20	*coffee break*
Session 2	Chair: Maarten van Bommel
11:20-11:40	**Matthijs de Keijzer**, Regina Hofmann - de Keijzer, *The early synthetic organic dyes: International patents*
11:40-12:00	**Art Ness Proaño Gaibor**, Johan Neevel, Birgit Reissland, Muriel Geldof, Frank Ligterink, *Use of a new sampling technique for identification of 19th century inks for drawing and writing*
12:00-12:20	**Anita Quye**, *Disguises, surprises and identity crises for 19th century early aniline dyes*
12:20-12:40	**Ilaria Degano**, Pietro Tognotti, Francesca Modugno, Diane Kunzelman, Maria Perla Colombini, *HPLC-DAD and HPLC-ESI-Q-ToF characterisation of early 20th century lakes and pigments from Lefranc archives*
12:40	Questions
12:50-14:00	*lunch break and posters*
Session 3	Chair: Jo Kirby
14:00-14:20	**Eva Eis**, *Fake lakes? The use of starch and other adsorbent substrates in paint manufacture*
14:20-14:40	**Francesca Sabatini**, Pietro Tognotti, Anna Lluveras-Tenorio, Ilaria Degano, *Aging and fading of eosin, a remarkable pigment in XIX-XX century painting*

14:40-15:00 **Maarten R. van Bommel**, Federica van Adrichem, Frank Ligterink, *Looking for the 'right' colour, virtual retouching of an early 20th century cabinet designed by Piet Kramer*
15:00 Questions

15:00-15:40 *coffee break and poster session*

Session 4 Chair: Dominique Cardon

15:40-16:00 Maurizio Aceto, **Elisa Calà**, Angelo Agostino, Gaia Fenoglio, Ambra Idone, Cheryl Porter, Charlotte Denoël, Monica Gulmini, *The Purple poor relatives: improvements in the identification of folium and orchil on manuscripts*
16:00-16:20 **Monika Ganeczko**, Bartłomiej Witkowski, Magdalena Biesaga, Monika Stachurska, Helena Hryszko, Agnieszka Laudy, Tomasz Gierczak, *Study of orcein decompostion by LC-ESI/MS/MS*
16:20-16:40 **Paula Nabais**, Maria João Melo, Maria Guimarães, Rita Araújo, Rita Castro, Conceição Oliveira, *Revisiting the purples of* Chrozophora Tinctoria
16:40-17:00 **Zvi C. Koren**, *Is it really real molluskan purple or just masquerading as such*
17:00 Questions

17:10 Announcements

19:30 Conference dinner

Friday, 7 October

09:00 Registration and refreshments, placement of posters

Session 5 Chair: Regina Hofmann-de Keijzer

09:20-09:40 **Annemette Bruselius Scharff**, *Dyestuff or natural pigmentation*
09:40-10:00 **Rosa Costantini**, Ina Vanden Berghe, Francesca Caterina Izzo, *Safflower red-dyed textiles: Degradation in illuminated and dark environments*
10:00-10:20 **Ewa Orlińska-Mianowska**, Monika Janisz, *Searching for historical names of the red colours in Polish language - based on the historical sources and dye analyses of the 16th and 17th century fabrics from the collection of the National Museum In Warsaw*
10:20-10:40 **Katarzyna Lech**, Damian Dąbrowski, Maciej Jarosz, *Colors of arrases: How LC-MS combines past and present times*
10:40 Questions

10:50-11:20 *coffee break*

Session 6 Chair: Irina Petroviciu

11:20-11:40 **Vanessa Habib**, *William Lauder Lindsay 1829-1880 – Three Scottish pattern books*

11:40-12:00 **Lore Troalen**, Rosie Upton, Claire Maugueret, Miriam Mcleod, Fergus McNab, Logan Mackay, Alison N. Hulme, *An enlightened approach towards the display of late 19th century fashion textiles: a UPLC-MS/MS and micro fade study of mauve and violet aniline dyes*

12:00-12:20 **Julie H. Wertz**, Anita Quye, David France, *Natural or synthetic? The Identification of anthraquinone dyes on historical Turkey red by UHPLC-PDA analysis*

12:20 Questions

12:30-14:00 *lunch break and posters*

Session 7 Chair: Anita Quye

14:00-14:20 **Ilaria Serafini**, Livia Lombardi, Camilla Montesano, Fabio Sciubba, Marcella Guiso, Roberta Curini, Armandodoriano Bianco, *Comparison of molecular pattern of American and Armenian cochineal dyed yarn, extracted through a new mild extraction technique*

14:20-14:40 **Jennifer Poulin**, *The application of GC-MS with TMTFTH extraction and derivatisation for the characterisation of natural dyes on museum objects*

14:40-15:00 **Irina Petroviciu**, Ileana Cretu, Florin Albu, Marian Virgolici, Andrei Medvedovici, *Identification of natural dyes in textiles and documents seal threads from the national museum of Romanian history*

15:00 Questions

15:00-15:40 *coffee break and poster session*

Session 8 Chair: Maria João Melo

15:40-16:00 **Recep Karadag**, *A natural dyeing method for obtaining Turkey red color*

16:00-16:20 **Karla Muñoz-Alcocer**, Laura Fuster-López, M. Luisa Vázquez De Ágredos-Pascual, Marcello Picollo, Giovanni Bartolozzi, Jose Luis Ruvalcaba-Sil, Miguel Ángel Maynez, Edgar Casanova-González, Isaac Rangel-Chávez, *Indigo and cochineal at 17th century Spanish colonial polychrome architecture in Chihuahua, Mexico: seeking the transmission of a millenarian technology*

16:20-16:40 **Laura Maccarelli**, Elizabeth Burr, Ioanna Kakoulli, Terry T. Schaeffer, And R. Ángeles Falcón, *Analysis of red yarns in textiles from the Huaca Malena archaeological site in Peru*

16:40 Questions

16:50 Closing remarks

LIST OF POSTER PRESENTATIONS

(in alphabetical order of the corresponding author)

[P1] **Kubra ALIYEVA**, Fariz KHALILLI, Sudabe MIKAYILOVA, *Application of natural dyes in dyeing of traditional carpet yarns*

[P2] **Susanna BRACCI**, Donata MAGRINI, Roberta IANNACCONE, *In search of color traces in ancient stone materials*

[P3] **Ottavio BRIGANDI'**, *The Dante's Perse Colour: A Study of Medieval Dyeing Applied to Italian Literature*

[P4] **Caterina CAPPUCCINI**, Adriana RIZZO, Federico CARÒ, Mechthild BAUMEISTER, Daniel HAUSDORF, *Multi-Analytical Identification Of Tannin-Based Stains On Wood*

[P5] **Rita ARAÚJO**, Maria João MELO, Paula NABAIS, Tatiana VITORINO, Maria Conceição OLIVEIRA, Conceição CASANOVA, Ana LEMOS, *Characterization Of Dyes Used In Bookbindings From Books Of Hours*

[P6] **Vincent DANIELS,** *Revealing the secrets of the madder dye and pigment vat*

[P7] **Lauren FORD**, Richard BLACKBURN, Chris RAYNER, *Complexities of lucidin chemistry in the extraction of textile artefacts dyed with dyer's madder (*Rubia tinctorum *L.)*

[P8] **Giulia GERMINARIO**, Inez Dorothé VAN DER WERF, Antonio MIRABILE, Luigia SABBATINI, *PY-GC-MS of some triarylcarbonium pigments: characterisation and identification in felt-tip pens*

[P9] **Mathieu HARSCH,** *The Italian Wood Trade in the Datini funds (Prato, Tuscany, at the end of the 14th century)*

[P10] **Patricia HOPEWELL**, Susanna HARRIS, *Accessible Or Exclusive? Blue Textiles In The Mediterranean 1000-500 BC*

[P11] **Sevim KARABULUT**, Türkan YURDUN, Gülbin ERDOĞAN, *Analysis of synthetic dyestuffs of two historical naval flags in the Istanbul naval museum with ion-pair chromatography*

[P12] **Damian DĄBROWSKI**, Jan GOZDALIK, **Katarzyna LECH**, Maciej JAROSZ, *Identification of resin based dyes using HPLC-UV-Vis ESI MS/MS*

[P13] **Livia LOMBARDI**, Ilaria SERAFINI, Claudia FASOLATO, Paolo POSTORINO, Camilla MONTESANO, Roberta CURINI, Fabio SCIUBBA, Marcella GUISO, Armandodoriano BIANCO, *Interpret SERS spectra of natural lake pigments: a SERS database of isolated compounds present in ammonia extracts obtained through HPTLC-SERS*

[P14] **Jeannette J. ŁUCEJKO**, Marianne VEDELER, Ilaria DEGANO, Maria Perla COLOMBINI, *Textiles From The Gokstad Viking Ship's Grave*

[P15] **D. Gizem ÖZKAN**, Halide SARIOĞLU, *Dye characterization of a Gürün wrap by using HPLC-DAD*

[P16] **D. Gizem ÖZKAN**, Türkan YURDUN, Halide SARIOĞLU, *Dye analysis of wool Gürün wrap (stylized as Persian wrap) yarns by HPLC-DAD*

[P17] **Adeola POPOOLA**, *Kinetics of dyeing and spectroscopic properties of dye from* Diallium Guinense *and* Pterocarpus Erinaceus *(African Rosewood)*

[P18] **Anita QUYE**, Jing HAN, Malcolm INNES, *The chemical effect of filtered visible light on light-sensitive dyes*

[P19] **Anita QUYE**, Dominique CARDON, Jennifer BALFOUR-PAUL, Lisa MOSS, *Assessing the Crutchley Archive of an early 18th century dye company in Southwark, London*

[P20] **Yoshiko SASAKI**, Ryohei FUKAE, Ken SASAKI, *Preliminary research about the application of the Fluorescence Lifetime Measurement for Cultural Properties*

[P21] Dong Il YOO, Kyunghi SON, **Younsook SHIN**, *Indigo dyeing of ramie fabric by bioreduction with saccharomyces cerevisiae*

[P22] **Ludo SNIJDERS**, **Art Ness PROAÑO GAIBOR**, *Ancient Mixtec colour technology: Experimental reconstructions of codex production*

[P23] **Georg STARK**, *"If Your Vat Turns To Death Refresh It With Mercury And Saffron… The Problem Was Always The Yellow!*

[P24] **Diego TAMBURINI**, Rebecca STACEY, Caroline CARTWRIGHT, St John SIMPSON, *A study of textiles from early nomadic cultures of Siberia*

[P25] **Emine TORGAN**, Recep KARADAG, *Multidirectional investigation of organic cotton fabrics dyed with Anatolian buckthorn and gallnut by historical recipes*

[P26] **Emine TORGAN**, Rezan ALKAN, Recep KARADAG, *Antifungal activity and HPLC analyses of silk fabrics dyed with madder and gallnut*

[P27] **Emine TORGAN**, Cemile TUNA, *Identification of the Ottoman tent textiles for sustainability of Cultural Heritage*

[P28] Claire MAUGUÉRET, **Lore TROALEN**, Stephen JACKSON, Alison N. HULME, *Dye sources used by May Morris in the embroideries from Melsetter House: a UPLC-PDA and MS study*

[P29] **Krista VAJANTO**, Sanna LIPKIN, Janne RUOKOLAINEN, *Blue textiles almost two millennia old from Northern Finland*

[P30] **M. Luisa VÁZQUEZ DE ÁGREDOS PASCUAL**, **M. Julia MARTINEZ GARCÍA**, *The ancient raw materials dyes reinterpreted at pharmacopeias of the Modern Europe*

[P31] **M. Julia MARTINEZ GARCÍA**, **M. Luisa VÁZQUEZ DE ÁGREDOS PASCUAL**, *Dyes "crocuses" of the Old and New world*

[P32] **Youngmi YEO**, Younsook SHIN, *The Dyeing Properties and Functionality of Nymphaea tetragona Leaves Extract*

[P33] Chanhee JUNG, **Younsook SHIN**, **Dong Il YOO**, *Application of Mixed Natural Colorants onto Hair dyeing: Basic Approach*

[P34] Chanhee JUNG, **Younsook SHIN**, **Dong Il YOO**, *Application of Mixed Natural Colorants onto Hair dyeing: Coloration System*

ABSTRACTS OF ORAL PRESENTATIONS

Listed in programme order

RED DYES IN THE FLORENTINE DYE COMPANY "FRANCESCO DI GIULIANO SALVIATI E COMP., TINTORI D'ARTE MAGGIORE", 1483-1498

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This presentation is the continuation of our common presentations at DHA33 and DHA 34. It is also based on our study of three registers, among the thousands preserved in the Salviati Archive, at the *Scuola Normale Superiore* in Pisa, Italy. These registers are the only three preserved account books of the company "*Francesco di Giuliano Salviati e Comp., tintori d'Arte Maggiore in Firenze*", a dye company settled in Florence. Francesco's father, Giuliano di Francesco Salviati, was involved, with two of his uncles (Iacopo di Giovanni and Alamanno di Averardo), in the production of broadcloth of high and medium qualities. Iacopo di Giovanni, his uncle, was also involved in the production of silk textiles. Francesco di Giuliano, through his dye company, was thus completing the activities of an important family business that operated in textile production.

The two first books record all commercial dealings, organized by products and providers (buying dyes and mordants, paying furnishers, dyers, local custom duties, etc.)

- Reg. 394 is their *Libro azzuro, seg. A*, corresponding to the years 1483 to 1486
- Reg. 395 is their *Libro giallo, seg. B*, corresponding to the years 1486 to 1491

The third one, Reg. 396, is a *Giornale*, recording all dailies activities from 1490 to 1498

Among the treasures of information the three books provide, we first chose to study the sourcing and use of two yellow dyes of historical importance, sawwort and weld, by this company (our presentation at DHA 34 in Thessaloniki).

We now report on the sourcing and use of red dyes: madders, kermes, *chermisi* scale insects and related adjuvants (polypore fungi), brazilwood.

This new research has again brought unique information:

- on the relative importance of red plant versus insect dyes in dyeing of broadcloth and silk textiles, respectively, within the Salviati sphere;
- on the areas and countries from which these red dyes were sourced;
- on their prices;
- on the quantities used.

Keywords:
Mediaeval red dyes; international trade; early industrial crops; colour names.

TEXTILES FROM MEDIEVAL WASTE LAYERS IN NEW TOWN PRAGUE– IDENTIFICATION OF ORGANIC DYES

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More than 1,500 archaeological textile fragments in an assemblage from waste layers in Prague's New Town dating to the 14th and 15th centuries were compared on the basis of textile parameters and contemporary colours. Wool fragments were divided into eight categories of colours – crimson, reddish-brown, dark red, brown, light brown, dark brown, grey and black. Silk fragments were only preserved in four colours – red, yellow, light brown and brown. The finest plain-weave cloth was preserved in shades of crimspon. A total of 173 samples (34 silk, 139 wool) were chosen from LC-HRMS analyses of original colour. Crimson worm, madder, brazilwood, woad, dyer's rocket/saw-wort/dyer's broom and tannins were interpreted as the natural dye sources. A single natural source was interpreted 65 times, a combination of two sources 60 times, a combination of three sources 19 times and four natural sources twice. The most common combinations of two sources was madder and woad (19 times), madder and dyer's rocket (12 times), crimson worm and madder (8 times) and tannins (6 times). Combinations of three sources involved madder, woad and tannins (7 times) and madder, woad and dyer's rocket (3 times). Combinations of four sources were comprised of crimson worm, madder, tannins and dyer's rocket (once) and crimson worm, madder, tannins and woad (once).

