

15 - 16 October, ASTRA Museum, Sibiu, Romania

# *Dyes in History and Archaeology*

39 DHA 2020  
ONLINE



39 DHA Conference 2020

15 – 16 October 2020

**39<sup>th</sup> DHA – Dyes in History and Archaeology**

*Online Conference*

ASTRA Center for Heritage, ASTRA Museum, Sibiu, Romania

### **Organized by**

ASTRA National Museum Complex, Sibiu

*with*

National Museum of Romanian History, Bucharest

the Romanian Association “Science and Cultural Heritage in Connection” (i-CON)

Muzeul Textilelor (*Textiles Museum*) Băița Hărtăgani

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Alina Astefanei

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Cristina Carșote

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## Programme

### Thursday, October 15

#### Session 1.

##### Chair Irina Petrovicu

- |               |   |
|---------------|---|
| 11.30 – 12.00 | Opening   |
| 12.00 – 12.30 | Jo Kirby<br><i>Dyes in History and Archaeology – the growth of a field of study</i> |
| 12.30 – 13.00 | Discussion  |
| 13.00 – 14.00 | Break and <a href="#">A Visit to ASTRA Museum</a> by ASTRA Film Studio              |

#### Session 2.

##### Chair Maria Melo

- |               |   |
|---------------|---|
| 14.00 – 14.20 | Ilaria Degano<br><i>Revealing the organic dye and mordant composition of Paracas textiles by a combined analytical approach</i> |
| 14.20 – 14.40 | Krista Vajanto<br><i>New insights for fibers and dyes from Snartemo V chieftain burial</i>                                      |
| 14.40 – 15.00 | Cristina Maria Barrocas Dias<br><i>The burial garments of the 14th-century Portuguese Archbishop Gonçalo Pereira (†1348)</i>    |
| 15.00 – 15.20 | Questions   |

### Short presentations (5 minutes each)

- |               |  |
|---------------|--|
| 15.20 – 15.40 | Márta Guttmann<br><i>Records of natural dyeing in Transylvania</i> |
|---------------|--|

Hedy M-Kiss

*Educational project, painting experiment with vegetable dyes*

Ruxandra Eugenia Socaciu

*Experimental printing using vegetal dyes – a sustainable approach in artistic expression*

Irina Petroviciu

*Natural dyes in contemporary textile art*

15.40 – 16.00 Break and Online Art Exhibition

### Session 3.

#### Chair Ilaria Degano

16.00 – 16.20 Hortense de La Codre

*Creation of a colour chart and building of a spectral data bank with spectroscopic techniques for the in-situ study of Aubusson tapestries of the 18th century*

16.20 – 16.40 Alina Astefanei

*Zooming in on historic colour charts of artists' paints of the early 20th century – The "Deutsches Farbenbuch" (1925)*

16.40 – 17.00 Jennifer Poulin

*A popularity contest: the statistics of manufacture for early synthetic colourants*

17.00 – 17.20 Questions

#### Short presentations (5 minutes each)

17.20 – 17.30

Cindy Connelly Ryan

*Documents from a revolutionary self-reinvention: Samuel Weatherill's dye notebooks, c. 1775-1785*

Ana Ursescu

*Sarmentum Tinctorial Garden: a bottom-up educational initiative*

17.30 – 17.50 Sarmentum Tinctorial Garden (video)

## Friday, October 16

### Session 4.

#### Chair David Peggie

- 11.30 – 11.50 Jantiene van Elk  
*Travel to learn: a network of dye professionals*
- 11.50 – 12.10 Paula Nabais, Maria João Melo  
*Organic colorants as markers for a chronology and geography of medieval scriptoria and workshops*
- 12.10 – 12.30 Márcia Vieira  
*Brazilwood lake pigments in the illuminated manuscripts of alfonso x: their first use in medieval european manuscripts?*

12.30 – 12.50 Questions

#### Short presentations (5 minutes each)

- 12.50 – 13.00  
Francesca Sabatini  
*Bright orange and scarlet red – first glance at “combined lakes” formulations*
- Maria Carolina Veneno, Paula Nabais, Vanessa Otero  
*Back from the Past: historical and experimental research of Winsor & Newton 19th-century recipes for Reseda Luteola*
- 13.00 – 14.00 Break and [Sibiu 825](#) by Dumitru Budrala – a video invitation to Sibiu

### Session 5.

#### Chair Alina Astefanei

- 14.00 – 14.20 Martina Bajoux Kmoníčková  
*Microscopic and spectroscopic characteristics of cochineal*

*lake pigments focused on tin mordants*

14.20 – 14.40 Kat Stasinska  
The most beautiful shade of red'. Re-discovering of Slavic folk recipes for dyeing with wild oregano (*Origanum vulgare* L.)

14.40 – 15.00 Questions

Short presentations (5 minutes each)

15.00 – 15.30

Vanessa Otero  
*Uncovering Al-Qalālūsī 13th-century treatise on ink making: new contributions to the study of medieval iron gall inks*

Neşe Çakir  
*Ink and paper characterization of 14th–18th century Ottoman period manuscripts*

Silvana Vasilca  
*Gamma radiation effect on natural dyes from historical textiles*

Valda Valkovska  
*Comparative study of the extraction of natural pigments from dyed woollen yarn using different acids*

15.30 – 15.50 Break and Visit to Textile Museum, Băița (video)

**Session 6.**

**Chair Jo Kirby**

15.50 – 16.10 Art Proaño Gaibor  
*Novel UPLC-PDA-HRMS method for natural, basic and acid dyes*

16.10 – 16.30 Ludmila Otilia Cintează,  
*Novel ZnO nanoparticle-based polymeric coatings for UV protection of natural dyes in historic textiles*

16.30 – 16.50 Questions

Short presentations (5 minutes each)

16.50 – 17.10

Theodora Năstasie

“If these walls could talk”. The advent of synthetic dyes and their highly-debated toxicity

Marc Holly

*Sharing colour – sharing knowledge. A new database for synthetic dyes and related materials*

17.10 – 17.30 Closing remarks



## Oral Presentation

## **Dyes in History and Archaeology – the growth of a field of study**

Jo Kirby

Independent scholar, Norwich; jokirbyatkinson@gmail.com

The first meeting of a small group of people interested in the analysis of dyes on archaeological and historic textiles took place in York in 1982. The success of this meeting and the active interest in dyes that it revealed led to a second meeting held in Edinburgh the following year and the group that was to become known first as Dyes on Historical and Archaeological Textiles (DHAT) and, at its seventh meeting in 1988, as Dyes in History and Archaeology (DHA) came into being. The early history and development of DHA was summarised by Vincent Daniels at the 25th meeting held in Suceava in 2006,<sup>1</sup> by which time the small group had grown into a larger and international collection of researchers, meeting in cities all over Europe while maintaining an informal and friendly atmosphere.