Keywords: medieval, textiles, colors, dyes, LC-MS

References:

[1] H. Březinová, D. Kohout(eds.) Medieval Textiles and Dyers Technology. Assemblage of Textile Fragments from Waste Layers of New Town Prague. 2016. In press

[2] D. Kohout, H. Březinová, An Assemblage of Medieval Archaeological Textiles from Prague: a Study of Current and Original Colours. In: K. *Grömer, F. Pritchard (eds.)*: Aspects of the Design, Production and Use of Textiles and Clothing from the Bronze Age to the Early Modern Era. NESAT XII. The North European Symposium of Archaeological Textiles, 21st – 24th May 2014 in Hallstatt, Austria. Archaeolingua Main Series 33. Budapest, 229-238.

THE EARLY SYNTHETIC ORGANIC DYES: INTERNATIONAL PATENTS

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Introduction

The presentation will discuss a topic which is related to our project 'the early synthetic dyes' and increasingly influenced the synthetic dye industry between 1857 and 1913, namely international patents. The lecture deals with the patent history and the share of dye patents in the dye producing countries; followed by patent affairs, such as patent struggles, patent suits, patent strategies and patent agreements on famous synthetic dyes. The last part shows the development of the synthetic dye Methylene Blue on the basis of patents.

Definition of a patent

A modern patent provides the right to exclude others from making, using, selling, offering for sale, or importing the patented invention for the term of patent, usually 20 years. A patent is, in effect, a limited property right that the government offers to inventors in exchange for their agreement to share the details of their inventions with the public.

Patent history

In Antiquity there is evidence that some form of patent rights was known. In medieval Europe monarchs granted special rights to the people with privileges, such as monopolies over trade. The oldest Patent Law in the world was born in the medieval Venetian Republic started with the Venetian Statute of 1474.
By the end of the 18th century three important countries of the world, England, France and the U.S., had created and enacted Patent Laws. In England the text of the Patent Law, known as 'Monopoly Act' (Statute of Monopolies), was created and the law was enacted in 1624. In the same year a royal grant was made to William Shipman for the cultivation and preparation of madder by: 'sowing, setting, or planting of a herbage called madder' and of using 'the misterie, arte and science of breaking, dyeing, dressing and preparing the same for dyeing' (Shipman's Patent, patent number 28 from 1624).
In the United States the first Patent Law was adopted in 1790 titled 'An Act to promote the process of useful Arts'. The first patent was granted to the American inventor Samuel Hopkins (1743-1818) for an improved method of producing potash (potassium carbonate).
The modern French patent system was created during the Revolution in 1791. Patents were granted without examination since the inventor's right was considered as a natural one. The patent law was revised in 1844.
After the unification of Germany in 1871 the creation of a comprehensive Patent Law was enacted in 1877, which was based on the principle of mandatory examination.
In Switzerland the first national patent law was enacted in 1888 by protecting only inventions that could be represented by mechanical models. Twenty years later the

German government threatened Switzerland with retaliatory measures, especially by the imposition of custom duties on the import of certain chemical products, such as aniline and synthetic dyes from Switzerland, if the patent law was not modified to include the protection of production processes by the end of 1907.

Patent affairs: patent struggles, patent strategies, patent suits and patent agreements
From the first day on patent struggles of synthetic dyes between dye factories were an issue. It seems that nearly every synthetic dye has its own patent story. In early days mauve and fuchsine were subject of many patent struggles, which reached the courts. The synthetics Hofmann's violet and aniline blue are examples for patent strategies. A patent alliance between Perkin & Sons and BASF gave Perkin in Britain a monopoly and prevented other British dye firms from entering the synthetic alizarin market. A combination of patent struggles, patent suits and a patent agreement between the German dye firms AGFA and Bayer is the Congo red case. In the beginning of the 20^{th} century the sulphur dyes were subject of patent struggles.

Methylene Blue and a series of patent suits
Especially the development of the synthetic dye Methylene Blue (Basic Blue 9, 52015), one of the 65 synthetic dyes in our project, can be studied by patents and patent suits. Discovered by the BASF research-director Heinrich Caro (1834-1910) in 1876 the structure of the blue dye was unknown. The German chemist August Bernthsen (1855-1931) solved the chemical constitution of Methylene Blue in 1884. Between its discovery and establishing the chemical constitution several German dye factories, such as AGFA, Ewer & Pick, K. Oehler and Hoechst, found new pathways, which threatened BASF's Methylene Blue.

USE OF A NEW SAMPLING TECHNIQUE FOR IDENTIFICATION OF 19TH CENTURY INKS FOR DRAWING AND WRITING

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The characterization of the organic constituents of inks present on drawings and writings is of crucial importance to reconstruct and predict their changing appearance over time and to understand their material biographies in general. Although various non-destructive spectroscopic techniques are available, in order to use more advanced chromatographic techniques and sampling method is required. Until very recently however, sampling ink from valuable artworks on paper could not be done, due to the damage that would be inflicted by available sampling methods.[1][2] This simple lack of a suitable sampling technique has obstructed the scientific investigation of inks on paper artworks.

In 2015 a new micro-sampling method was developed at the Cultural Heritage Agency of the Netherlands.[3] With an inert *magnesium oxide micro sampling* (MOMS) rod only a few particles are scraped off the ink surface. As this sample is very small, it can be taken anywhere without any visible damage. The sample can be analysed with different techniques, including Scanning electron microscopy with Energy-dispersive X-ray spectroscopy (SEM-EDX) and Ultra-high performance liquid chromatography with Photodiode array detector attached to Electrospray ionization mass spectrometer (UHPLC/PDA/ESI-MS). Also, Surface Enhanced Raman Spectrometry can be applied.

With this method it now is possible to analyse both the inorganic and the organic components of the ink sample. MOMS was applied with great success to investigate inks on drawings and letters by Van Gogh in the REVIGO research project. The analytical results make clear that Van Gogh often used a variety of commercially available inks such as brightly coloured aniline inks, like methyl-violet and fuchsine, chrome-logwood inks and mixtures of both inks. We begin to see that essentially all his currently faded and brown ink drawings originally were brightly coloured or deep blue/black.

Keywords: Ink analysis, Drawings, Paper, Sampling techniques

References:

[1] J.G. Neevel: "The Identification of Van Gogh's Inks for Drawing and Writing", Marije Vellekoop, Muriel Geldof, Ella Hendriks, Leo Janssen & Alberto de Tagle (Eds), Van Gogh's Studio Practice, Van Gogh Museum, Amsterdam, Mercatorfonds, (2013) Brussels, pp.420-433

[2] Daria Confortin et all.: Crystal violet: Study of the photo-fading of an early synthetic dye in aqueous solution and on paper with HPLC-PDA, LC-MS and FORS, J. Phys.: Conf. Ser. 231- 012011 (2010), Padova

[3] A. N. Proaño Gaibor, Birgit Reissland, J Neevel: A novel in-situ sampling technique / Identification of inks and other media (Preprint), International Assosiation of Book and Paper Conservators XIIIth Congress, (2015), Berlin

DISGUISES, SURPRISES AND IDENTITY CRISES FOR 19TH CENTURY EARLY ANILINE DYES

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Distilled histories of landmark synthetic dyes by name, discovery date and simplified chemistry imply that historical synthetic dyes can be neatly characterized and distinguished. Such misunderstanding leads to over-optimistic research expectations for textile conservation and dress history which often cannot answer the questions asked[1].
By turning to 19th century technical books written by industrial dyers and dye chemists about the manufacture, names and use of synthetic dyes, a more realistic story emerges. But it is a complex one. Most troublesome were the early anilines dyes which sparked the synthetic revolution in the mid-1800s. Today these are of most interest for historical collection preservation, significance and interpretation. Hence they deserve to be better understood.
This paper draws upon evidence gathered in the Dye-Versity project[2] from technical dye books published in Britain between 1862 and 1908 by eminent and respected chemists and dyers, including Green[3] and Crace-Calvert[4]. Chemical characteristics, names and manufacturing relationships for commercial aniline red, violet and blue dyes, including magenta, are compared and connected. Their history reveals chemical disguises and confusing identities even for those who knew them firsthand.
After the commercial success of Perkin's purple in 1857, many new aniline dyes went to market over the next 20 years, with a slow but steady trickle continuing into the late 1890's. Subtle synthetic variations and recycling of aniline dyes in the competitive 1860's race for discovery coupled with their use in the 1870s and 1880s as starting materials for new dyes give anilines an overlapping chemistry and long chronology. And despite patents, manufacturers could choose their own trade name for essentially the same dye.
Whilst challenging to untangle, such primary evidence from historical technical sources contributes an important perspective to advance research for early synthetic dyes.

Keywords: commercial manufacture, trade names, dyeing

References:

[1] A. Quye. The power of two: uniting chemical and historical research of 19th c. early synthetic dyes for conservation. Paper presented at the Icon 2016 2nd triennial conference of the Institute of Conservation, Birmingham, 16-17 June 2016.
[2] A Quye. Dye-Versity: chemical variability of aniline dyed textile samples in 19th c. dye books. Funded by a Research Initiative Grant from the Carnegie Trust for the Universities of Scotland.
[3] A.G. Green. A systemmatic survey of the organic colouring matters. London: Macmillan and Co. 1908
[4] F. Crace -Calvert. Dyeing and calico printing: including an account of the most recent improvements in the manufacture and use of aniline colours. Edited by John Stenhouse and Charles Edward Groves. Manchester: Palmer and Howe. 1876

HPLC-DAD AND HPLC-ESI-Q-TOF CHARACTERISATION OF EARLY 20TH CENTURY LAKES AND PIGMENTS FROM LEFRANC ARCHIVES

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The characterisation of atelier materials and of the historical commercial formulation of paint materials has recently gained new interest in the field of conservation science applied to modern and contemporary art. Assessing the composition of the original materials purchased by artists can guide not only their identification in actual works of art, but also their restoration and preventive conservation.

In studying the transition period corresponding to industrial revolution, when many such variants or combinations were hypothetically possible in paint formulation [1], 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.

In this frame, more than thirty historical red lakes and colorants (dating from 1890 to 1921), provided by the Lefranc&Bourgeois Archive in Le Mans (France), have been investigated through a combined analytical approach based on chromatographic and mass spectrometric techniques. The focus of the research was to develop and apply a methodological approach based on the application of the techniques of election for the identification of such complex and interesting organic materials, namely: High Performance Liquid Chromatography using DAD or ESI-Q-ToF detectors. HPLC-DAD and HPLC-ESI-Q-ToF analyses allowed us to identify minor components in lakes and dyes composition, to discriminate between different recipes for the extraction of colours from the raw materials, and ultimately to distinguish among natural and synthetic formulations [2].

Keywords: early synthetic dyes; synthetic alizarin; HPLC-DAD; HPLC-ESI-Q-ToF

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FAKE LAKES?
THE USE OF STARCH AND OTHER ADSORBENT SUBSTRATES IN PAINT MANUFACTURE

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In 1895 an anonymus author complains about "*faked colours*" in Dingler´s Polytechnic Journal.[1] He refers to an analysis carried out by the Research Laboratory for Painting Techniques in Munich[2], which had shown that several pigments, especially materials used in decorative painting had been "*faked*" in "*an irresponsible manner*". Colours which were called "*Wall green*", "*Lime green*" or "*Fashion blue*" had turned out to be clay or heavy spar, dyed with aniline dyes instead of lightfast mineral pigments.

But producing such colours was actually common practice in pigment manufacture. Recipes for pigments made by dyeing starch, kaolin or green earth with synthetic dyes frequently appear in 19th century sources. But if no mordant was used for the precipitation of a dye, can those „lake pigments" really be considered lakes?

A recipe collection, which was compiled by a paint manufacturer between 1888 and 1894 contains several recipes for such colours. „*Wall green*" could be produced by dyeing green earth with various types of Malachite green, and "*Brilliant Red*" was made by mixing potato starch with Fuchsine.[3] Apart from that, other green, blue, violet and red dyes are mentioned in late 19th century recipes. For better understanding of properties, reproduction of some of these colours has been carried out.

Manufacture of these "lakes" was simple and they provided cheap substitutes with bright colours. The production of „adsorption lakes" is even described in paint manufacturing literature. Although their stability did not remain undiscussed, "fake lakes" were produced at least until the first half of the 20th century.

Keywords: fake lakes, lake pigments, adsorption lakes, historic recipes, 19^{th} century paint manufacture

References:

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[2] Versuchsanstalt der deutschen Gesellschaft zur Beförderung rationeller Malverfahren
[3] The mentioned recipes for „*Wandgrün*" and „*Brillantroth*" are part of the recipe collection of the "*Farbenfabrik Heinrich Wiesel*", which is the focus of my research.

AGING AND FADING OF EOSIN, A REMARKABLE PIGMENT IN XIX-XX CENTURY PAINTING

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Eosin, also called Pigment Red 90 or Acid Red 87, is a synthetic organic pigment dated to 1871 and commercialized as Geranium lake. It has been one of the most brilliant hues in the palette of the Impressionist painter Vincent Van Gogh. Unfortunately, the eosin lakes have shown a high photosensitivity that have caused the evident fading of the intense pink colorations of the canvas into lighter ones.

In the present work a multi analytical approach based on micro-destructive techniques, such as HPLC-DAD-MS-Fluorescence, was developed in order to characterize eosin and its degradation products. An ultra-sensitive HPLC-Fluorescence method, able to detect eosin at 0.1 ppb concentration levels, was optimized. This method succeeded in revealing degradation compounds of eosin not detectable with DAD. Some paint model systems were prepared using eosin lake, different kinds of white pigments (white lead, zinc oxide and titanium dioxide) and linseed oil as binders or isopropanol as solvent. The mock-ups were artificially aged selecting different UV-Vis irradiation ranges and irradiation times. Thus, the most influent parameters on eosin aging process have been evaluated and differentiated intermediates and final degradation products have been found. Two possible degradation pathways have been hypothesized on the basis of the products detected.

In addition, the data collected by thermo-analytical techniques and FT-IR together with those obtained with a non-destructive approach (analyses performed by Università di Perugia) provided us complementary information to confirm and better understand the degradation mechanisms occurring in this challenging case study. In the end, the ultra-sensitive multi analytical approach developed could be considered a promising starting point to optimize methods for characterising different groups of synthetic organic pigments in heterogeneous painting matrices.

Keywords: Eosin, HPLC-DAD-MS-Fluorescence, Degradation pathway

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LOOKING FOR THE 'RIGHT' COLOUR, VIRTUAL RETOUCHING OF AN EARLY 20TH CENTURY CABINET DESIGNED BY PIET KRAMER

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Synthetic dyes are known for their poor light fastness. In addition to the application of these dyes for textiles, similar colourants were often use to stain furniture in such way that the pattern of the wood remains visible. However, some synthetic dyes applied on furniture fade very fast, sometimes even within months after application as will be shown during this presentation.

During the 31st DHA meeting, held in Antwerp, research devoted to make reconstructions based on historical recipes was presented [1].This part of the research aimed to determine the most significant parameters in staining recipes which affects the overall colour. Based on the reconstruction, it became clear that sometimes (often?) vivid colours were obtained; colours which are now gone. To continue the research, ageing experiments were carried out which will be presented during this presentation. However, all the knowledge obtained is difficult to transfer to the professional and general public. To overcome this issue, a virtual retouching experiment was carried out in which a cabinet of Piet Kramer was illuminated with coloured light. The 'right' colour was determined based on a careful study of the object, reconstructions, colour measurements and the use of widely available software to map the cabinet in such way that the faded parts were retouched using coloured light. During this presentation, the process will be explained and some results will be shown.

Keywords: Synthetic dyes, furniture, reconstruction research, virtual retouching

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THE *PURPLE POOR RELATIVES*: IMPROVEMENTS IN THE IDENTIFICATION OF FOLIUM AND ORCHIL ON MANUSCRIPTS

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The use of *folium* and *orchil* on painting artworks and on textiles is cited in several treatises since Roman age [1] which suggested their employment as substitutes of the far more expensive *Tyrian purple* dye. Despite this, their identification on artworks has been rarely reported, possibly as a consequence of lack of diagnostic information that only recently has been improved [2] with particular concern to non-invasive analysis. In the view of the scarcity of scientific knowledge, it is mandatory that a characterisation study on these dyes must begin with accurate historical reconstructions, starting from reliable raw matters. In this study, following the preparation of folium from fruits of *Chrozophora tinctoria* (L.) A. Juss. plant and of orchil from different lichen species, we recorded standard spectra with UV-visible diffuse reflectance spectrophotometry with optic fibers (FORS) and spectrofluorimetry and used them as references for the identification of the two purple dyes on illuminated manuscripts. A survey on books held at different libraries in Italy and France allowed us to identify their presence in several instances and to define a time range and typical ways of employment. In particular, folium seemed to be mainly suitable for filigrees, while orchil appeared to be more versatile, being used for painting miniatures, filigrees and for colouring parchment. The use of the *poor relatives* of the Tyrian purple dye resulted to be wider than expected: folium is documented from 9th to 15th century, while for lichen dyes the range is larger, being from 6th to 16th century. These limits were presently set on the base of the already performed chemical analyses. New identifications on further manuscripts will contribute to shape the picture.

Keywords: folium, orchil, non-invasive, illuminated manuscripts, FORS

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STUDY OF ORCEIN DECOMPOSTION BY LC-ESI/MS/MS

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In this work, high performance liquid chromatography coupled to the electrospray tandem mass spectrometry (LC-ESI/MS/MS) was used for the identification of natural dyes in standard solutions and historical textiles samples. As the part of the detailed analysis of 192 medieval liturgical vestments currently stored in the National Museum in Gdańsk and textiles from the royal chambers from Museum of King Jan III's Palace at Wilanów, Poland, the identification of selected natural dyes present in these samples was carried out.
The obtained data shown a presence of orchil in the analyzed historical textiles; a lesser purple dye prepared for a different species of lichens e.g. *Roccella/Ochrolechia/ Varialaria* [1-2]. In the currently available literature, there is very little data regarding orchil analysis with HPLC/MS. Therefore in this work, analysis of the main orchil colorants was carried out, in addition to the degradation mechanism of the orcein derivatives found in orchil.
Degradation of hydroxyl and amine orcein derivatives were studied in the aging chamber. The aging chamber constructed in the laboratory allows for exposing the sample to UV-Vis irradiation at different wavelength and intensities for various periods of time. Obtained results allowed for proposing the decomposition mechanism for the compounds under study. For example compound with molecular mass of 376 Da, a likely orchil decomposition product, was detected in the aged sample.

Keywords: LC-MS/MS, natural dyes, orchil

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REVISITING THE PURPLES OF *CHROZOPHORA TINCTORIA*

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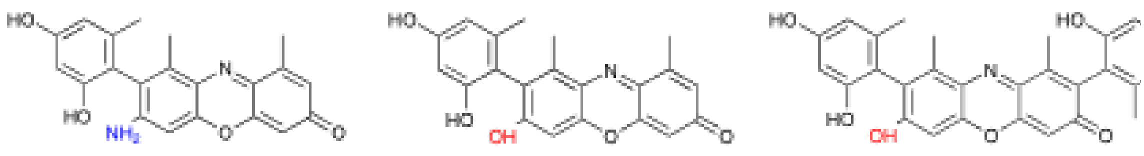
Purple dyes obtained from liquen species such as *Roccella, Lecanora,* and *Varialaria* and the seeds from the flower *Chrozophora tinctoria* were possibly used since Antiquity to dye textiles. Purple was an important colour in Antiquity as well as in the Middle Ages, and "true" purple was obtained from Mediterranean shellfish of the genera *Purpura*. The high status of the wearer of purple-dyed textiles in the past was never to be surpassed by any other colour, natural or synthetic. Purples obtained from the above mentioned plants carried symbolic meanings, and we know that in the Early Middle Ages and from the 14th c. on, orcein purples were used in the illuminations of precious manuscripts [1]. Franco Brunello in "*L'arte della tintura*" argued that this dye was used in Antiquity and Early Middle Ages, but during the High Middle Ages, in Europe, fell into oblivion, only to be later rediscovered.

In the 1960s, Musso and coworkers [2] disclosed the fundamental molecular structures for purples extracted from liquens: orcein purples depicted in Figure 1. The same cannot be said about the colours extracted from *Chrozophora tinctoria*, for which, despite the pioneering contribution of Krekel [3] that was followed up by the research carried out by Aceto *et al.* [4], it has not been possible to propose a structure.

Since it is a Portuguese indigenous plant and the studies by Krekel were made using plants harvested locally, we propose to revisit these colours. In this work the main chromophores present in *Chrozophora tinctoria* will be disclosed based on HPLC-DAD-HRMS analysis. We will further discuss if it is possible to distinguish between orcein and *Chrozophora tinctoria* purples based on fiber optics reflectance spectroscopy and microspectrofluorimetry.



α-aminoorcein **α-hydroxyorcein** **β-hydroxyorcein**

Figure Molecular structures for the main orcein chromophores

Keywords: illuminations, orcein, liquens, C*hrozophora tinctoria*, purple dyes.

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IS IT REALLY REAL MOLLUSKAN PURPLE OR JUST MASQUERADING AS SUCH

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For the past 25 years of performing analyses on historic and archaeological colorants, I have been privileged to identify *bona fide* molluskan purple as a textile dye and as a paint pigment on a rare number of important cultural heritage objects [1–4]. These items include textiles and a marble jar – some of them of a royal affiliation – and span a millennium of purple-production, dating from about 500 BCE to 500 CE from ancient sites in Persia, the Judean Desert in Israel, Egypt, and beyond. In addition, I was able to successfully identify the malacological provenance of the authentic purple colorant by means of a multi-component HPLC analysis of the pigment, which can contain as many as about 10 colorants and not just the 6,6'-dibromoindigo dye, the common denominator of all purple pigments. Thus, the identification of the molluskan species used for the purple-dye production, especially the use of the *Hexaplex trunculus* mollusk, is based on the presence or absence of a significant quantity of the 6-monobromoindigo chromatic marker [4].
Based on the above methodology, in a few analyzed Roman Period textile dyeings and the paint on a stele, the detection of a possible molluskan purple source would be perplexing as there appears to be no logical reason for these textiles to have been dyed with real purple. Or is there a hidden factor here? These mystifying examples – for which I will describe them as "Anomalous Purples" – will be compared with other "purple"-dyed textiles ranging from blue to violet (bluish-purple) to reddish-purple. Additionally, these Anomalous Purples may have undergone several successive or simultaneous dyeings with one or more different dyestuffs, a process not previously seen in such textiles. The *raison d'être* of these dyeings, the inevitable questions surrounding them, and their significance will be discussed in my talk.

Keywords: HPLC, molluskan purple, dibromoindigo, monobromoindigo, *Hexaplex trunculus*

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DYESTUFF OR NATURAL PIGMENTATION

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Many of the woven Iron Age textiles that were found in the inhumation graves from a Danish burial site in Western Jutland (Lønne Hede) were either striped, checkered or with different colored warp and weft. They have therefore undoubtedly been made of colored wool. Furthermore several textiles contain white wool yarns, which show that the surrounding soil didn't seem to have any coloring substances that could be absorbed by the wool. The textiles were found in a partly waterlogged sandy soil, which apparently preserved the colors better, compared to textiles from waterlogged bogs, which normally mostly are brown.

Dyestuff analysis of the colored wool by HPLC- DAD shoved mainly no evidence for dyeing. Occasionally it was possible to detect a blue or a yellow dye source, but never any red, even though many samples were either red, maroon or orange. The question was therefore if the wool color could be attributed to natural pigmentation.

Natural pigmentation occurs in the fibers as pigment granules, either rice- grain like eumelanin (max size 0.5x1.2µm) or spherical phaeomelanin (0.2- 0.4 µm). Normally they can be recognized as dark opaque spots by transmitted light microscopy (TLM) of whole mounts or in cross sections of fibers, but according to Ryder (1990) [1] and my own observations, it can sometimes be difficult to verify a content of natural pigmentation, when you are dealing with degraded archaeological fibers. Ryder mentions that breakdown of pigment granules can give a diffuse color effect similar to dyed fibers.

Many of the fibers from the Lønne Hede textiles are clearly colored, transparent fibers. These colors could perhaps origin from disintegrated pigment granules since the identification of dyestuffs seldom has occurred. To test this hypothesis, red and maroon samples were analyzed by TLM and transmission electron microscopy (TEM). Furthermore, acid extracts of the samples were analyzed by UV/Vis spectroscopy and compared to extracts of new and degraded (in waterlogged peat) white and brown wool.

The result show that TEM is the only method that gives exact information on the status of the pigment granules, whether they are intact, partly or totally disintegrated. The work is in progress and the results will be presented at the meeting.

Keywords: Archaeological wool, dyestuff, natural pigmentation, disintegration, TEM

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SAFFLOWER RED-DYED TEXTILES: DEGRADATION IN ILLUMINATED AND DARK ENVIRONMENTS

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In this work we present a multi-analytical study on safflower red dyestuff and its degradation processes.
The research was based on the identification, through HPLC-PDA analysis, of safflower red within several historical European silks (dated from the 17th to the 19th century), stored by the Victoria and Albert Museum of London and showing fading of pinkish colours.
To evaluate the stability of safflower red, specific ageing tests were carried out on new silk samples, prepared according to traditional dyeing procedures. For the artificial ageing, the effects of light, temperature, humidity and ozone were investigated through HPLC-PDA analysis, Vis-reflectance spectrophotometric measurements and colorimetric examinations.
It is well known that carthamin, the main red dye contained in safflower petals, is highly unstable to light exposure [1]; therefore, in order to study the actual influence of the other parameters, the treatments were carried out in a dark environment.
The results showed and confirmed that safflower red degrades in a fast and continuous way when exposed to light but interestingly, considering the recalculated chromatographic peaks areas, it was observed a significant decrease of carthamin also for the samples aged in dark environments (cold and humid; hot and dry; RH 60%; RH 90%; ozone-rich). However, detectable chromatic variations ($\Delta E > 50$) were proven to only occur at RH 90% in the dark: in this condition, the textiles visibly yellowed and a yellow compound (not revealed in the undyed aged silk and before the treatment) was detected and appeared to increase during the time lapse of ageing (100 days). These findings can be useful for the preventive conservation of fabrics dyed with Carthamus tinctorius L. which are displayed or stored by museums.
Furthermore, the dye baths employed were analysed by HPLC-PDA, leading to interesting new observations on safflower markers.

Keywords: safflower; carthamin; HPLC-PDA; artificial ageing; preventive conservation

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SEARCHING FOR HISTORICAL NAMES OF THE RED COLOURS IN POLISH LANGUAGE - BASED ON THE HISTORICAL SOURCES AND DYE ANALYSES OF THE 16TH AND 17TH CENTURY FABRICS FROM THE COLLECTION OF THE NATIONAL MUSEUM IN WARSAW

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Popularity of the red colour in Poland is connected both with the tradition of acquiring it from the Polish cochineal, as well as cultural connotations of this colour. The linguistic richness of names of red shades applied in descriptions of fabric colours in Poland is also the subject of research of linguists. Linguistic research, as well as historical documents and ethnographic research are the sources of knowledge about the formerly used dyes. Interesting signs of use the red dyes are preserved in Polish and other Slavonic languages[1]. Since the Renaissance the dictionary of red colours names in Poland has been regularly enriched thanks to long and intense trade relations with Italy and the presence of Italian merchants. In the 17th century along with the development of dyeing technology and changes of fashion there appeared many names of red shades of Italian origin[2]. Italian merchants resident in Polish cities brought not only commercial names of silk fabrics as well as names of their colours. This fact is well documented by account books containing lists of fabrics imported from Italy and posthumous inventories of movable property specifying cloths and valuable textiles. Many Italian names of colours have been preserved to this day in the Polish language. For textile and fashion historians it is extremely important to search preserved in museum collections examples of fabrics corresponding to the historical names of colors[3]. In 1970s Maria Taszycka made an attempt to compare the 17th century Italian silk fabrics with their historical names specified in account books of Italian merchants resident in Kraków[4]. Following this path, we will try to compare the 16th and 17th century fabrics from the collection of The National Museum in Warsaw with the historical names of reds and analysis of dyes.

Keywords: Historical textiles, Insect dyes, Colour names, Reds

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COLORS OF ARRASES: HOW LC-MS COMBINES PAST AND PRESENT TIMES

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Arrases belonging to the collection of the Wawel Royal Castle are unique works of art and they create the largest preserved collection of tapestries in Poland. Originally it counted on about 160 fabrics and even though it is not the largest collection of tapestries in Europe, it is the largest collection assembled by one sovereign. The set consisted of figurative fabrics, verdures, above-door, windowbags and parapets fabrics, grotesque and fabrics covering furniture. Currently, the set includes 136 fabrics (134 of them are in the collection of the Wawel Royal Castle, the other two are in the possession of the Royal Castle in Warsaw and the Rijksmuseum in Amsterdam).
Arrases were ordered in Brussels probably in the late 1540s by King Sigismund Augustus. The first fabrics appeared on the Wawel Castle in 1553 on the occasion of the wedding of the King and his third wife Catherine of Austria, while the whole collection until 1560. Although the fabrics have been produced in various weaving centers, they were formed around one joint styling, to decorate the Wawel Castle.
Most of dyestuffs contain more than one coloring matter, so analytical methods used for their identification must include separation steps. The use of high performance liquid chromatography (HPLC) allows separating various colorants, that belong to different groups (i.e., anthraquinones, flavonoids, carotenoids, indigoids, protoberberines, quinochalcones and orceins). They can be identified with use of spectrophotometric (UV-Vis) or tandem mass spectrometric (MS) detection, while the later one may give also information about structure of unknown compounds.
HPLC–UV-Vis–ESI MS/MS method was used for characterization of natural dyes present in four historical arrases. Based on these results, it has been found that most of the threads were dyed with dyes of plant origin. Apart from that, the dyes prepared from scale insects and lichens were identified.

Keywords: arrases, HPLC-UV-Vis-ESI MS/MS, natural dyes

WILLIAM LAUDER LINDSAY 1829-1880 – THREE SCOTTISH PATTERN BOOKS

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An enlightened physician and passionate botanist, Lauder Lindsay spent his professional life caring for patients at Murray's Royal Institution for the Insane in Perth, Scotland. In his free time he collected and studied lichens. He was an energetic investigator particularly in the field of colour producing lichens which he regarded as a 'new and open' area of chemistry. He compiled three volumes of dyed fabric samples now in the collections of the Royal Botanic Gardens in Edinburgh. Many pages include detailed Notes, drawings and actual examples of lichens and their locations. Much of this work was included in his book 'The History of British Lichens' published in 1856.
Since the discovery of aniline in the 1820's the field of organic chemistry had become particularly active and included the search for novel colourants and dyes. Lauder Lindsay carried out systematic experiments on over 500 specimens of Scottish lichens and the best imported examples in an attempt to create a stable dye fast to washing and light (1). His work was overtaken by the work of William Henry Perkin on coal tar which had unexpectedly and dramatically produced a bright purple dye later named mauveine. A link between the two men was the dye company of Robert Pullar and Sons of Perth who advised Perkin on the commercial possibilities of the new dye. Underlying the work of both men, however, was the study of chemistry and the developing field of colour chemistry. This paper will examine Lauder Lindsays pattern books and the legacy of his work within the 19thc Scottish dye trade.