Since these early years, the history and use of dyes has interested a wide range of historians, archaeologists and scientists working on different types of artefact, not only textiles, and in archives and on biological sources as well as in different fields of chemical analysis. The number of analytical techniques available has increased, including non-invasive methods. Increasingly sensitive chromatographic and spectroscopic techniques can provide different types of information. As well as studies of the dyes themselves, methods of extraction and analysis are also discussed. In addition to the natural dyes used for centuries, early synthetic dyes have become a significant subject for examination. However, the audience and subject field remain grounded in the history of the use of dyes: however advanced the analytical method, it must be applicable to a rare, fragile historical object and needs to be explained in this context.

1. Daniels, V. (2017) '*Dyes in History and Archaeology: the early years*', *DHA E-Newsletter*, occasional newsletter, London: Archetype, August 2017.

## **Revealing the organic dye and mordant composition of Paracas textiles by a combined analytical approach**

Francesca Sabatini<sup>1</sup>, Martina Bacigalupo<sup>1</sup>, Ilaria Degano\*<sup>1</sup>, Anna Javér<sup>2</sup>, Marei Hacke<sup>3</sup>

<sup>1</sup> Department of Chemistry and Industrial Chemistry, University of Pisa, Via Moruzzi, 13, I-56126 Pisa (Italy)

<sup>2</sup> Collection coordinator, The Cultural Administration, Department of Museums, Norra Hamngatan 8, 411 14 Gothenburg (Sweden)

<sup>3</sup> Department for Conservation, Unit for Heritage Science, Riksantikvarieämbetet/Swedish National Heritage Board, Box 1114 SE-621 22 Visby (Sweden)

The object of this study is a wide selection of cotton and camelid samples from an important collection of 2000-year-old Paracas textiles, now at the Museo Nacional de Arqueología, Antropología e Historia del Perú (MNAAH; Lima; Peru) and at the National Museum of World Culture (NMWC; Gothenburg; Sweden). The threads, chosen as representative of the whole palette, were selected from eighteen different textiles. A combined spectroscopic and spectrometric analytical approach was selected to characterize the composition of this wide set of samples. In particular, technical photography was used to gain a general overview of the samples, X-Ray Fluorescence (XRF) was employed for identifying the mordants and mapping the elemental distribution in the threads, while Liquid Chromatography coupled with Diode Array Detector and with High-Resolution Mass Spectrometry (HPLC-DAD, HPLC-HRMS) were used for characterizing organic dye composition.

This study provides fundamental pieces of information on the mordants used in the dyeing processes, rarely investigated up to now, and to the varieties of vegetal sources employed in Paracas textiles. The widening of Andean dyestuff database is highly important not only to acquire knowledge on Paracas culture, but also to ease the dye characterization of archaeological textiles from Peruvian region and South American area region in general.

## **New insights for fibers and dyes from Snartemo V chieftain burial**

PhD Krista Vajanto<sup>1</sup>, Maarten R. van Bommel<sup>2</sup>, doctoral student Jenni Suomela<sup>3</sup>, PhD Jani Seitsonen<sup>1</sup>

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<sup>2</sup> University of Amsterdam, the Netherlands; [m.r.vanbommel@uva.nl](mailto:m.r.vanbommel@uva.nl)

<sup>3</sup> University of Helsinki, Dept. of Cultures, Finland; [jenni.suomela@helsinki.fi](mailto:jenni.suomela@helsinki.fi)

Several woolen luxury textiles from the Migration period (450 AD) Snartemo V burial were found in Norway already at 1930's, with a gold-plated ring-hilt sword, a glass beaker, a bronze kettle, a gold ring, a gold-gilted fibula. The textiles have been treated with conservation agent Modocoll, that has been long seen problematic for any dye analyses. Some dye analyses were made at 1980's by TLC. In 2018, 13 more samples were analyzed in Amsterdam by UHPLC-PDA, to find out if modern analysis methods can give results despite the old conservation stuffs.

The visible colors of the Snartemo textiles vary from different brownish shades to, blueish and reddish hues. The UHPLC-PDA dye analysis detected indigotin isatin, alizarin, rubiadin and luteolin compounds – as well as a group of unknown colorants. Source of the dyestuffs could be woad, madder and weld. The wool of the Snartemo finds might be underwool of the local Spelsau sheep, although in the finds the fibers are extremely fine: the plied yarns are often 0.5 millimeters in diameter, with 6 ply twists per 5 millimeters. Most probably the colorants were not gained from local sources but were transported to the Iron Age Norway as dyestuffs – or in dyed textiles made of fine wool.

One of the Snartemo findings is a patterned tablet woven band, that has been woven with a very complicated motif using at least five differently colored yarns. Reconstructions of this textile rely on the visual colors: blue, green, yellow, red and purple. However, the role of naturally pigmented fibers has emerged, because chromatographic analyses did not give a proper explanation for the reddish and yellow yarns. According to our analysis with different means of microscopy (TLM, SEM, TEM), we suggest that the reddish hue is a result of dark natural pigmentation of the wool– and the yellow hue is white wool, with no dyeing.

## **The burial garments of the 14<sup>th</sup> century Portuguese Archbishop Gonçalo Pereira (†1348)**

Barrocas Dias, C.<sup>1,2</sup>; Monteiro, P.<sup>3</sup>; Serro, M.<sup>4</sup>; Manhita, A.<sup>1</sup>, Claro., A.<sup>5</sup>; Candeias, A.<sup>1-3</sup>

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<sup>3</sup> Laboratório José de Figueiredo-Direcção Geral do Património Cultural (LIF/DGPC), Lisboa, Portugal

<sup>4</sup> Textile Conservator Freelancer, Lisboa, Portugal

<sup>5</sup> CHAM – Centre for the Humanities, Universidade NOVA de Lisboa/Universidade dos Açores, Portugal

In 1344, D. Gonçalo Pereira commissioned his burial chapel in the Cathedral of Braga (North of Portugal), the Chapel of Nossa Senhora da Glória, where his tomb effigy depicts a middle-aged man in pontifical rich vestments. In 1992, during renovation works in Cathedral, the tomb was open, and some woven and embroidered fragments of the textiles that had been used for dressing the archbishop were removed before the tomb was closed again.

Silk fibres and gilt leather strips recovered from the different fragments were analysed using optical microcopy, SEM-EDS, FTIR and HPLC-DAD-MS. A graphical reconstruction of the decorative motives (Fig.1, for the “Lion” Lampas) was done based on macro digital especially treated images and stereo-microscope observation of the textile fragments, fundamental for perceiving the weave structure and identify the respective decorative motifs.