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AN ENLIGHTENED APPROACH TOWARDS THE DISPLAY OF LATE 19TH CENTURY FASHION TEXTILES: A UPLC-MS/MS AND MICRO FADE STUDY OF MAUVE AND VIOLET ANILINE DYES

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The identification of aniline dyes in late 19th century Fashion textiles is challenging. This is due to the large range of related dyes that were patented and marketed until the early 20th century, rendering difficult the identification of a specific aniline dye. Of these, Mauve synthesised in 1856 by W.H. Perkin, has hitherto been the most extensively studied [1, 2].
As part of the development of new galleries at National Museums Scotland, a survey of Fashion dresses dated to the 1860s and thought to have been dyed with mauve or related aniline dyestuffs was undertaken. One of the aims of this work was to gain a better understanding of the variable fading rates of mauve and violet aniline dyes in order to plan the rotation of these unique garments. A selection of textiles was subjected to Micro Fade Testing (MFT) and dye analysis, to assess the variability in their fading rates and also their compositional variation.
The textile samples were analysed using a Waters Ultra Performance Liquid Chromatography instrument coupled to Photo Diode Array analysis (UPLC-PDA) and Electrospray Ionisation tandem Mass Spectrometry (ESI MS/MS) conducted in positive ion mode using a Waters Synapt G2 Q-ToF. This method allowed the characterisation of the main dye components present in these complex dyes by the simultaneous determination of their UV-Vis and *m/z* data [3]. The fragmentation of the aniline dye components was investigated using Accurate Mass data, which was acquired on a 12T Solarix FT-ICR (Bruker Daltonics). Mass spectra were recorded with an average peak resolution of 200,000 and mass accuracy of greater than 100 ppb facilitating the determination of a unique molecular formula based on the observed mass.
This study revealed a much more complex variation in the dye compositions than first expected, together with noticeable variation in their light sensitivity. This work will set the ground for a more informed display of Fashion Textiles at National Museums Scotland.

Keywords: fashion textile, photo-degradation, aniline dyes, mauve, violet

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NATURAL OR SYNTHETIC? THE IDENTIFICATION OF ANTHRAQUINONE DYES ON HISTORICAL TURKEY RED BY UHPLC-PDA ANALYSIS

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The 19th c. Turkey red (TR) industry consumed a huge quantity of *Rubia tinctorum* madder plant roots prior to the commercial production of the dye's synthetic equivalent, alizarin. Alizarin, a major component of *R. tinctorum*, was the first naturally occurring dye compound to be successfully replicated, and was available in 1869, a year after its discovery.[1] Dyers and chemists of the time realized that synthetic alizarin (also called alizarine) was not pure and, like madder, a mixture of hydroxyanthraquinones. They determined that synthetic alizarin also contained anthrapurpurin (1,2,7-tri-hydroxyanthraquinone, also called isopurpurin) and flavopurpurin (1,2,6-tri-hydroxyanthraquinone) in varying quantities depending on the synthesis reaction conditions.[2] These compounds have not been reported in modern analyses of madder extracts, making them potentially useful markers of synthetic alizarin for dating or provenancing an historical textile.
Dye analysis by high performance liquid chromatography (HPLC) is well established in the study and conservation of historical textiles. Recent advances have improved separation and detection with UHPLC (ultra HPLC) technology, enabling better results from smaller sample sizes. Extensive analytical research of textiles dyed with madder exists, but no HPLC study has focused on TR specifically. Early synthetic dyes are another area with much to be explored and only recently have anthrapurpurin and flavopurpurin been identified on an historical textile.[3]
This paper discusses the anthraquinones identified by UHPLC with photodiode array detection (PDA) for 19th c. TR textiles in the collections of the University of Glasgow Scottish Business Archives and the V&A Museum. The results are compared to extracts of madder root, and to dyed samples and powders of historical synthetic alizarin and also garancine, a dye also used by mid-19th century TR dyers and made by treating madder with sulfuric acid.

Keywords: UHPLC, Turkey red, madder, early synthetic alizarin

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COMPARISON OF MOLECULAR PATTERN OF AMERICAN AND ARMENIAN COCHINEAL DYED YARN, EXTRACTED THROUGH A NEW MILD EXTRACTION TECHNIQUE

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Cochineal dyes are representing in the last years one of the more interesting challenge for researchers in conservation field. Widely used during the century, object of investigation in several studies, mainly because of several compounds unknown, until a short time ago. Recent studies [1, 2, 3] have been focused on the elucidation of these unknown structures, moved by the idea that, in studying artworks and dyes employed, it is not possible to look at few molecules, thought as responsible for the colour, as "marker" molecules, easily detectable, to discriminate the matrix employed. However, this approach is not sufficient if we need to preserve the artwork, understand which matrix has been employed the provenance and, at least, hypothesize the degradation path. Considering complex matrices such as cochineal, we need to consider also other compounds, which could influence the hue during the dyeing processes.
We present the results of the application of the new alkaline mild extraction technique [4], initially thought for madder dyes, to lake and textile, made from cochineal extracts from American cochineal and Armenian cochineal. The application of this methodology to cochineal matrix led to a modification in the extraction protocol, in order to avoid the formation of alteration products. The characterization of compounds was performed through HPLC-MS (in SIM mode and MRM), ^{1}H-NMR, ESI-MS experiments in a first step. In addition, 2D NMR analysis confirmed the presence of O-glycosyl anthraquinones, extracted and conserved with this mild approach and MRM transition allowed to discriminate between the several glycosyl compounds. Then, the extracts of dyed yarns with American and Armenian cochineal were analyzed and compared to identify which molecules or class of compounds would had been fixed on the yarn during the colouring processes and compare to data from literature [1, 2, 3].

Keywords: Cochineal dyes; ammonia method; HPLC-MS

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THE APPLICATION OF GC-MS WITH TMTFTH EXTRACTION AND DERIVATISATION FOR THE CHARACTERISATION OF NATURAL DYES ON MUSEUM OBJECTS

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For more than a decade at the Canadian Conservation Institute (CCI), natural dyes from historical textiles and other dyed substrates have been analysed using gas chromatography-mass spectrometry (GC-MS). This methodology was first published for the analysis of indigo and associated degradation products.[1] A key first step in the procedure is the use of the alkaline derivatising agent *m*-(trifluoromethyl)-phenyltrimethylammonium hydroxide (TMTFTH) to extract the dyed substrates. Subsequent analysis by GC-MS allows not only for the identification of colourants, but also dye degradation products, non-dye marker compounds, dye bath auxiliaries, and substances present on the object through original use or later contamination.

An important supplement to the method is the use of extraction ion software (such as Chemstation) or deconvolution software (such as AMDIS) with purpose-built mass spectral search libraries. These tools enable the operator to extract target peaks from a chromatogram based on either chosen ion fragments, or through complete mass spectrum matches. The use of these software greatly increases the signal to noise ratio (S/N) and highlights peaks of interest.

This presentation will provide an overview of the methodology and discuss the compounds identified through the reactions of TMTFTH with flavonoid dyes (e.g., old fustic, dyer's buckthorn and red sandalwood), quinone dyes (e.g., madder, *Galium* and butternut), indigoid dyes (e.g., indigo and Tyrian purple) and some lichen species. The presentation will also show that identification of dyestuff is possible based on non-dye marker compounds that are unique to certain plants. The analysis of extracts of a selection of historical dyed textiles and Canadian First Nations decorative objects analyzed at CCI will be provided as validation of the methodology. Both the advantages and disadvantages of this approach will also be discussed.

Keywords: natural dyes; gas chromatography-mass spectrometry; TMTFTH; AMDIS

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IDENTIFICATION OF NATURAL DYES IN TEXTILES AND DOCUMENTS SEAL THREADS FROM THE NATIONAL MUSEUM OF ROMANIAN HISTORY

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A large number of textiles from Romanian collections have been studied in the last years in terms of dye analysis. Dated between the 15th and the 20th century, they include the most representative classes of textiles in local collections: liturgical embroideries (15th-19th c.), court cloth brocaded velvets (15th-16th c.), Oriental knotted carpets and kilims (15th-20th c.), ethnographical textiles (19th-20th c.), documents seal threads (15th c.). Madder, lac dye, Mexican Cochineal, redwood type dyes, weld and dyer's broom were the most frequently used biological sources while kermes, wild madder, young fustic, *Rhamnus* berries, sawwort, isparak and bastard hemp were also detected [1-3].
The National Museum of Romanian History (MNIR) preserves more than 1000 textile objects dating back from the 15th to the 20th century. Textile components could be also find in furniture, bookbinding and documents. Masterpieces of art or historical evidence, they all stand as witnesses of the history and the artistic development of the three Romanian provinces - Wallachia, Moldavia and Transylvania.
The present work discusses the results obtained on dye analysis performed on selected objects from the MNIR collection: liturgical vestments from Transylvania (15th-16th c.), seal threads in 15th and 17th c. documents, a 17th c. velvet gospel cover, 19th c. vestments and 19th-20th c. ethnographical textiles. Analysis were performed by liquid chromatography with UV-Vis and mass spectrometric detectors, connected in line (LC-DAD-MS/MS) [4].
The results of the dye analysis performed are in perfect agreement with those previously obtained, enrich the existing knowledge on the selected objects and add new evidence on the variety of sources used in the three Romanian provinces in the 15th-20th c.

Keywords: dye analysis, textiles, liquid chromatography, mass spectrometry

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A NATURAL DYEING METHOD FOR OBTAINING TURKEY RED COLOR

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The present invention relates to a natural dyeing method which enables to dye 100% cotton fiber and fabric products by using roots of madder plant in particularly textile sector and to obtain Turkey red color. Although Turkey red is a color which is known theoretically since 15th century, obtaining cotton textile products with Turkey red color still requires difficult and long steps. When all steps are not applied as it should be or in cases where it is not waited for necessary periods, the desired color tone cannot be obtained completely.

In this study; coloring compounds, mordant materials and color value were analyzed in the different historical Turkey red textiles in the Topkapi Place Museum and Military Museum in Istanbul. All the analysis results were used for obtaining Turkey red color by developed dyeing machine (Fig.1) and developed dyeing process. The developed process was result in take out a patent.

According to the analysis results of historical Turkey red textiles and developed Turkey red color have same characterizations. In addition to fastness and antimicrobial tests were done on the developed Turkey red color.

Fig. 1: Modified and developed dyeing machine for natural dyes.

Keywords: Turkey red, analysis, process, patent

INDIGO AND COCHINEAL AT 17TH CENTURY SPANISH COLONIAL POLYCHROME ARCHITECTURE IN CHIHUAHUA, MEXICO: SEEKING THE TRANSMISSION OF A MILLENARIAN TECHNOLOGY

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In the last years a comprehensive conservation project has been carried out at several 17th century Spanish colonial churches of Nueva Vizcaya (Chihuahua, Mexico), that have in their interior decorative European designs on wooden ceilings and walls. In parallel a natural resources survey has been done to identify local materials from those that were possible imported through the royal trade that connected Mexico City with the Northern Spanish Frontier.
Recent FTIR, FORS and XRF analysis [1] have evidenced the presence of indigo and cochineal at the polychrome wooden ceilings at the Jesuit mission church of Santa Maria de Cuevas and at the Royal Mine church of Cusihuiriachi.
Indigo dye (*Indigofera Suffruticosa Mill., Indigofera Jamaicensis or Indigofera Mucrolata, among others*) in inert substrates of white color and clay nature, such as atapulgite or sepiolite [2] was used to produce the hybrid pigment of Maya Blue in Central America since Late Pre-Classic (ca.150A.C) [3]. It was also used by other civilizations of Ancient Mesoamerica, as Teotihuacan (Central Mexico) or Chupicuaro culture (Western of Mexico). Current studies are seeking to determinate if the blue pigment is made only with indigo or Maya blue, prepared with a local clay. Until now, there is no record that indigo had been part of Chihuahua's Tarahumara Indians' palette. However, the presence of *Indigosfera Suffructicosa* has been registered by local botanists at the deeper levels of the Sierra Tarahumara Canyons; located at eight hours distance (400 km) from Santa María de Cuevas and Cusihuiriachi (323 km).
The domestication of the cochineal by the Mesoamerican indians has been well documented and described by the Franciscan Bernardino de Sahagún in middle 16th century. However as it is with Indigo, there is no record that pre-Hispanic indians in Chihuahua used cochineal to tine their vestments, paint their ceramics or wood artifacts. Not even today is known as pigment by the local community. However, a cactus (Opunita) with manifest of cochineal (*Dactylopus coccus)* was found at 10 km from the church of Santa Maria de Cuevas. The cactus was transplanted and transported to the lab for its study [4].

All this suggests that the use of indigo and cochineal was brought to Nueva Vizcaya by the missionaries to decorate their missions' architecture. In this sense, it is known that indigo and carmine dyes had a great economic and symbolic value in pre-Hispanic times, and therefore both colors were exchanged by the trade routes of ancient Mesoamerica, as was described in historical writings, such as the Matricula de Tributos (ca.1522-30), a document that describes the goods that different regions and villages of Ancient Mesoamerica paid to Mexico-Tenochtitlan, the capital of the Aztec Empire, in XVI the century.
In this paper, the analysis of micro samples together with *in situ* spectroscopic studies and the study of other local natural materials collected around Santa Maria de Cuevas and Cusihuiriachi that could have been used to produce such colors is presented. The main aim of this research is to understand if indigo or possible Maya blue and carmine were transported from central Mexico or if they were produced locally.

Keywords: Mayan Blue, Carmine, Spanish colonial missions, Mexico, Chihuahua, FTIR, FORS, XRF

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ANALYSIS OF RED YARNS IN TEXTILES FROM THE HUACA MALENA ARCHAEOLOGICAL SITE IN PERU

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Several pre-Incan cultures (e.g. Wari and Tiwanaku) interacted in the Asia Valley on the South Central coast of Peru during the Middle Horizon period (ca 7th century to 11th century CE). Ceramics and textiles from the Huaca Malena site in this valley display significant inter-cultural influence in their iconography, materials, and technology [1]. In the last century of occupation of the site, an immense platform served as a mausoleum, where thousands of textile objects and fragments have been recovered [2].
Earlier cultures occupying the Valley used *Galium spp.* as a red dyestuff, but the Wari culture is known to have used cochineal alone or in combination with other dyes [3]. For dye analysis, red and pink yarn samples were taken from seven textiles recovered from the Huaca Malena mausoleum site: a bag, two bands, an uncu, and three textile fragments. Two of the textiles are recognized as Wari on the basis of stylistic attributes while the others represent coastal styles, three of which are found only in the Malena region.
Yarn construction and fiber morphology were assessed by polarized light microscopy (PLM) and scanning electron microscopy (SEM). Dyes in the yarns were analyzed by three techniques: surface enhanced Raman spectroscopy (SERS) [4], high performance liquid chromatography with diode array detection (HPLC-DAD), and fiber optic reflectance spectroscopy (FORS). Yarns dyed with cochineal, *Galium hypocarpium* and *Galium ciliatum* were used as reference materials.
The archaeological yarns were all made of camelid fibers. The only dye found in major quantity was carminic acid, indicating that all the samples had been dyed with cochineal. This result is consistent with Wari dyeing custom previously reported for the late Middle Horizon period [3]. Significant amounts of other dyes such as those from *Galium spp* were not observed, which suggests that the yarns analyzed were not dyed with mixtures of dyestuffs.

Keywords: SERS, Huaca Malena, HPLC-DAD, Natural red dyes, Pre-Colombian Archaeological Textiles

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ABSTRACTS OF POSTER PRESENTATIONS

Listed in alphabetical order

APPLICATION OF NATURAL DYES IN DYEING OF TRADITIONAL CARPET YARNS

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Interesting results of application of natural dyes over carpet yarns by traditional way were displayed upon researches conducted within the project "The Role of Women in Rural Lifestyle Development" in June 2016 in Gagali, Bijo and Gashad Villages of Agsu region. There exist over 100 natural dyes in the area of Azerbaijan. The mostly known of them are walnuts shells, pomegranate and onion peels, sumach, the kind of mushroom, grown in the hull of mulberry tree which were used in three villages.
Black colour is obtained from the mushroom, colour from light yellow up to dark brown from the pomegranate peel; from wallnut shell- light saffron colour to dark brown colour (green layer protecting wallnut while forming). They are dyed with various colours of golden yellow and dark red. However, for last 20 years these natural dyes are not used and the methods of their dyeing are to be forgotten. Not only carpets, but also rugs are woven with natural dyes. The rugs were woven by dyer who did carpet yarns with artificial dyes in Agsu region. Rugs and carpets woven with woolen yarns dyed with these artificial dyes mix their colour while being washed and lose their look and therefore the carper-makers are not able to sell their carpets.
The purpose of our project is to teach carpet-makers the aforementioned natural dyes in Gagali, Bijo and Gashad villages of Agsu region of Azerbaijan, to try to improve quality of the carpets they wove, therein restoring previous reputation of Azerbaijani carpets, including Shirvan. The survey implemented amidst the women of three villages revealed that, the women were ready to learn these methods of dyeing in order to weave more qualitative carpet and afford selling their carpets. The project managers plan to teach dyeing with natural dyes.

Keywords: carpet, palaz, dye, Agsu, women

IN SEARCH OF COLOR TRACES IN ANCIENT STONE MATERIALS

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Although many ancient civilizations are known to have made use of polychromy on sculptures and in general on stone artifacts, today much of these colors have been lost. For this reason, in the minds of a very large majority, the original stones have remained un-colored until today.

In recent years a strong interest focused on the study of the original polychromy on ancient sculptures has emerged[1].

The small amount of these traces lead to a new approach for their characterization in order to limit sampling and hopefully, avoiding it. The non-invasive approach permits the examination of a very large number of artworks with a virtually limitless number of analytical acquisitions allowing to perform measurements *in situ*. Already during the measurement process, this approach leads to a fundamental exchange of views among scientists, archaeologist, conservators and museum experts.

The application of a protocol based on imaging techniques integrated with data obtained from single spot techniques such as X-Ray fluorescence (XRF) and Fiber Optic Reflectance Spectroscopy (FORS), provides high-quality information. In this paper some examples of analyses conducted in different contexts from museums to archeological sites will be presented. These analyses are included in a wider research project aimed to enlighten the use of colors on the sculptures in ancient time and to better define materials used in the past[2,3]. In this context particular attention will be devoted to the use of organic materials.

Keywords: ancient stone, polychromy, integrated protocols, red lakes

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THE DANTE'S PERSE COLOUR: A STUDY OF MEDIEVAL DYEING APPLIED TO ITALIAN LITERATURE

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This talk will be the first time that I will present some recently published findings from a paper on Medieval Dyeing applied to Italian Literature [1].

According to this paper, Dante's expressions mentioning the colour perse are to be connected with wool drapery trades and dyeing processes, in use in Florence as well as in the rest of Europe between the XIII and the XVI century. French documents suggest the colour perse to almost exclusively be a dark nuance of blue. If this can at least explain the perse's occurrence within a Dante's early work, the remaining Dante's quotations allude to black, at times fading to red tones especially in the *Convivio*'s definition of perse: "Perse is a colour that is a blend of purple and black, but with black predominating, so that perse is designated by a term similar to black". Despite this, many texts until XVI century (including various *Divine Comedy*'s comments) mention the perse's blue tones even if the *Convivio*'s red nuances were well known by then.

All these facts make sense thanks to the professional context of wool dyeing in Florence, where a reddish version of perse called *perso fiorentino* imitates the French quality, promoting the same variety which the poet's works probably allude to. This paper refers to some dyeing related words such as *sanguigno* (bloody) and *purpureo*, considering also another imitated colour called *nero di perso*. The possibility of seeing French perse through the whole Dante's life leads to the question of why the poet does not seem to talk about it. Finally, the paper considers the dyeing metaphor in a famous *Inferno*'s passage: "O living being, gracious and benign, / who through the darkened air (*aere perso*) have come to visit / our souls that stained the world with blood (*tignemmo il mondo di sanguigno*)". Here the tragic story of two lovers Paolo and Francesca expresses a vivid allusion to medieval colour processing of Florentine perse, representing a temporarily brilliance (due to red intervention) which immediately lacks power and is cancelled by the dominant Hell's colour.

Keywords: Dante, French Perse, Florentine perse, Italian literature, dye imitation

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MULTI-ANALYTICAL IDENTIFICATION OF TANNIN-BASED STAINS ON WOOD

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While several papers exist on tannin-based inks, very few analytical studies have focused on tannin-based stains on wood. The identification of the stains is challenging but it can inform on artists/craftmen's techniques and intentions as well as conservation treatments.
This study focuses on researching, reproducing and analyzing wood-stains derived from natural organic colorants, in particular vegetable tannins that have been traditionally used to darken wood. The aim was to develop a protocol that could be used for determining the composition of this type of stains on wooden decorative arts.
At first, traditional recipes for dark stains, containing vegetable tannins, natural organic colorants and iron sulfate or iron acetate were selected based on the most commonly found in literature. Then the stains were prepared and applied on oak and maple wood, in consideration of their very different tannin contribution. Some samples were also finished with a layer of shellac, since on historical objects a varnish is usually applied to protect and improve the appearance of the stain. The stain solutions and the stained wood were studied by FTIR, HPLC-PDA, XRF, Raman spectroscopy and SEM-EDS. Samples of stained wood were also prepared as cross-sections in order to observe and characterize the stains and their extent of penetration in the substrate.
FTIR and Raman allowed to identify the complex ferrous-tannate whose distribution inside of the sample could be further examined in the chemical image obtained by FTIR coupled with a Focal Plane Array (FPA) detector. In addition, SEM-EDS was useful for the elemental mapping in cross-section. After optimizing the method of extraction of the stains from the wood, natural organic colorants and vegetable tannins were then characterized by HPLC-PDA.
The analytical data obtained from the mock-ups has been useful for the identification of black and brown tannic-stains used on a selection of the Metropolitan Museum's furniture.

Keywords: wood-stains, tannins, wooden furniture, FTIR-FPA, HPLC-PDA, Raman

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CHARACTERIZATION OF DYES USED IN BOOKBINDINGS FROM BOOKS OF HOURS

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The identification of dyes is fundamental to artefact preservation and interpretation. In this sense, the dyes used to colour the textile bookbinding of two 15th c. books of hours were characterized by a multi-analytical approach. This study is part of a research on the bindings of books of hours preserved in Portugal, aiming to disclose their protective action and to contribute to rise awareness on the history of bookbinding and production techniques of the Western book.
The micro-samples, from a blue dark velvet from a binding likely dating from the 15th-16th centuries, and a scarlet velvet from a binding probably from the beginning of the 17th century were analysed by µ-Raman spectroscopy, µ-spectrofluorimetry and Surface-Enhanced Raman Spectroscopy (SERS). The analysis of the dark blue textile revealed the presence of indigotin chromophore [1]. In turn, the analysis of the scarlet velvet allowed the identification of a dye from animal origin due to the presence of carminic acid [2].
Carminic acid is the main chromophore in the Euro-Asian cochineal of the genus *Porphyrophora spp*., and in the American cochineal of the genus *Dactylopiusv spp*.. The latter was introduced in Europe in the 16th century and replaced the other insect species due to its higher colorant content and better quality [2-4].
The micro-sample from the scarlet textile binding will be further analysed with HPLC-HRMS (High - Performance Liquid Chromatography - High Resolution Mass Spectrometry). Comparison of the results with different species of Euro-Asian and American cochineal insects will allow to identify which species was the source of the carminic acid-containing scarlet dye [4]. This information will bring us closer to the accurate provenance and dating of the raw materials used in the production of the textile bookbinding and contribute to the development of methodologies to better preserve the artefact.

Keywords: bookbinding, dyes, carminic acid, cochineal

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REVEALING THE SECRETS OF THE MADDER DYE AND PIGMENT VAT

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When madder pigments are made from an aqueous extract the vast majority of soluble colouring material is incorporated into the pigment. The composition of such pigments is thus critically dependent on the composition of the aqueous extract which in turn is determined by the solubilities of the constituent hydroxyanthraquinones. There is very little published solubility data for the key components, pseudopurpurin, purpurin, alizarin and ruberythric acid. The solubilities of the aforementioned compounds have been determined in both water and a 5% alum solution over a range of temperatures. This data together with results of investigations of the stability of the solutions enables conclusions to be drawn on how best to obtain pigment products of desired composition. The results also have implications for the dyeing of textile fibres. Solubility results will be presented and the results of several experiments which demonstrate the usefulness of this data in pigment making.

Keywords: Madder, pigment, solubility, pseudopurpurin, alizarin, purpurin

COMPLEXITIES OF LUCIDIN CHEMISTRY IN THE EXTRACTION OF TEXTILE ARTEFACTS DYED WITH DYER'S MADDER (*RUBIA TINCTORUM* L.)

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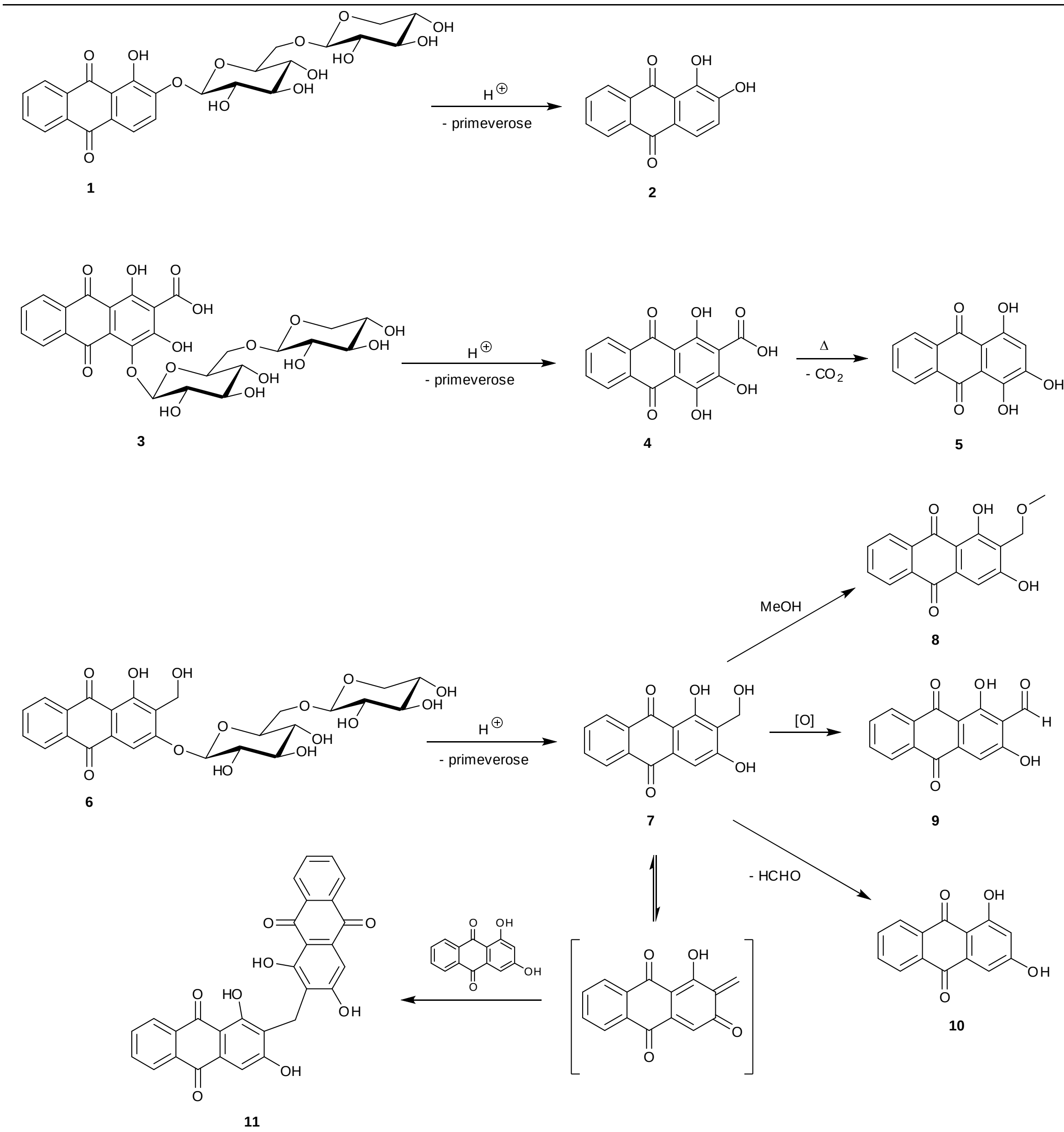
Extracts from the roots of Dyer's Madder (*Rubia tinctorum* L.) have been used for centuries as red dyes for textiles. The main components *in planta* are the glycosides ruberythric acid (**1**), galiosin (**3**), and lucidin primeveroside (**6**). These compounds are hydrolysed into their algycons in acidic conditions, particularly those used in extraction, which is problematic in the field of dye analysis and leads to loss of information.[1] Losing information related to the original composition of the dye causes difficulties in identification of the original dye species, variety and origin;[2] moreover, aglycons observed are often only alizarin (**2**) and purpurin (**5**) (*via* pseudopurpurin; **4**), but lucidin (**7**) is seldom detected. Lucidin is an unstable aglycon with an array of complex equilibrium chemistry, making its detection in historical textiles very difficult. This chemistry is dependent on solvent and pH and small changes can push the equilibrium to previously unidentified products.

Herein we prepare lucidin by a synthetic route and investigate these equilibrium pathways through the use of HPLC, LC-MS and NMR analysis. Using these techniques, degradation pathways that occur under various extraction conditions can be quantified. Certain observations were made: as expected, hydrolysis of lucidin primeveroside into lucidin glucoside occurs under acidic conditions, followed by a second deglycosylation to lucidin as concentration of acid and/or extraction time increases. Lucidin reacts with methanol to form lucidin methyl ether (**8**), which changes retention time and UV absorption; oxidation of lucidin forms nordamnacanthal (**9**); a retro-aldol reaction of lucidin forms xanthopurpurin (**10**); and a lucidin dimer (**11**) is formed when DMSO, acidic and oxidising conditions are used in extraction. Another parameter that has an effect on the composition of the extract is reaction kinetics – HPLC-DAD is applied to investigate consequential reactions taking place at increasing time intervals.