With this study it was possible to identify the burial vestments of the archbishop, some of which made with textiles likely from Central Asia or China. The uniqueness and richness of some textiles suggests that the care and detail followed by D. Gonçalo Pereira in the construction of his burial chapel was extended to his choice of burial garments.



Figure 1 – “Lion” Lampas: a) Right cuffs/ Photo: Jorge Horácio Oliveira (LJF/DGPC); b) Detail/ Photo: Madalena Serro; c) Graphical reconstruction/ Madalena Serro and Paula Monteiro.

**Creation of a colour chart and building of a spectral data bank with spectroscopic techniques for the in-situ study of Aubusson tapestries of the 18th century.**

Hortense de La Codre<sup>1</sup>, F. Daniel<sup>1</sup>, C. Marembert<sup>2</sup>, L. Servant<sup>3</sup>, R. Chapoulie<sup>1</sup>, A. Mounier<sup>1</sup>.

1 IRAMAT-CRPA (UMR 5060 CNRS / Université Bordeaux Montaigne) Institut de Recherche sur les ArchéoMATériaux Centre de Recherche en Physique Appliquée à l'Archéologie Maison de l'Archéologie 33 607 Pessac – France

2 Atelier Myrobolan, teintures naturelles artisanales Bruxelles

3 Institut des Sciences Moléculaires (UMR 5255 CNRS/Université de Bordeaux) 33405 Talence – France

Aubusson, located in central France, is famous for its tapestry factory. In 2009, the knowledge in the art of making Aubusson tapestries was added on the List of Intangible Cultural Heritage of Humanity by UNESCO. In the 17th century, when it earned its title of *Manufacture Royale*, were born the "Verdures fines" representing landscapes. These fine tapestries were made with specific techniques and materials supposed to provide them superior quality, according to the use of "Grand teint" dyes, reserved for high quality tapestries. A specific methodology has been introduced to allow the identification of the main components of tapestries (textile, dye and mordant) using most of the time non-invasive and *in-situ* methods.

This project contains several stages, the first of which consisted in the creation of a colour chart. The dyeing recipes were listed thanks to several treaties of the 18th century [1,2,3]. The list of dyes is long, the yellows have for example at least five different plants (weld, broom, dyers sarrette, yellow wood and fenugreek), that's why, more than 100 recipes based on " primitive colours " (blue, red, yellow, fawn and black) and 150 mixed dyes emerged from this research. Among these samples, "test" recipes were made by varying different parameters (dyes, quantities and composition of mordants, pH, soaking time...) in order to observe the influence of these different elements on the colour & on their identification. The experimentation thus made it possible to show the compromises to be made in order to obtain a colour that is both beautiful and solid, worthy of the Grand teint. This colour chart of about 250 samples was made on wool and silk, thanks to a collaboration with a Belgian dye house (Myrobolan).

In a second step, reference spectra of these samples were recorded with several non-invasive analytical methods from ultraviolet to near-infrared range (HSI-VIS-NIR, FORS, LED $\mu$ SF...) in order to create a reference spectral database [4,5,6].

Finally, this spectral data bank shows spectral differences due to the variation of the different components and their proportions in the recipes. This exhaustive database makes it possible to improve the results obtained in two “Verdures” with Brühl's count coat of arm, kept at the Cité Internationale de la Tapisserie in Aubusson. Indeed, thanks to the power of hyperspectral imagery, a powerful visual tool, it has been possible to map the restoration areas and the textiles used (wool or silk); to identify certain dyes and mixtures (indigo mixed with cochineal...) and to have additional information on the mordants used.

[1] D. Cardon, *Le monde des teintures naturelles*. Belin, 2003.

[2] J. Hellot, « L'art de la teinture des laines et des étoffes de laine en grand teint et petit teint », Paris, (1750).

[3] C-L. Berthollet, « Éléments de l'art de la teinture », Paris, (1791).

[4] A. Mounier et al., *COLOR research and application*, 41 (2016) 302-307.

[5] D. Tamburini, *J. Dyer, Dyes and Pigments*, 162 (2019) 494 – 511.

[6] A. Mounier et al., *Microchemical Journal*, 140 (2018) 129 – 141.



## **Zooming in on historic colour charts of artists' paints of the early 20th century - The "Deutsches Farbenbuch" (1925)**

Alina Astefanei<sup>1</sup>, Clarimma Sessa<sup>2</sup>, Christoph Steuer<sup>3</sup>, Heike Stege<sup>3</sup> and Maarten van Bomme<sup>1,4</sup>

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The "Deutsches Farbenbuch" was the result of a long discussion about the quality of commercial paints that began at the "1<sup>st</sup> Conference for Painting Technique" held in Munich in 1893.

The book aimed at establishing quality assurance and correct denotation standards for commercial paints and to fight against "Farbenschwinde!" (paint deception). It was published by the chemist and paint producer Heinrich Trillich in 3 parts (1923-1926); the second part (1925) was dedicated to artists' paints (TRILLICH 1925). The book contains several commercial colour charts of different German paint producers such as Schoenfeld, Schmincke, Pelikan, Bössenroth and others.

In this work, we present the use of a combination of spectroscopic (Raman and SERS) and mass spectrometry (UPLC-MS) techniques for the accurate identification of organic pigments and dyes in artists' colour charts of the "Deutsches Farbenbuch". We have identified a significant number of different synthetic organic pigments, lakes and dyes belonging to different chemical classes and often present in mixtures. The identified colorants have mainly poor to fair, and only few have good fastness to light. These findings indicate that the conservation and exhibition of artworks from this period must be performed with special care. Furthermore, the results demonstrate the need of combining different complementary analytical tools such as Raman, SERS and LC-MS for a comprehensive characterization such complex samples.

## **A Popularity Contest: The Statistics of Manufacture for Early Synthetic Colourants**

Jennifer Poulin<sup>1</sup> and Eric Hagan<sup>1</sup>

<sup>1</sup>Canadian Conservation Institute, 1030 Innes Road, Ottawa, Ontario, K1B 4S7 Canada

From the invention of Perkin's Mauve in 1856, to publication of the first edition of the *Colour Index* in 1924 more than 1,200 synthetic colourants were introduced to the world market. Some achieved commercial success that was short-lived or long-lasting, while others were rarely used for various reasons, including high cost, low fastness, or toxicity. This turbulent period of innovation was largely driven by the demand of the textile industry; therefore, identifying common synthetic colourants is especially relevant to the study of textile collections and their preservation. The risk of fading during exhibition is of particular concern due to the observed low lightfastness of many synthetic colourants.

In preparation for a CCI research project on synthetic dye identification and lightfastness, work was carried out to catalogue the most prominent of the early synthetic colourants used in North America. This poster will outline how information was gathered and filtered from sources that include multiple editions of the *Colour Index*, its predecessor *Farbstofftabellen*, and government documents related to the manufacture and trade of synthetic colourants. As an example of the findings, only about 25% of the materials listed in the *Colour Index* (1924) were manufactured within, or imported into, the United States in 1920. Working with a more concise grouping of popular North American colourants, the materials were assessed for the existence of published lightfastness ratings and 19<sup>th</sup>-century specimens were gathered for future analysis.

The results of this effort offered a clearer picture of the synthetic dye industry and highlighted materials of significance. It also reinforced the need for further work in assessing the light sensitivity of many colourants under conditions similar to the museum environment, and the creation of an accessible database of marker compounds for dye identification using modern analytical techniques.

## Travel to Learn: a Network of Dye Professionals

Jantiene van Elk<sup>1</sup>

<sup>1</sup>Librarian Textiel Museum Jantiene.van.elk@textielmuseum.nl

The craft of dyeing has been learned from people to people for centuries. Travelling was an essential means of learning and sharing new information on dyeing. The Industrialisation didn't change this practise immediately, but slowly. In the Textiel Museum we keep the travel books of the Leidsche Katoen Maatschappij, which are an illustration of this part of the history of dyeing.

For many generations, the art of dyeing textiles has been taught by masters to apprentices. The Industrial Revolution led to the appearance of lots of technical books. It also led to the establishment of technical schools at the end of the nineteenth / beginning of the twentieth century. This change was not abrupt, as new research on the importance of information, knowledge and skills shows. The early modern world of artisans, craft workers and their institutions are an intrinsic part of the industrialisation, argues Jan de Vries in *Rethinking Protoindustry : Human Capital and the Rise of Modern Industry*<sup>1</sup>.

Travel was essential for the transmission of dye knowledge, though books began to play a more important part in sharing information especially in the eighteenth century<sup>2</sup>. In the first half of the eighteenth century people earned a living by travelling around with their trade secrets<sup>3</sup>. Especially in calico printing, colourist, as these dye specialist were called, played an important part in the diffusion of knowledge all over Europe. Colourists travelled from Colmar, Paris, Jouy, Deville,

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<sup>1</sup>Vries, Jan de. „Rethinking protoindustry : Human Capital and the Rise of Modern Industry.” In *Reinventing the Economic History of Industrialisation*, Anne Gerritsen, Pat Hudson and Giorgio Riello Kristine Brulan. London; Chicago: McGill-Queen's University Press, 2020.

<sup>2</sup>Graaff, J.H. & Roelofs, W.G.Th & Bommel, Maarten R.. *A Colourful Past: The Origins, Chemistry and Identification of Natural Dyestuffs*. London: Archetype publications, 2007, p. 6.

<sup>3</sup>Fox, Robert, en Augustí Nieto-Galan, . *Natural Dyestuffs and Industrial Culture in Europe, 1750-1880*. Canton: Science History Publications, 1999, p 231.

Rouen, and Mulhouse in France to Switzerland, Russia, and Germany<sup>4</sup>. A network of chemist-dyers existed which provided authority and allowed for continuous innovations.

This practice of travelling continued well in the nineteenth century. Professional education in chemistry and dyeing textiles was yet to develop. To demonstrate this soft change from an artisanal dyers world to an industrialised dyers world, I will show the travel books of the Leidsche Katoenmaatschappij, which are in the Textiel Museum's library. The Driessen family owned the Leidsche Katoen Maatschappij, a calico printing company which existed from 1836 till 1936. Manuscripts were essential to keep the knowledge of the company, as the handwritten manuscripts by meesterknecht Faes from 1816-1836, Fabricage- en receptenboek by Oswald Leonard Heubner from 1860, the description of the Foxhill Bank Printing Company by Felix A.H. Driessen in 1877 and Stalenboek van Engelse katoendruk by Felix Driessen from 1876 show.

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<sup>4</sup>Fox, Robert, en Augustí Nieto-Galan, . *Natural Dyestuffs and Industrial Culture in Europe, 1750-1880*. Canton: Science History Publications, 1999, p. 126.

## **Organic colorants as markers for a chronology and geography of medieval scriptoria and workshops**

Paula Nabais<sup>1</sup>, Maria João Melo<sup>1,\*</sup>, João A. Lopes<sup>2</sup>, Márcia Viera<sup>1</sup>, Rita Castro<sup>1</sup>, Aldo Romani<sup>3</sup>

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<sup>2</sup> iMed.Ulisboa-Research Institute for Medicines, Faculty of Pharmacy, University of Lisbon, Av. Prof. Gama Pinto, 1649-003 Lisbon, Portugal

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Microspectrofluorimetry presents several advantages comparing with other techniques, such as the simultaneous acquisition of emission and excitation spectra, offering high sensitivity and selectivity combined with good spatial resolution and the possibility of in-depth profiling [1]. However, it lacks the molecular fingerprint as disclosed in vibrational spectra. Using chemometric modeling of the data acquired from the spectrofluorimeter, we intend to overcome this disadvantage, by identifying the colorant present while addressing the complexity behind the color formulation. Recipes' specificities can provide insight into chronological and location particularities, such as scriptoria, enabling a better understanding of the making of the artists' materials.

In a previous work, we proved the efficacy of the modeling strategy applied to a database of historically accurate reproductions of four natural red colorants, used during the Middle

Ages: lac dye, kermes, cochineal, and brazilwood [2]. Following this methodology, it was necessary to address the complexity of naturally aged color paints, such as those found in artworks. The red colorants selected for this study, lac dye and brazilwood, were identified by molecular fingerprint techniques in medieval manuscripts (11<sup>th</sup> – 15<sup>th</sup> c.).

The modeling applied allowed for the discrimination between the colorants tested as well as a deeper understanding of the making of the colors and paint formulations present in historical artworks, enabling advances in art technological source research. For the first time, we could pinpoint a formulation in which lac dye and brazilwood chromophores are admixed, in manuscripts from the Alcobaca scriptorium, while probing the recipes' specificities. A third part, in

future development, consists of the preparation of an algorithm-based software which performs statistical modeling to generate a prediction, the colorants' identification

References:

1. Melo MJ, Claro AAcc Chem Res. 2010;43(6):857-66. DOI: 10.1021/ar9001894.
2. Nabais P, *et al.* Herit Sci. 2018;6:13. DOI: 10.1186/s40494-018-0178-1.