Keywords: Lucidin, Madder, *Rubia tinctorum*, Lucidin primeveroside, Degradation

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PY-GC-MS OF SOME TRIARYLCARBONIUM PIGMENTS: CHARACTERISATION AND IDENTIFICATION IN FELT-TIP PENS

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Triarylcarbonium dyes were patented in the early 1900s and were first employed in the textile industry. Nowadays they are used as pigments in modern paints and inks, although characterised by a relatively low photostability.
Here a systematic pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) study of five commonly used blue, green and violet triarylcarbonium pigments (Basic Blue 11, Acid blue 22, Acid green 5, Basic violet 3, Basic violet 14) of different subclasses was carried out. Pyrolysis temperatures ranging from 300°C up to 800°C were applied in order to study the pyrolysis products generated at each temperature. At temperatures above 550°C for each of these pigments characteristic pyrolysis products could be identified [1].
The occurrence of these pigments could be efficiently evidenced in the pyrograms that were acquired for some felt-tip pens used for sketches by the Brazilian modernist architect and industrial designer Lina Bo Bardi (1914, Rome - 1992, São Paulo) and in commercially available felt-tip pens. Unfortunately, the inks are usually very sensitive to light and chemical agents and the exact knowledge of their composition, especially of the pigment contents, may be important to define the optimal conservation treatment and/or storage conditions. Our data showed that it is possible to reveal triarylcarbonium pigments in complex matrices. Although not all the pyrolysis products of the reference pigments could be detected, efficient identification of these pigments could be accomplished thanks to the presence of specific markers.

Keywords: triarylcarbonium, Py-GC-MS, felt-tip pen, inks

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THE ITALIAN WOAD TRADE IN THE DATINI FUNDS (PRATO, TUSCANY, AT THE END OF THE 14TH CENTURY)

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Today, the importance of the woad in the cloth manufacture of medieval Tuscany is well-known, and the main Italian production areas of this dye are quite well-identified since the pioneer work of Franco Borlandi who located three principally zones: in Tuscany, in Lombardy and in the Bolognese country [1].
However, such a geography of the medieval Italian woad trade has to be reviewed with more accuracy. Moreover, a comparative study of the various regional varieties of this dye remains to be done.

Both these issues can be examined thanks to the rich archives of Francesco Datini of Prato, which contain almost the whole accounting of the *bottega della tinta* of Niccolò di Piero di Giunta Del Rosso, the dyer with whom the famous merchant was associated at the end of the 14th century.
In this sense, I intend to expose at the DHA conference, research I made within the Daniela Degl'Innocenti's project "*In origine era il panno*". Through an analysis of the *Libro del Guado* (1393-1397) [2], which was opened to register all the purchases in woad made by the Del Rosso dyer, I will present the large-scale distribution network of this single dyeing workshop's wood, and I will demonstrate how the prices and the qualities of this dye could vary according to its origin.

Besides, as this accounting-book covered a first period in which Del Rosso was the single owner of his dyeing *bottega* (before December 1st, 1395), and a second one in which he was in partnership with Francesco Datini (after), I will outline how the purchase into capital of the famous trader could has changed the day-to-day work of the dyeing company. To conclude, I will put this specific case back in the broader context of the history of the Italian woad trade between the 14th and the 16th century.

Keywords: Woad, Tuscany, Prato, Datini, Distribution network

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ACCESSIBLE OR EXCLUSIVE? BLUE TEXTILES IN THE MEDITERRANEAN 1000-500 BC

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Colourful textiles are often considered by archaeologists to be valuable, exclusive items. Yet, to what extent were different coloured textiles accessible to people in past societies and what may have limited this? The aim of this research is to consider the exclusivity of blue textiles in the early Iron Age Mediterranean from a perspective of resource availability, skill and time in woad production, processing and dyeing. The research focuses on Italy from 1000-500 BC. To establish the role of blue textile during this period, we consider published dye analysis of preserved textiles and the coloured textiles represented in Etruscan tomb paintings. Using historical records, interviews with traditional woad-dyers and controlled dye experiments, we calculate how many woad plants are required to dye one kilogram of wool yarn, the time taken and skills involved.

The dye experiments used fresh woad leaves, balls and pigment to dye two weights of single ply wool a target shade of blue. A variety of dye recipes was used for the experiments with varying levels of success. The woad dyeing methods employed, especially the fermentation, was challenging due to many variables that affect the outcome, notably the effect of soil and weather conditions on the indigotin content of the leaves. Results from these experiments together with information from the historical sources and woad-dyers today allow us to suggest the quantity of plants necessary to dye one kilogram of wool. Woad production also relies on time and skilled labour, which was potentially as relevant in the past as it is today.

Keywords: Blue, woad, experiment, Iron Age, Italy

ANALYSİS OF SYNTHETİC DYESTUFFS OF TWO HİSTORİCAL NAVAL FLAGS İN THE ISTANBUL NAVAL MUSEUM WİTH ION-PAİR CHROMATOGRAPHY

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Identification of the dyestuff on historical textiles is important information source for the restoration and conservation of the cultural heritage artifacts. Although extensive research has been done on the analysis of natural dyestuffs, the analysis of early synthetic dyestuffs is still a somewhat unexplored area when dealing with historical or art objects.

In this study, the synthetic dyestuff components of two historical naval flags were investigated qualitatively applying ion-pair chromatography.

Historical textile samples were obtained from Naval Ensign Collections of Istanbul Naval Museum (inventory number 0698-A; dimension: 135 × 290 cm and inventory number 0714; dimension: 300 × 200 cm).

In this study, the dark blue colour of sample 0698-A and the red colour of sample 0714 were analysed and determined. And they were determined as acid red 52 and brilliant blue FCF dyestuffs. Depending on the information obtained from the analysis results, naval flags were dated.

Keywords: Synthetic Dyestuff, Historical Textile Objects, HPLC-DAD, Ion-Pair Chromatography

IDENTIFICATION OF RESIN BASED DYES USING HPLC-UV-VIS ESI MS/MS

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Presented study concerns identification of organic dyes and pigments obtained mainly from resins such as dragon's blood, lac dye and gamboge. These resins were used in historical paintings but to this date, are poorly characterized and their chemical composition is not well-known.

Resins consist of many different chemical compounds, not all of them are coloring agents, and because of this proper method of separation and detection must be developed. Therefore, extracted components of resins were separated by high performance liquid chromatography (HPLC) using reversed phase phenyl column and detected by UV-Vis spectrophotometry and tandem mass spectrometry (MS/MS). In order to differentiate colorants from other components of resins numerous UV-Vis chromatograms were collected for different wavelengths, corresponding to absorbtion maxima of different dyes. Pigments observed in these chromatograms were further identified by electrospray ionization mass spectrometry (ESI MS).

To characterize structures of organic dyes they have to undergo fragmentation process in which specific dissociation of compound occurs. Fragmentation may go through decomposition of substituents: cleavage of *O*-glycoside bond, cross-ring cleavage in *C*-glycosides; loss of neutral particle such as H_2O, CO or CO_2, and other, more advanced fragmentation pathways of core compound [1]. Thus, product ion (fragmentation) mass spectra of selected quasi-molecular ions of these coloring compounds were collected in order to determine their chemical structure.

Keywords: tandem mass spectrometry, resin dyes, dragon's blood, lac dye, gamboge

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INTERPRET SERS SPECTRA OF NATURAL LAKE PIGMENTS: A SERS DATABASE OF ISOLATED COMPOUNDS PRESENT IN AMMONIA EXTRACTS OBTAINED THROUGH HPTLC-SERS

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Planar chromatography has proved to be very useful for the analysis of natural products. The chromatograms obtained are not only a fingerprint of the natural raw material, but are a source of extensive data. In fact, the chromatographic tracks can be scanned spectro-densitometrically, UV/visible spectra of the separated chromatographic zones can be recorded and a number of other analytical techniques (MS – NMR - FTIR and Raman/SERS) can be applied [1].
In this work the application of this technique to the creation of a SERS database of isolated compounds present in ammonia extracts of natural lake pigments is presented.
To analyze lake pigments it is necessary to break the complex and extract the dyes. To reach this result, our new mild extraction method [2], that demonstrated to preserve a major amount of glycosides respect to other proposed mild protocol, has been applied.
In the first step of the research, samples of lakes prepared from various natural raw materials (different species of Rubiaceae, *Reseda luteola* L., American cochineal, Armenian cochineal, *Kermes vermilio*) were prepared, following the recipes contained in ancient and medieval treatises [3]. The ammonia extracts obtained were analyzed by HPLC (SIM mode-MRM), NMR and ESI-MS, to identify the compounds present in the extracts. Then HPTLC-SERS was performed.
For what concern the application of SERS to real cases, we developed a new analytical protocol based on the use of a Ag-gel matrix for the micro-sampling of lakes from painted surfaces associated with SERS analyses and designed a specific KIT [4]. To interpret the SERS spectra of lake micro-samples from our Ag-gel matrix, we use as reference database the spectra obtained from HPTLC-SERS analyses. In this way, we identified useful signals to discriminate the presence or absence of glycosylated compounds or characteristic aglicones, important to obtain information about the process of preparation or the provenance of lakes.

Keywords: natural dyes; mild extraction technique; SERS; micro-sampling; HPTLC-SERS

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TEXTILES FROM THE GOKSTAD VIKING SHIP'S GRAVE

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Studies of the dyestuff in archaeological textiles can contribute considerably to the understanding of visual outlook, provenience and dating of objects. They may also be valuable in deciding how they should be conserved and displayed.

We have studied six samples from the Viking Age grave at Gokstad, Norway. The prestigious grave, containing the best preserved Viking ship ever found, was constructed in the years around 900 AD in Norway. A huge man that died in his 40`s was laid to rest there. His ship was equipped with a lot of objects considered needed for his travel, including several beautiful textiles. What might have been the ship`s sail as well as a very special piece of embroidery with silk and gold threads was found in this grave, both turned out to be dyed with madder. The high quality materials used underlines the impression of a high status grave at the Norse society's very top level.

HPLC-UV/Vis and HPLC-ESI-Q-ToF methods were applied in order to identify flavonoids, anthraquinones, tannins and indigoid components in the textile samples. The methods enable an easy identification of dyestuffs by the detection of preserved molecular markers in old textiles.

By the analyses we identified the typical markers of madder type dyestuff: alizarin, purpurin, pseudopurpurin and anthragallol, and degradation products of protein-based fibers: 4-hydroxybenzoic acid and phenols.

Keywords: dyestuff, textiles, HPLC methods

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DYE CHARACTERIZATION OF A GÜRÜN WRAP BY USING HPLC-DAD

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In order to contribute to Ankara Ethnography Museum and protect cultural values, yarn samples of stored Gürün wrap is examined by the help of high-performance liquid chromatography method for detecting the dye type of yarn for each color. Gürün district, which is situated in the province of Sivas in the Middle Anatolian region of Turkey with approximately 20.000 population, hosts technically rich, unique and very famous historical hand woven fabrics called Gürün wraps. The patterned Gürün wrap fabric's warp and weft yarns are wool. It has an Ottoman hand writing embroidered with yellow thread on it. Gürün wrap fabrics have been used as men's and women's outer wear and in the decoration of the houses by the locals. Typical Gürün wraps are weaved in spread, interconnected, interlocked and striped patterns and have almonds, flowers, leaves and branches as ornaments. In most cases white color dominates the ground pattern.

In order to characterize the natural dyes used for fabric, a reversed-phase high performance liquid chromatography (RP-HPLC) with diode array detection (DAD) method was used. The dye extractions were carried out with 37% HCl/MeOH/H_2O (2:1:1 v/v/v) mixture. Dye compounds of the samples, which were identified according to the HPLC analysis, are as follows: Carminic acid, Flavokermesic acid, Alizarin and Purpurin.

Fig. A: General appearance of the wrap

Fig. B: Detailed appearance of the pattern and embroidered Ottoman hand writing

DYE ANALYSIS OF WOOL GÜRÜN WRAP (STYLIZED AS PERSIAN WRAP) YARNS BY HPLC-DAD

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In this poster presentation, dye analysis of a Gürün wrap obtained from Ankara Ethnography Museum will be introduced. Gürün district, which is situated in the province of Sivas in the Middle Anatolian region of Turkey with approximately 20.000 population, hosts technically rich, unique and very famous historical fabric called Gürün wrap. According to the inventory information of Ankara Ethnography Museum, this particular Gürün wrap contains similar features with Persian wraps. Some of the Gürün wraps combine the design and weaving techniques of Indian and Iranian wraps. For this reason, it is possible to call these sort of Gürün wraps as stylized Persian wraps. Gürün wraps were woven in Jacquard hand looms. The Gürün wrap fabrics were 1.20 m. in width and the fabric batch was usually cut out 2.52 m. in length for each wrap. While white color dominates the simplicity of the fabric ground in typical Gürün wraps, ornaments stand out in the Gürün wraps stylized as Persian wraps. Apart from the white, red-yellow or red-blue colors were largely used on the ground of the Gürün wraps stylized as Persian wraps.

Both warp and weft yarns of this particular Gürün wrap are wool. In order to detect the natural dye sources of the wrap a reversed-phase high performance liquid chromatography (RP-HPLC) with diode array detection (DAD) method was used for 13 yarn samples. The dye extractions were carried out with 37% HCl/MeOH/H_2O (2:1:1 v/v/v) mixture. Dye compounds, which were identified for 13 yarn samples according to the HPLC analysis, are as follows: Carminic acid, Laccaic acid-D, Indigotin and synthetics. Using natural and synthetic dyes together indicates that, the wrap was produced in the late 19th or early 20th century.

Fig. A: General appearance of the wrap

Fig. B: Detailed appearance of the pattern

KINETICS OF DYEING AND SPECTROSCOPIC PROPERTIES OF DYE FROM *DIALLIUM GUINENSE* AND *PTEROCARPUS ERINACEUS* (AFRICAN ROSEWOOD)

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Red dyes have been extracted from two tropical plants *Diallium guinense* and *Pterocarpus erinaceus* (African rosewood) and their colouring properties studied on cotton fabrics. Both dyes were extracted by the use of organic solvents using the soxhlet technique and purified by re-crystallization processes.
The dyes were standardized before use by measuring their wavelengths of maximum absorption and adherence to Beer-Lambert law established.
Both plants gave shiny red crystals that transmitted between λ_{max} of 490 – 500nm. A yield of 5% for *Diallium sp* and 17.3% for *Pterocarpus sp.* Both dyes were characterized using FTIR technique in addition to the UV-visible standardization. The common functional groups found from these scans showed the presence of C=C (ca. 1620 – 1470cm^{-1}). NH_2 absorption characteristics of NH- stretch at ca. 3590- 3400cm^{-1} and C=O (ca. 1602cm^{-1}) for *Pterocarpus sp.* while *Diallium sp.* showed prominent peaks at OH (ca. 3417cm^{-1}), C-H sp^3 at ca 2923cm^{-1} and also C=O and C-O bands at 1614 and 1055cm^{-1} respectively.
GC-MS scan for *Diallium* extract showed probable presence of a long extended conjugated product of an acid or ester.
Both dyes were substantive to mordanted cotton fabrics dyed in hydroxyl solvents (locally distilled alcohol) and their dyeing kinetics studied.

Keyword: Rosewood, soxhlet, Dye, Beer-Lambert, Cotton Fabric.