## **Brazilwood lake pigments in the illuminated manuscripts of Alfonso X: their first use in medieval European manuscripts?**

Márcia Vieira<sup>1</sup>, Paula Nabais<sup>1,2</sup>, Graça Videira Lopes<sup>2</sup>, Laura Fernández<sup>3</sup>, Maria João Melo<sup>1,2,\*</sup>

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<sup>3</sup> Department of Art History, Faculty of Geography and History, Complutense University Madrid, Av. Profesor Aranguren s/n, 28040, Madrid, Spain

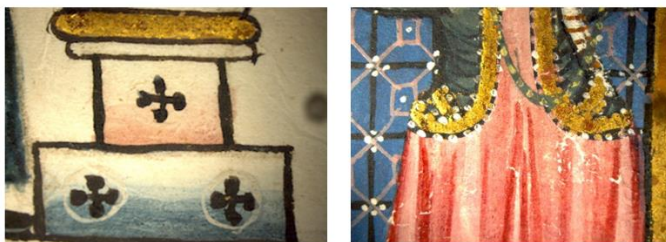
Brazilwood was an important source for lake pigments and organic dyes in the Middle ages up until the 19<sup>th</sup> c. [1-3]. Its preparation is described in several medieval treatises such as “The book on how to make all colours paints for illuminating book” [3]. Our systematic studies have confirmed its application in 15<sup>th</sup>-century books of hours [1]. In 2016, examples of brazilwood paints were identified in the Ajuda Songbook (*Cancioneiro da Ajuda*), a monument to Galician-Portuguese medieval lyric containing an exceptional series of illuminations [4]. Unfortunately, we do not have accurate information about its commissioning or where and when it was produced. It is tentatively dated from the 13<sup>th</sup>-14<sup>th</sup> centuries, which would make these brazilwood paints the oldest examples known in European medieval manuscripts.

In November 2019, to assess if the Ajuda Songbook could have been produced in the scriptorium of Alfonso X of Castile “The Wise” (1221-1284), we made a preliminary identification of the molecular colour palette used in this scriptorium. Selected by art historians, five manuscripts preserved at the Real Biblioteca del Monasterio de El Escorial, including two of one of the greatest medieval European monuments *Cantigas de Santa Maria* (Songs of Holy Mary): “Códice Rico” RBME MS T-I-1 (ca. 1280-82) and “Códice de los músicos” RBME MS b-I-2 (1282-1284) [5, 6], were analyzed *in situ* by reflectance spectroscopy, microscope, and Raman spectroscopy. In all five manuscripts, it was observed a pink-rose applied beautifully and extensively in architecture and vestments, and the most fascinating aspect is its similarity in hue and *shade* to the pink used in Ajuda Songbook, Figure 1. However, we could not establish with certainty the colorant used in these pink-rose colours.

With the database of reconstructions that we have been building for the past 15 years, it was possible to suggest, based on UV-Visible spectra, the presence of brazilwood in the Alfonso X scriptorium [2]. Since Alfonso X manuscripts precede the Ajuda Songbook, the confirmation of brazilwood paints in these manuscripts with other analytical techniques will establish them as the earliest known examples of the use of brazilwood in European medieval manuscripts and even in textiles.

This future identification may also indicate that the Ajuda Songbook could have been produced in this scriptorium. However, a more in-depth study of the paint is necessary to fully identify its formulation and uncover the recipe specificities [2, 7]. To prepare it, a throughout research of Iberian treatises with brazilwood recipes was undertaken encompassing the 11<sup>th</sup>-17<sup>th</sup> centuries, which will ultimately be reproduced with as much historic accuracy as possible. The knowledge obtained from the study of the reconstructions of the Iberian recipes will contribute to know more When and Where the Ajuda Songbook was produced. Therefore, in this poster, we intend to present and discuss the similarity of the pinks used in Alfonso X scriptorium and Ajuda songbook and the contribution of the research made in Iberian treatises and resulting reconstructions for its characterization.

### Alfonso X scriptorium



### Ajuda songbook





Figure 1 – Comparison between the pink-rose colour found in the vestments and architecture of Alfonso X manuscripts and the brazilwood paints of the Ajuda songbook.

### Acknowledgments

The authors would like to thank the Real Biblioteca del Monasterio de El Escorial, especially Ricardo Pichel, Rosa Rodriguez Porto, and D. José Luis del Valle Merino, and the Biblioteca do Palácio Nacional da Ajuda for their generous support and collaboration.

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## **Microscopic and spectroscopic characteristics of cochineal lake pigments focused on tin mordants**

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The cochineal (*Dactylopius coccus*) is a species of a scale insect parasitizing on a cacti of the genus *Opuntia*. Its high content of crimson antrachinon colorant, mainly carminic acid, was the reason of its popularity for dyeing textile and artistic use after its import in 16th century. At first the dyes made with textile shearings were used. From 17th century the lakes prepared directly from insects became more common, typical mordants were aluminum salts like potash alum. Salts of tin were used for the first time in 17th century by Dutch inventor Cornelius Drebbel. In 18th century this method spread in Europe and was well known for its brighter scarlet colour.

This presentation displays the procedure of creation of lake pigments and summarizes the properties of lake pigments originating from different methods of precipitation of cochineal described by historical sources. The focus is on lakes prepared with different tin based mordants considering their different properties such as manipulability. However, the potash alum as mordant was also employed to compare properties with tin mordants lakes.

Microscopic and spectroscopic properties of prepared lakes were determined. The possibilities of differentiation of tin salts mordants lakes by UV-VIS reflectance spectroscopy were explored. This type of information is important to evaluate the possibilities of analytic methods for identification of cochineal lakes in artworks, to understand the origin of the lake and can help for example with the dating of an artwork.

This work was supported from the grant of Specific university research – grant No A2\_FCHT\_2020\_060.

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**'The most beautiful shade of red'. Re-discovering of Slavic folk recipes for dyeing with wild oregano (*Origanum vulgare* L.)**

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'Kultura ludowa Slowian' ('Slavic folk culture') the monumental work of Polish ethnographer, Kazimierz Moszynski, contains intriguing mention about the certain shade of red considered as a most beautiful one amongst the common folk. This mysterious colour was supposedly received from wild oregano (*Origanum vulgare* L.) flowers. Different variations of the recipe were described (with additions such as a wheat malt or apple tree leaves). Some other sources about folk textile dyeing also mention the oregano flowers as a dyestuff. There is no consistency though if the immersion or fermentation dyeing should be applied I made attempt to recreate the recipe, researching mentions from ethnographic sources and performing the series of dyeing experiments, with the usage of experimental archaeology methods.

Both unmordanted and alum mordanted samples were tested; experiments were performed on linen and woollen fibres. Dyed samples were tested for lightfastness and wash fastness. The received results will be described and analysed during presentation.

## **Novel ZnO nanoparticle – based polymeric coatings for UV protection of natural dyes in historic textiles**

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Natural dyes, widely used for decoration in historic textiles, paper paintings and other work of art are subjected to constant degradation under various stressors, UV exposure being one of the most dangerous. In the present work coatings based on ZnO nanoparticles were synthesized and characterized as protective materials for textile decorated with natural dyes.

ZnO nanoparticles with various average size and different shapes have been synthesized using a hydrothermal method and another greener method, assisted by plant extract.

The size and morphology of ZnO NPs were investigated by using dynamic light scattering DLS and scanning electron microscopy SEM. The interaction of as prepared ZnO nanopowders with model components of common natural dyes used in traditional Romanian textiles was investigated through FTIR and UV-Vis spectroscopy. Model dyes were subjected to accelerated degradation under UV light exposure and the effect of the metal oxide nanoparticles presence was studied.

The ZnO nanopowders were dispersed in polymeric matrix in order to increase the stability of the suspensions and fabricate a suitable transparent coating materials to be applied on various substates such as textile and paper.

The application of nanoparticle – based coatings significantly decreased UV light-induced degradation of dye component quercetin and carminic acid, due to the UV-blocking effect of ZnO material.

The resulting hybrid nanostructured material exhibit promising perspective to develop inexpensive coatings for preventing dye discoloration during the

exposure to light, thus results in an effective protective material for decorated historic textiles or documents.

#### ACKNOWLEDGEMENT

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## **Short presentation**

## Records of Natural Dyeing in Transylvania

Guttman Márta<sup>1</sup>

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Three recently published books (written in Hungarian) will be briefly presented, each of them containing historic records on dying in East and South-East Transylvania.



The first two are written by a textile artist, Csókos Varga Györgyi (1926-2012), who collected many historic dyeing receipts (manuscripts and verbal communications) and reproduce them, also taught them to young artists at the artist colony she founded in Etyed, Hungary. The books not only list the historic texts, but contain more explanations and technical details, relaying on literature, collaboration with ethnologists, chemist and other specialists and the author's personal experience. The plants used for the different colours are listed.

The third book, edited by Szőcsné Gazda Enikő, presents the until recently unknown legacy (recordings and studies) of the ethnologist Roediger Lajos (1854-1941), museologist at the Szekler National Museum in Sfântu Gheorghe in the first part of the 20th century. One chapter of the book contains some tens of receipts on wool.



## **Educational project, painting experiment with vegetable dyes**

Assist.Prof.PhD.Habil Hedy M-Kiss<sup>1</sup>

<sup>1</sup>West University of Timișoara Romania

This communication is based on the experiment of painting with vegetable dyes, accomplished by the students from the West University of Timisoara, Faculty of Arts and Design, Department of Visual Arts, Conservation-Restoration. Disciplines aimed at Methodology of conservation and restoration of textile objects and techniques textile technologies involve knowledge and deepening of the characteristics of natural textile fibers as well as traditional dyes used in the past. The situation from the 2- nd semester of the 2019/20 study year was carried out online with the guidance of students in order to carry out personal projects, home made experiments, dyeing with vegetable dyes of natural wool and cotton textiles. The resulting material was accompanied by a paper on the topic of vegetable dyes in which aspects were mentioned regarding the working method of the chosen plants, the name in Latin, etc. The purpose of this experiment was made in order to use textile yarns dyed with vegetable dyes, in preserving the restoration of textile objects and their use in the artistic creation of students. I believe that the knowledge and use of natural textiles and natural dyes, based on the past traditional experience, has a major importance, especially in this area of saving heritage and textile design creations. If the tradition is respected even today, we can hope that in the future we can have a solid foundation in this regard, the effort now made by the young generation will give results in a few years. This communication is a synthesis and a statistic on the plants used, chosen according to preference, and the result of the chromatics obtained by those involved in the project.

## **EXPERIMENTAL PRINTING USING VEGETAL DYES – a sustainable approach in artistic expression**

Ruxandra Eugenia Socaciu<sup>1</sup>

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In the context of globalization and migration spreading and culture, as a living entity, evolving toward an universal language, the cultural loss appear.

Regarding the cultural heritage viewed from the perspective of cultural recovery of its constitutive elements, lost along the evolution of society, experimenting with the use of vegetal pigments, and improving lost techniques in artistic expression in order to adapt to contemporary conceptual exigency, can be considered a sustainable attitude in artistic creation process.

Sustainability as a new pursuit is currently omnipresent in almost every aspect regarding human activities. The themes of sustainable energy, economy or agriculture, can be identified as central point of regular debates. It is only natural that it becomes a challenge for artists and artistic creations, too.

Synthetic dyes are immediately available, cheap and ready to use, offering a wide range of intense colours. By comparison, vegetal dyes give pale colours extracted in a complex and time consuming process, assuming the completion of a long cultural route that involve harvesting the plants, extracting the pigments, preparing the dye and finally dyeing.

Accessibility, reducing time and production costs, decrease of wooded areas and natural meadows overstated the economic aspect and contributed in the loss of natural dye knowledge.

The low cost production using synthetic dyes determined the perception of clothes and other dyed products to migrate from long term use to single use consume object.

This experimental study of printing on paper, canvas and natural fibers textile, using vegetal pigments extracted from plants specific to Romania's geographic area, aims, through experiential approach of the specific complex *from material to artwork* process, to achieve the goal of material, cultural and social sustainability in artistic creation.

The experiential approach is expressed by translating scientific experiments in artistic creations, as samples of failure or success, impregnating the artwork with

the marks of ups and downs of creation process itself and involving the artist *all the way* from the material producing to artistic conception and execution.

Viewed from the perspective of artisanal execution, achieving standardized recipes and techniques as results of conducted experiments, determine predictability in results and allow repetition of processes.

Although printing might seem similar to dyeing, the main technique challenges in printing using vegetal dyes are related to the colour solution consistence, the means to apply the dye onto the material and fixing the dye if the case.

For the viewer, the present study final product consist in a mainly visual experience of samples, details and full view artworks containing the personal experiential journey of the artist, while passing through the cultural/sustainable/experimental path from idea to artwork, walking in the footsteps of, metamorphosed through personal experience, recovered cultural elements. But also consist, for the reader, in a material that aims documenting the experience of the creation experience with recipes and technical processes description.

## Natural Dyes in Contemporary Textile Art

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<sup>3</sup> ASTRA National Museum Complex

"Natural Dyes in Contemporary Textile Art" is an exhibition which aims to create a bridge between cotemporary art and Romanian, European and worldwide textile heritage, through natural dyes. The project is based on the interdisciplinary research performed, since 1997, by Romanian specialists, on textiles from local collections dated 15-th to 20-th century. These studies, presented at DHA 18-38 meetings, included dye analysis on liturgical embroideries, brocaded velvet court cloths, oriental carpets and traditional (ethnographic) textiles and evidenced the use of a large number of natural dyes, of vegetal and animal origin, from local and traded biological sources.