THE CHEMICAL EFFECT OF FILTERED VISIBLE LIGHT ON LIGHT-SENSITIVE DYES

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Despite best efforts to remove damaging UV and short wavelength light from museum displays, dyes on historical textiles can still fade or change colour if visible light causes chromophoric compounds to form or degrade. For known light-sensitive dyes, better understanding of the impact of visible wavelengths on them could lead to innovative tuneable LED lighting that offers protection by removing the more damaging wavelengths without perceived colour change to the exhibit or light source.
Published studies about museum lighting mainly concern aesthetic impact on artworks[1] with very few reporting chemical changes[2]. Textile dyes specifically remain un-investigated, so the Filtered Light Project pilot study was initiated to assess visible light effects on major chemical components of the light-sensitive historical dyes safflower, turmeric and basic magenta (fuchsine).
Silk fabrics direct-dyed with carthamin, curcumin and fuchsine were exposed for up to 672hrs to a xenon arc lamp (1.1 Wm^{-2} @ 420nm) in a QSun XE1 accelerated light chamber at 26±1°C. The lamp light passed through a daylight-through-glass filter[3] and then an array of 10nm and 60nm bandpass filters, from 395nm to 755nm and 470nm to 780nm respectively, over the silks. Colour changes to exposed dyed areas were tracked by fibre optic reflectance spectroscopy and exposed dyed areas were sampled regularly for analysis by ultra-high performance liquid chromatography with photodiode array detection[3] to detect and monitor chemical markers of change[4].
Initial results reveal new compounds in samples filtered at and near visible wavelength maxima for their dye chromophores: curcumin ~400mm (faded after 48hrs exposure), carthamin ~510nm (yellowed after 120hrs) and pararosaniline ~560nm (bluer after 168hrs). This novel study of the chemical impact of visible light on photosensitive dyes therefore suggests that tuneable LED museum lighting for textiles could be protective and so will be studied further in the Filtered Light Project.

Keywords: safflower, turmeric, magenta, photo-degradation, LED lighting

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ASSESSING THE CRUTCHLEY ARCHIVE OF AN EARLY 18TH CENTURY DYE COMPANY IN SOUTHWARK, LONDON

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The Crutchley Archive is a remarkable yet unknown assemblage of early 18th century documents associated with a dyer called John Crutchley and a dye company in Southwark, London on the south bank of the River Thames. In 2011 Crutchley's descendants donated fourteen documents of dyeing instructions and calculations, pattern books and cashbooks spanning 1722 to 1740 to the Southwark Local History Library and Archive (acquisition no. 2011/5). The collection's significance to dyeing history went unrecognised until examined by Anita Quye in 2014[1].

The Crutchley Archive reveals a large dye company specialising in 'topping' with madder and cochineal. Three large and neat books dated '1736-38', '1739/40' and '1740' present beautiful dyed woollen fabrics (patterns) alongside dyeing instructions (receipts). Colours range from vibrant oranges and reds to subtle pale pinks and lilacs. Turmeric, safflower and weld are amongst other dyes mentioned in the receipts.

There are also five dye recipe books with copious receipts for madder and cochineal, seemingly with alum mordant alone, and a number of associated patterns, predominantly bright red. Two of these books have receipts transcribed from Dutch or Flemish into English. Three fragile ingredient books for dyeing, one dated 1726, bear evidence of use in the dye house, and there is also one book of dyeing calculations. Finally, two cash books, one dated 1722 to 1732-3, list people's names alongside financial details ranging from £1 to a costly £3,000.

A six-month assessment by the authors began in June 2016, funded by The Dyers' Company and the Textile Conservation Foundation. Presented here are the researchers' initial findings from documentary evidence, colour measurements and exploratory dye analysis. An outline of their plan for a collaborative cross-disciplinary investigation of the Crutchley Archive and comparison with Dominique Cardon's study of a similarly-dated French dyeing archive is also discussed[2].

Keywords: pattern books, dyeing receipts, topping, woollen cloth

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PRELIMINARY RESEARCH ABOUT THE APPLICATION OF THE FLUORESCENCE LIFETIME MEASUREMENT FOR CULTURAL PROPERTIES

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Berberine showing strong fluorescence emission is main ingredient of Amur cork tree and related species. The unique emission and excitation spectra of this were useful for the identification of Amur cork tree.

The fluorescence lifetime: τ is another parameter derived from florescence radiation, and can be measured non-invasively and without contact, which is appropriate for the valuable cultural textile.

Fluorescence lifetime is dynamic parameter that can be obtained by the observation of the relaxation processes from excited state with pico or nano second pulse laser photolysis. Since the τ values in the same solvent or matrix are constant, lifetime measurement can be used for the identification of the dye materials. The τ values are also sensitive to the change of the circumstance around the dye, and could be used as a parameter to reflect the micro-environment of the dye molecules.

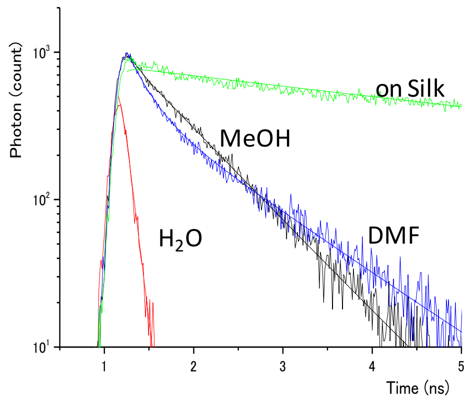

Fig. 1 Fluorescence decay of berberine depend on the solvent

We started the preliminary research for the fluorescence lifetime measurement of berberine and silk dyed with Amur cork tree. Fluorescence decay profiles of berberine in various solvents and dyed silk were showed in Fig.1. Fluorescence intensity of berberine rapidly decreased and the curve was fitted by single- or two-exponential decays. Longer τ values than in water were observed in MeOH, DMF and on silk. Prolonged lifetime (10 times more) of dyed silk compared with in MeOH was observed, suggesting the decrease of non-radiative thermal process.

In this presentation, we will report the application of fluorescence lifetime measurement to cultural textile dyed with Amur cork tree.

Keywords: fluorescence life time, time resolved fluorescence spectrum, fluorescence decay, Amur cork tree, cultural textile

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INDIGO DYEING OF RAMIE FABRIC BY BIOREDUCTION WITH *SACCHAROMYCES CEREVISIAE*

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The indigo dye is insoluble in water and thus, the reduction of indigo to leuco-indigo is an important process in textile industry. Chemical reducing agent (sodium dithionite) is preferred to use for the formation of leuco-indigo in industry. The oxidised products of this chemical reduction such as sodium sulphate (Na_2SO_4), sulphite ions ($SO_3{}^{2-}$) and thiosulphate ions ($S_2O_3{}^{2-}$), are main pollutants in the wastewaters of textile dyeing industry. For these reasons, many attempts have been made to replace the use of chemical reduction agents with more environmentally friendly alternatives [1-3]. The aim of this study is to investigate the efficacy of *Saccharomyces cerevisiae* strains to reduce natural indigo and to develop an eco-friendly reduction process of indigo as an alternative choice to replace polluting chemical reducing agents. *Saccharomyces cerevisiae* strains were separated from baker's yeast and rice wine and used for indigo reduction. Their indigo reducing activity was evaluated by color yield on ramie fabric and monitored time-based changes in K/S value and the pH of reduction medium. On the basis of the results obtained, it was confirmed that *Saccharomyces cerevisiae* strains were able to reduce indigo sufficiently enough to dye fabrics. Therefore, it is possible to develop eco-friendly process of indigo reduction using *Saccharomyces cerevisiae* strains.

This research was supported in 2016 by the MOE (The Ministry of Education), Republic of Korea, under the BK21 plus project (S16AR43D0801) supervised by the NRF (National Research Foundation of Korea).

Keywords: biotechnological process, *Saccharomyces cerevisiae*, indigo reducing activity, bioreduction.

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ANCIENT MIXTEC COLOUR TECHNOLOGY: EXPERIMENTAL RECONSTRUCTIONS OF CODEX PRODUCTION

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A vibrant writing tradition existed in Mesoamerica before the arrival of the Europeans. Of this tradition less than twenty books survive today. These pictographic and hieroglyphic books are materially very complex. They are made on strips of gesso-covered leather or bark paper on which figures were drawn using mostly organic colorants. Very little is known about the creation process of these manuscripts. Their rarity has prompted their custodians to implement a strictly non-invasive research policy. Non-invasive investigation, using XRF, Raman, UV-Vis and IR spectroscopy has revealed some of the main ingredients for these books [1, 2], but has trouble with the secure identification of organic materials, adhesives, and additives that are present in low concentrations. To come to a better understanding of the creation process, researchers from Leiden University and the Cultural Heritage Agency of the Netherlands collaborated to experimentally reconstruct sections of Codex Selden, Bodley and Vaticanus B. These reconstructions were based not only on the results of the non-invasive investigations, but also on information gathered from early colonial Spanish descriptions, such as the work by Bernardino de Sahagún [3]. Next to these sources, present day knowledge of indigenous peoples is essential for the identification of materials and related production processes [4]. The experiments have given great insight into the creative process of the Mesoamerican scribes, and the possibilities and limitation of the materials they were working with. Having broadened the range of materials needed to make a codex, it has also becomes clear that these books are the result of both long distance interaction through trade or tribute, as well as intensive cross-craft interaction.

Keywords: Mesoamerica, Manuscript, Organic paint, Experiment, Reconstruction

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"IF YOUR VAT TURNS TO DEATH REFRESH IT WITH MERCURY AND SAFFRON… THE PROBLEM WAS ALWAYS THE YELLOW!

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A recently discovered manuscript from around 1600 shows the engagement of the alchemists/early chemists in developing first steps in using indigo for dying linen. The recipe was found in the archive of one of the most important courts fostering alchemy at this time, the court of „Moritz the Scientist“ at Kassel in northern Germany.

Although having no knowledge of the reduction processes needed for dying indigo on cellulose fibres the author hit sometimes the right chemical use and on the other side shows us typical misunderstandings. The use of „mercurius sublimatus corrosivus", operment and Saffron to cure a failed indigo vat is discussed. The recipe gives us an insight of an alchemists thinking: the "magic bullet" for solving nearly every problem was first the mercury sublimate.

In this special problem of a "dead" indigo vat the alchemist knows that adding something yellow is important to revitalize the vat, so operment or leaves of a birch tree are proposed as a help.

The astonishing use of the expensive saffron indicates the long-lasting influence of antique imaginations of the life-yellow spending plant "crocus sativus" - an echo of the spring-ceremonies of the antiquity in early vat-technolgy. The use of brazilwood instead of madder hits the necessary input of something reddish to improve the dying process but it was the wrong "red"…

The research was done in collaboration with Jens Bartoll (Lab Stiftung Preussische Schlösser, Potsdam, Germany), Dr. Peter Schmidt (Indigo Synthese BASF, Ludwigshafen, Germany) and on the basis of the heritage of the late Dr. H. Cassebaum: The appearance of the operment-vat in the 17th and 18th century, Magdeburg 1965.

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A STUDY OF TEXTILES FROM EARLY NOMADIC CULTURES OF SIBERIA

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The excavations of the Pazyryk valley, situated in the eastern part of the Altai mountains near to the Russian border with Mongolia and China, were mainly carried out by Rudenko in 1947-9. A series of burial mounds dating back to the 4th century BC was revealed in exceptionally good state of preservation, as freezing occurred inside the barrows [1, 2].
The finds included horse and human mummified bodies, as well as the most ancient carpet ever found. Garments, saddles, rugs, jewels, ornamental and everyday life objects were also present. This confirmed the existence of an early nomadic culture in this region making efficient use of natural resources and developing a distinctive form of "Animal Style Art", including body art such as tattoos that are still visible on some of the human bodies.
In collaboration with the Hermitage Museum of St. Petersburg this project aims to examine the textile production of Pazyryk peoples, using SEM-EDX for fibre characterisation and HPLC-ESI-Q-ToF for dye analysis. This will help determine if the textiles were locally produced or acquired through trade contacts. Comparisons will be made between textiles used for different purpose, i.e. carpets, clothes, horse-trappings, as well as between textiles from other Siberian archaeological sites, i.e. Oglakhty, and the results also compared with those obtained in publications [3, 4]. In addition, the frozen burial environment offers a rare opportunity to examine material preservation in terms of both structural (fibres) and molecular (dyes). Investigations will be performed in order to highlight how the micro/chemical preservation compares with the apparent excellent preservation of these objects, and if any changes are present that are unique to the frozen burial environment. An introduction to the project and some preliminary results are presented in this contribution.

Keywords: Pazyryk, textiles, dyes, HPLC-ESI-Q-ToF, SEM-EDX

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MULTIDIRECTIONAL INVESTIGATION OF ORGANIC COTTON FABRICS DYED WITH ANATOLIAN BUCKTHORN AND GALLNUT BY HISTORICAL RECIPES

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Natural dyes have the advantage that their production implies the use of renewable resources, causes minimum environmental pollution and has a low risk factor. In former times, wool, cotton and silk fibres were always dyed with natural dyes extracted from plants or animals. The Anatolian buckthorn (*Rhamnus petiolaris* Boiss.) and gallnut (*Quercus infectoria* Olivier) plants have a very important place in the history of natural dyes and have long been used in Turkey [1-2].

In this study, four organic cotton fabrics was dyed with Anatolian buckthorn and gallnut plants using different dyeing process. Alum [$KAl(SO_4)_2.12H_2O$] was used as mordant. Firstly, four cotton fabrics were washed with 10 % nonionic soap in hot water (about 50 ^oC) for 20 minutes, rinsed and so they were dried. Then, they were mordanted with alum ($KAl(SO_4)_2.12H_2O$) a constant temperature of 100 ^oC for 60 minutes and were dyed with Anatolian buckthorn (*Rhamnus petiolaris* L.) and gallnut (*Quercus infectoria* Olivier) of 100 ^oC for 30 and 60 minutes. In these four dyeing, buckthorn percentages remained constant while gallnut percentage increased. Used rates are for buckthorn plant 10 % and for gallnut plant 5 and 10 %.

L*, a* and b* values were measured for the dyed four fabrics. In accordance with results of colour measurement, colour of the fabrics as dark yellow was gradually observed with added gall oak plant and increase dyeing time. pH values of the dyed fabrics were determined by surface pH meter and results were they are approximatelly 6. HPLC-PDA was used for identification of the dyestuffs. According to the HPLC results, vanilic acid, ellagic acid, isorhamnetin, rhamnetin and emodin were detected in the dyed cotton fabrics. SEM-EDX was used for surface image of the dyed and undyed organic cotton fabrics and SE (seconder electron detector) for imaging was preffered. Washing, light, rubbing and perspiration fastnesses of dyed organic cotton fabrics were performed according to ISO 105 C06:A2S; ISO 105 B02:1995 / G:6; ISO 105x12 and ISO 105 E04 standarts respectively. Antimicrobial tests were performed against gram-positive and gram-negative bacteria by the AATCC 100 quantitative test method.

Financial support by the Scientific and Technological Research Council of Turkey (TUBITAK) 1507 project (Project No: 7150407) is gratefully acknowledged.

Keywords: natural dyeing of organic cotton fabrics, antimicrobial activity, fastness tests, HPLC-DAD, SEM-EDX.