Within the project, young artists - students and graduates from the National University of Arts Bucharest, Faculty of Decorative Arts and Design, Department of Textile Arts and Textile Design, coordinated by teachers, will use a selection of biological sources identified in textiles from Romanian collections – indigo (*Indigofera species* or *Isatis tinctoria*), madder (*Rubia tinctorum* L.), dyer's greenweed (*Genista tinctoria* L.), American Cochineal (*Dactylopius coccus*), buckthorn (*Rhamnus bark*) and weld (*Reseda luteola* L.), together with other plants from the local flora, to make textile objects, decorative panels and artistic installations. These will be exhibited together with traditional textiles from the ASTRA Museum Sibiu in an exhibition associated with the DHA 39 meeting.

The exhibition, which will remain open until the end of November, aims to promote contemporary visual arts, and more particularly textiles and to highlight natural dyes as a resource in contemporary art. It also intends to create a connection between contemporary and traditional textiles through natural dyes and to highlight the results of interdisciplinary research by providing scientific information to the public. Innovative, it also spotlights contemporary textile art in dialogue with the textile heritage.

Perfectly framed into the "eco-friendly" concept, the exhibition hopes to be a message to the general public about the variety of materials offered by nature as

resources in visual arts, with a direct impact on our health and the environment in which we are living.

The exhibition, coordinated by The Romanian Association "Science and Cultural Heritage in Connection" (i-CON), having as partners National University of Arts Bucharest (UNArte) and ASTRA National Museum Complex, supports artistic production and research as well as cultural dialogue at national and international levels.

The project is co-financed by AFCN (Administrația Fondului Cultural Național) – The Administration of the National Cultural Fund.

**Documents from a Revolutionary Self-Reinvention: Samuel Weatherill's dye notebooks, c. 1775-1785.**

Cindy Connelly Ryan<sup>1</sup>

<sup>1</sup>Library of Congress Preservation Research and Testing Division

The Library of Congress Manuscripts Division holds a collection of ephemera and records from the Weatherill family firm in Philadelphia, PA. Two slim notebooks in this archive contain a collection of textile dye and ink recipes, attributed to Samuel Weatherill Sr. (1736-1816). Weatherill's biography reveals a remarkable ability to repeatedly re-invent himself both professionally and personally as the dramatic events of the American Revolution rippled through the fabric of Philadelphia society, altering public discourse, civic structures, industries, and trade networks. This modest notebook of colorant recipes provides a window into one of these radical changes in Weatherill's life, a carpenter who reinvented himself as a textile weaver and dyer out of a sense of civic duty, and a pacifist Quaker who actively supported the cause of revolution and took up arms himself to defend the city. The notebooks document dyestuffs available and techniques in use in the Colonies at the time, and while prepared for personal use, have parallels in publications and learned societies that emerged in late 18thC –early 19th C Philadelphia. Laboratory reconstructions of select recipes confirm their practical utility. Textual analysis of one section of the text, "Colours for Washing of Maps", has identified Weatherill's sources for this part of the collection, and provides insights into both the date and the manner of the notebooks' composition.

Illustrations:

Notebook pages – first page, map-washing colors page

Picture of Weatherill

Title pages of the two source texts for the map-washing colours section

Select reconstructions of the map-washing colours

## Sarmentum Tinctorial Garden: a Bottom-up Educational Initiative

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We know from books and documents that, during the XIXth century, natural dyeing was widely spread in Romania as a household industry, but subsequently it almost disappeared due to industrialization and emergence of the synthetic dyes. Recently there is a revived interest in natural dyeing and related traditional crafts in our country. Social media made possible the aggregation of an online group with almost 2500 members. This active community gathers and shares information and experience, bibliography and recipes. Besides theoretical and virtual information exchange, joint workshops and hands-on experience came out as a need.

As a consequence, with the support of the Sarmentum Association, a series of 14 events including conference and workshops were organized since December 2019. A strong community of 40 people learned and practised natural dyeing contributing to create awareness and interest on the subjects in the hand made communities at national level.

Complementary, the Sarmentum tinctorial garden (STG) was launched. Sarmentum means twig in Latin and it symbolises the educational mission of the Association which hosts the STG project.

STG is a place where it is experienced the arrangement and cultivation of several reference plants for dyeing, with multiple purposes: learning and education, promoting an ancient traditional craft, testing and experimenting (identifying the suitable dyeing plants), team-working, producing necessary materials for dyeing.

It contains a selection of tinctorial plants which include: ornamental plants with great tinctorial potential (*Tagetes* sp., *Cosmos* sp., *Centaurea* sp., *Dahlia* sp., *Calendula officinalis*, *Helianthus* sp., *Rudbeckia hirta*, *Solidago Canadensis* and *Gaillardia aristata*), plants which were traditionally used in our country to dye, either cultivated (*Rubia tinctoria*, *Carthamus tinctorius*) or from the spontaneous flora of those times but rare now (*Anthemis tinctoria*, *Genista tinctoria*, *Serratula*

*tinctoria*, *Isatis tinctoria*) and plants that do not grow normally in our area but are easily adaptable (*Polygonum tinctoria*).

The interdisciplinary and trans-disciplinary educational potential of the STG is to be exploited through the connections with many other fields. It encompasses from biology and Latin as an indication of historical use to ecology and geography, from chemistry of the mordants and categories of colourants to colour theory, from textile crafts and ethnography to art and history and from horticulture to landscape architecture.

STG aims to gather specialists in the above mentioned domains, to raise awareness for the natural dyeing field and to increase the knowledge base of the community.



## Bright orange and scarlet red –first glance at “combined lakes” formulations

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The huge number of complex formulations of synthetic dyes and pigments commercialized in the 19<sup>th</sup> century makes their comprehensive characterization both difficult and fundamental for their successful identification in artworks. This entails both the description of the exact starting composition of a wide collection of reference materials along with the study of the challenging photo-degradation processes in which most of the early synthetic dyes and pigments are involved.

In the late 19<sup>th</sup> century, synthetic dyes were quickly adopted for industrial paint manufacture. A completely new set of colours became available, and an even wider palette could be achieved by combining two or more dyes in one lake pigment. The dyes could either be mixed and precipitated together, or one after the other, using one or several different precipitating agents in the process. These so-called “combined lakes” were mainly produced to achieve orange, red, brown or green colours.<sup>5</sup>

The combination of several dyes makes their analytical characterization extremely complicated and brings up new, intriguing questions. Does the stability and fading phenomena of such a pigment differ from a single dye lake pigment? What are the effects of different precipitating agents? And how do two or more dyes interact in such a lake pigment?

In order to address these questions for the first time, 9red-orange lakes (Figure 1) were studied. The pigments were reproduced according to historic recipes from the Wiesel collection.<sup>6</sup> Recipes with up to three dyes (Orange II, Ponceau R and Fuchsin) were chosen for this study. All lakes were precipitated onto an alumina substrate but using different precipitating agents (tin chloride or barium chloride). The dyes were precipitated alone as well as in combination.