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ANTIFUNGAL ACTIVITY AND HPLC ANALYSES OF SILK FABRICS DYED WITH MADDER AND GALLNUT

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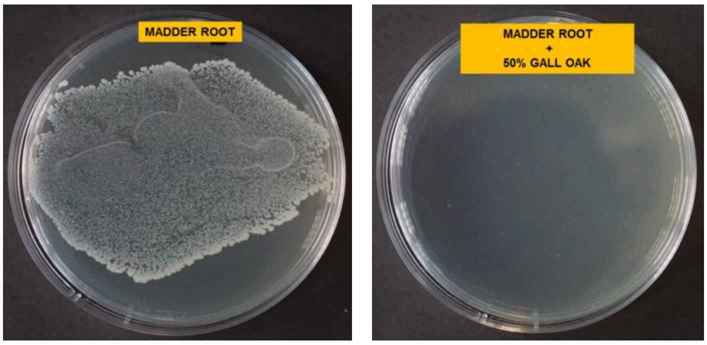
Antimicrobial clothing and textile materials have recently attracted consumers and manufacturer. In former times, wool and silk fabrics were always dyed with natural dyes extracted from plants or animals [1]. Natural dyes are reported as potent antimicrobial agents owing to the presence of a large amount of compounds such as anthraquinones, flavonoids, tannins, napthoquinones etc. which possess strong antimicrobial properties. Antifungal activities of *Rubia tinctorium* have been previously published [2]. *Candida albicans* is special type of yeast that is naturally found on the surface of various mucosal layers of the human body [3]. It is also an oppurtunistic pathogen in human. It can cause disease in immunodeficient individuals such as AIDS patients, organ transplant recipients, cancer patients. They can be spread from person to person by direct contact.
In this study, five silk fabrics are separately dyed madder (*Rubia tinctorium* L.) and gallnut (*Quercus infectoria* Olivier) in different percentages and so they are tested for antifungal activity against *Candida albicans* DSMZ 1386 (Şekil 1). In addition, coloring compounds and their peak high in dyed silk fabrics are detected by HPLC-PDA. Colour values of the dyed silk fabrics are measured by CIEL*a*b* spectrophotometer.



Şekil 1. Images of antifungal activity of dyed silk fabrics against *Candida albicans* DSMZ 1386.

Keywords: natural dye, antifungal activity, HPLC, madder, gallnut.

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IDENTIFICATION OF THE OTTOMAN TENT TEXTILES FOR SUSTAINABILITY OF CULTURAL HERITAGE

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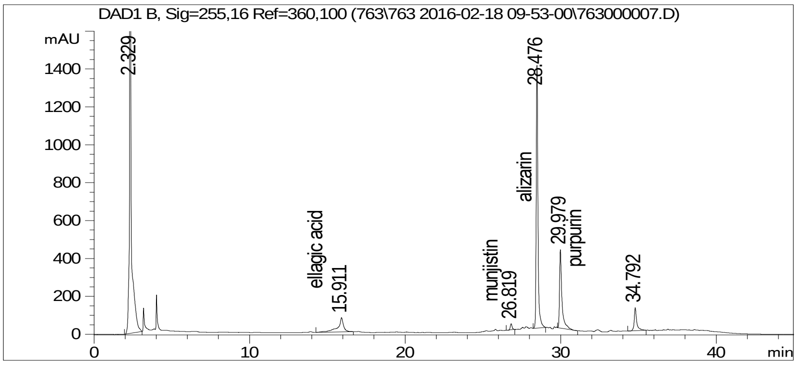
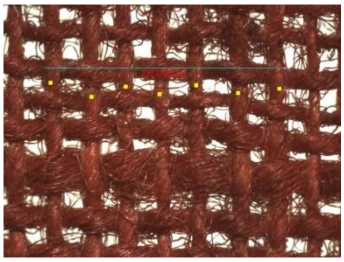
Turkic communities, throughout their semi-settled life in Inner and Central Asia and Anatolia, traditionally have lived in tents made of a rich variety of hand woven fabrics. Tents have served Turks as indispensable housing for daily life, for showy ceremonies, for reverent prayers and during macabre wars. Rich variety of textiles used in Ottoman tents which are in the collections of Turkish and European museums are identified [1].
In this study, color, dye and technical analyses of the fabrics used in the production of Ottoman tents were examined. The samples were provided from unused pieces during restoration of Ottoman tents in Istanbul Topkapi Palace Museum and Harbiye Military Museum. Non-destructive and micro analyses methods were used what HPLC-PDA for identification of dyestuffs, CIELAB spectrophotometer for color measurement and optical microscopy for technical analyses [2]. Colour measurements are very important for restoration and conservation of historical textiles. Each color on the historical textile can be measured by using CIEL*a*b* spectrophotometer. Warp and weft density, weaving and knitting techniques, the twist direction of the yarns are determined by optical microscopy. According to results of dyestuff analyses, ellagic acid, munjistin, alizarin, and purpurin were identified in most of the red colours (Şekil 1). This work was supported by the Armaggan company and Turkish Cultural Foundation (TCF) Cultural Heritage Preservation and Natural Dyes Laboratory and are gratefully acknowledged (www.armaggan.com, www.turkishculturalfoundation.org, www.tcfdatu.org).





Şekil 1. (left) Chromatogram of the red color, (right) Image of optical microscopy of the red color.

Keywords: Ottoman tents, dyestuff analyses, technical analyses, cultural heritage.

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DYE SOURCES USED BY MAY MORRIS IN THE EMBROIDERIES FROM MELSETTER HOUSE: A UPLC-PDA AND MS STUDY

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In 2014, National Museums Scotland purchased two large embroideries, remarkable examples of the work of May Morris, the daughter of William Morris. The hangings were made for Melsetter House on the Orkney island of Hoy, in around 1900, worked collaboratively by May Morris and her friend and client, Theodosia Middlemore.
Based on a design of 1891 for the curtains of her father's bed at Kelmscott Manor, Oxfordshire, these two embroideries exhibit the same design worked in different colours and stitches. Each of them depicts a central pomegranate tree between rosebushes and floral trails against a square trellis background. A number of different birds, and a rabbit, animate the space.
During conservation treatment for exhibition in a new gallery at National Museums Scotland, the opportunity arose to sample both pieces for dye analysis, providing a unique opportunity to learn more about the dyes used in the wools selected by May Morris. Several samples of the main colours were investigated using a Waters Ultra Performance Liquid Chromatography instrument coupled to Photo Diode Array analysis (UPLC-PDA) and Electrospray Ionisation Mass Spectrometry (ESI MS) conducted in positive mode using a Waters Synapt G2 Q-ToF. This method allowed the simultaneous characterisation of the main dye component present is these complex mixture of dyes by combining their UV-Vis and *m/z* data.[1]
Our study revealed that May Morris used a range of natural and synthetic dyes (aniline and azo) [2] sometimes in combination to achieve specific hues. This poster will present the results obtained from the investigation of both pieces.

Keywords: UPLC-PDA / MS, dye analysis, Melsetter House, May Morris, 19th century

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BLUE TEXTILES ALMOST TWO MILLENNIA OLD FROM NORTHERN FINLAND

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A unique find from the Northern Finland contained six tiny textile fragments sized with ca 1 cm^2. These have been preserved in direct contact with a bronze bracelet, which has protected the wool material from decaying in cemetery of Kaakkuri in Välikangas in Oulu. The finds are dated to AD 200–400, which makes them one of the oldest preserved woollen textile find of Finland.
The fragments are brownish in visual analysis, but with a blueish tint. They have been woven using s- and z-spun yarns, which can be interpreted as spin pattern and/or the use of differently coloured yarns. The bronze artefacts of the burial have parallels in Southern Scandinavia.
Optical microscopy (TLM and fluorescence) as well as electron microscopy (SEM) and element analysis (SEM-EDX) were applied to identify the blue colourant. In TLM, the fibres are clearly blueish and that colour was fluorescent. In SEM, heavy degradation appeared in fibres, but also copper (Cu), iron (Fe) and phosphor (P). These findings suggest that, the most likely sources for blue colour were either indigotin or azurite (that contains Cu) or vivianite (that contains Fe and P). No HPLC was applied, because it would have required too much archaeological material.
In TLM, indigo-dyed modern references, indigo powder and other archaeological fibres with UHPLC-ensured woad were clearly fluorescent. Inorganic pigments azurite and vivianite are not fluorescent.
Thus, we interpret that the textile contained indigotin.

Keywords: optical microscopy, fluorescence, indigotin, SEM-EDX, azurite, vivianite

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THE ANCIENT RAW MATERIALS DYES REINTERPRETED AT PHARMACOPEIAS OF THE MODERN EUROPE

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The organic raw materials used as dyes was described in written sources as *Naturalis Historia*[1], and medical treatises or pharmacopoeias as the written of Theophrastus, Disocorides, Galenus, Nicandri, Paulus Aegineta, etc. Likewise, these plant dyes, are prescribed in the recipes of Greek alchemy treaties for textiles dyeing, glass, and other materials [3]. Similarly, these dyes form part, since antiquity, of compounds used as pharmacological remedies. Botanical products were essential in these formulations.
Its use goes back to ancient Egypt [4]. In these remedies such as essences, tinctures, and medicinal drinks were used the sap, fruits, roots, branches, bark, oils and resins from plants dyes such as: saffron, madder, Alkana, lotus, juniper, henbane, safflower, opium, etc. These raw materials appear already quoted in the Ebers Papyrus and the texts of the temples of Edfu and File. A very interesting example of vegetable mixture of this type is the *Kyphi*. This is a ritual, magical and medicinal scent very appreciated in the Ancient and Greco-Roman Egypt.
Although the identification of modern plants with Egyptian names is complicated, we have lists and descriptions of Theophrastus, Dioscorides, and the lists of the Arab authors. These were essential to learn about these ancient plants, and to connect them with the plants used during the Middle Ages and Modern times in different contexts. The joint analysis of these sources and ancient recipes, present in alchemical treatises and compilations from different times, has allowed us to prove the use of certain plants dyes, both for dyeing, as forming part of alchemical, pharmacological and magical-medicinal formulations, from antiquity. These applications, mentioned in the written sources, they were corroborated through of research and analysis the remains preserved in apothecaries and pharmacies of the modern Europe.

Keywords: plant dyes, drugs, Alchemy, Pharmacopoeia.

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DYES "CROCUSES" OF THE OLD AND NEW WORLD

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Ancestral beliefs have syncretised yellow colour with some metals, such as gold. The symbolic value of these metals, symbol of wealth, likewise the assimilation of yellow colour with to power of the solar star and the fire, made this colour was highly regarded between the ancient cultures of the Old World. Also, yellow was a colour associated to the goddess Artemis. The girls who had to prepare for marriage were under the tutelage of Artemis, and this was the colour of the *crocota* [1]. The yellow colour was one of the common shades in women's dress in Antiquity [2]. Many Old World plants, mentioned in ancient sources: saffron, safflower, Reseda, celidonia, etc., [3] are capable of producing this yellow dyes.
For its part, in the ancient Pre-Columbian cultures of Mesoamerica yellow also had important meanings. In the Mayan civilization, for example, this colour was linked to the God of corn. The death and rebirth of this God, in accordance with the myth, became it the divinity that symbolized the life and its perpetual regeneration among the ancient Maya. In addition, the raw material that the gods used for the Creation of the Man was corn, whose yellow colour becomes again symbol of the life [4]. But the main saffron of Mesoamerica, named *achiote* (*Bixa Orellina* L.) [4], was orange instead of yellow, a colour between yellow and red, which also symbolized life among the ancient Maya by its close relationship with the vital liquid of the men (the blood). *Achiote* had great importance in the arts, medicine and food among ancient Mesoamerican cultures. Its orange colour contrasts with other vegetal and floral species that offered high intensity yellow colouring materials with medicinal properties, such as the dye obtained from "the flower of the dead" (*Tagetes erecta* L.). In this study we analysed the different plants that produced the saffron dyes, yellow and red, of the Old and the New World.

Keywords: Antiquity, saffron, art, drug, ritual

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THE DYEING PROPERTIES AND FUNCTIONALITY OF *NYMPHAEA TETRAGONA* LEAVES EXTRACT

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The effect of roots of Nymphaea tetragona is excellent in anti-aging of skin, thus being used as material for functional cosmetic, whereas their leaves are thrown away usually. This study was to investigate the practicality and functionality of *Nymphaea tetragona* leaves as a natural dye while searching for various dyeing methods to utilize them. After the leaves were soaked in methanol for 5 hours, it was filtrated, dried and powdered. After dyeing of cotton, silk and wool with *Nymphaea tetragona* extract, the optimal dyeing conditions were investigated by measuring the K/S values. The optimum dyeing of fabrics was carried out in the condition of liquor ratio 1:50, 100℃, dye concentration 2.5%(o.w.b) and 60min. Aluminum, Iron, Copper, Titanium were used as mordant. Dyeing properties and surface colors were different according to used mordant in the condition of liquor ratio 1:50, dye concentration 3%(o.w.f), 40℃ and 30 min. The mordant increased the K/S values and exhibited various colors such as green, khaki, brownish yellow, dark brown, dark gray and so on. As for color fastness, the silk fabric dyed with *Nymphaea tetragona* extract showed the highest rating regardless of the type and method of mordant in light fastness(3~4, 4~5 rating), washing fastness(4~5, 5 rating) and rubbing fastness(4, 4~5 rating). The silk and wool fabric dyed with *Nymphaea tetragona* leaves extract showed very good antimicrobial activity of 99.8% against *Staphylococcus aureus*. *Nymphaea tetragona* leaves extract is worth to be used as a natural dye because they are excellent in dyeing properties, color fastness and antibacterial activity.

Keywords: *Nymphaea tetragona Leaves, K/S value, mordant, color fastness, antimicrobial activity*

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APPLICATION OF MIXED NATURAL COLORANTS ONTO HAIR DYEING: BASIC APPROACH

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Because synthetic dyes are resistant to microbial degradation and toxic to environment, natural ones are taking attention in hair dyeing. But hair dyeing by using natural resources has many restrictions in color variation and durability to washing and light[1]. To cope with the limitations during research stage, wool is sometimes introduced as the substitute of natural hair because they are very similar in morphological and chemical structure[2].
We selected sappan wood, gardenia fruit blue, phellodendri cortex, and log wood to represent red, blue, yellow, and purple shades. Colorant mixtures were applied onto wool at some dyeing conditions. Bleached hair sample was coated with the mixed paste, wrapped in aluminium foil, kept in an oven at 40℃ for 30min. cooled down at room temperature, washed with commercial shampoo solution. the dyed samples of wool and hair were evaluated from the date of color measurement. Compared with sappan wood and log wood, K/S values of wool were a little lower than those of hair when gardenia fruit and phellodendri cortex were used.

Keywords: natural hair dyeing, color measurement, sappan wood, gardenia fruit blue, log wood.

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APPLICATION OF MIXED NATURAL COLORANTS ONTO HAIR DYEING: COLORATION SYSTEM

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There are many limitations to extract the colorants from the natural resources of high efficiency[1]. However in hair dyeing, natural materials are regarded as environmentally more safer than synthetic ones[2]. As the substitute of synthetic coloring materials, we selected some natural ones for hair dyeing such as sappan wood(red), gardenia fluit(blue), phellodendri cortex (yellow), and log wood(purple). Conventional techniques were applied to extract coloring materials from natural resources. Hair dyeing onto bleached sample was applied as follows; coated with the mixed paste, wrapped in aluminum foil, and then kept in an oven at 40℃ for 30min. Color properties of the dyed wool and hair were evaluated in terms of H(hue), V(value)/C(chroma) values and L, a*, b* values using the CIE, Munsell conversion program. Dyed wool showed wider color variation than dyed hair in the mixed color system. The use of colorant mixtures enables human hair to get wider range of color spectrum than that of single ones. In Munsell hue diagram, better linearity in hue was obtained by controlling dyeing conditions including concentration and additives.

Keywords: natural hair dyeing, color property, Munsell system, CIE system

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