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<sup>5</sup> Zerr, Georg/Rübencamp, Robert: A Treatise on Colour Manufacture. London 1908, p. 509-510.

<sup>6</sup> The Wiesel collection is a compilation of recipes, collected between 1888 and 1894 by Hermann Wiesel. A complete transcript of the collection has been published recently: Eis, Eva: Die “Farben-Recepte” der Firma Heinrich Wiesel. Transkription und Auswertung der Rezeptsammlung eines Farbenfabrikanten aus dem ausgehenden 19. Jahrhundert. Bad Langensalza 2020.

Reference paint layers were prepared, and their ageing and possible fading was monitored for six months by analysing two sets of paint model systems by colorimetry. One was exposed to indoor natural light, while the other was subjected to accelerated ageing in a Solar box. The composition in terms of organic colouring components and possible photo-degradation products was assessed by High Performance Liquid Chromatography with Diode Array UV-Vis (DAD), Fluorescence (FD), and High Resolution Mass Spectrometry (LC-HRMS) detection. The kinetics of fading of the different lakes were evaluated, and preliminary results on the stability of the formulations will be presented herein.



Figure 1: The nine red-orange lakes object of this study.

## **Back from the past: historical and experimental research of Winsor & Newton 19<sup>th</sup> century recipes for *Reseda luteola***

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Yellow dyes were used for millennia up until the advances in modern chemistry. They were explored in the medieval textile industry and by illuminators and painters to create precious masterpieces. However, they are one of the most challenging materials to identify in artworks, and their conservation is a major concern. Furthermore, these highly light-sensitive dyes have “lost” their original colour due to degradation; yellow glazes turned transparent, and greens are now blue. The original appearance of unique artworks and the intention of the artist are thus forever altered [1-3].

Treatises and recipe books are unique primary sources of information on the artists’ philosophy and practices, providing new perspectives on the study of original artworks [2]. Winsor & Newton (W&N) was a leading artists’ colourmen established in the 19<sup>th</sup> century that supplied renowned painters as J. W. Turner (1775-1851) and John Constable (1776-1837). The W&N 19<sup>th</sup> Century Archive is the most comprehensive historical archive of detailed instructions for the manufacture of artists’ materials available for researchers [4].

In a time of chemical development, especially of artificial dyestuffs, it is very interesting to note that W&N was producing and selling natural yellow lakes. From a total of 1511 database records for yellow pigments, 42% pertains to yellow lakes.

This project intends to explore the technology of preparing weld lake pigments (*Reseda luteola*) by W&N in the 19<sup>th</sup> century. The recipes will be deconstructed, and the pigment reconstructions will be characterized by a multi-analytical methodology that will include high-performance liquid chromatography. The knowledge gain will contribute to dating and provenance studies.

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## Uncovering al-Qalalūsī 13<sup>th</sup>-century treatise on ink making: new contributions to the study of medieval iron gall inks

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Iron gall inks are a vital element of our written cultural heritage that is at risk of a total loss due to their degradation. Their dark colour, perceived as black, results from Fe<sup>3+</sup>-polyphenol complexes. However, their structure, as well as the key factors and mechanisms that lead to their degradation, are yet to be fully understood [1]. Within the interdisciplinary project “Polyphenols in Art - Chemistry and biology hand in hand with conservation of cultural heritage” we aim at better understanding their behaviour and evolution over time and thus advancing knowledge towards their preservation [2].

This poster will uncover the medieval preparation of iron gall inks found in the Andalusian technical treatise, Tuḥaf al-ḥawāṣṣ fī ṭuraf al-ḥawāṣṣ, written in the thirteenth century by the poet and civil servant Muhammad ibn Muhammad ibn Idrīs ibn al-Qalalūsī (1210-1308). The version used was that translated to Italian by Sara Fani [3]. There are 25 recipes on the production and performance of iron gall inks encompassing different manufacturing procedures and the addition of other elements such as pomegranate juice besides the common ingredients: a phenolic extract from gallnuts, Fe<sup>2+</sup> obtained from iron salts and gum arabic. A rationalisation of these recipes will be presented, and a preliminary selection will be reproduced with as much historical accuracy as possible. The inks will be characterised by a multi-analytical approach that combines high-performance liquid chromatography-diode array detector, Raman and Infrared spectroscopies; the results will be compared with those acquired in medieval manuscripts. This study will contribute new knowledge of science and technology in Al-Andalus, and new reference materials will be available for degradation studies.

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## **Ink and paper characterization of 14th-18th century ottoman period manuscripts**

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Deterioration in the physicochemical, chemical and optical properties of historic paper documents stored in libraries and archives is responsible for an enormous loss of cultural heritage. In order to develop appropriate conservation and restoration of paper documents, it is important to understand the factors that cause degradation and its mechanisms in relation to properties of paper. Whether arises from external and internal sources, acidity is the main problem in degradation of cellulose-based material [1].

The papers used in Ottoman period manuscripts, either European or Turkey originated, have mainly been produced by cotton rags. Generally two specimens of black ink have been used in Osmanlı manuscripts. First one is mainly composed of soot and oil, latter one contains iron (II) sulfate (green vitriol), tannin containing ingredient (i.e. gull) and oil. Besides, iron (II) sulphate is also added to soot and oil consisting ink formulations with the aim of providing brightness on paper. The acidity arising from the iron (II) ions by ageing have induced enhanced deterioration of cellulose and thus tearing was observed particularly near the letters of manuscripts [2].

In this study, fragment of manuscripts belonging to 14 - 18th century have been granted from the Süleymaniye Manuscript Library. Severe losses, stains and discolorization were observed in all paper samples. The optical properties of paper samples were measured by CIELAB color parameters. The acidity of paper samples were determined by surface pH measurements. Characteristic signals obtained from NMR spectrum indicated that cloth was the raw material for all of the paper samples. It is well known in literature that the conservation state of paper is correlated with the crystallinity degree of the cellulose fibers [3].

Crystallinity degrees computed from the peak areas of NMR spectrum concluded that European originated sample belonging to 16th century has the maximum crystallinity degree with 67%.

X-ray fluorescence (XRF) analysis was used to characterize the elemental composition of inks. XRF results showed that all the unwritten parts contain calcium, black inked parts contain lead in addition to calcium, red inked parts contain mainly lead, sulphur and mercury. The obtained data were compatible with investigated Ottoman period ink recipes.

Keywords: Osmanlı Manuscripts, Paper Degradation, Ink

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## **Gamma radiation effect on natural dyes from historical textiles**

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Biodegradation is a natural process in which metabolic activity is interconnected by organisms growth, maintaining equilibrium in the matter transformation cycle. Biological agents affect Cultural Heritage objects, causing colour or appearance changes, resistance loss, partial or total structural alteration due to chemical changes like modifications in polymerization degree or molecular structure. The fungicide and bactericide effect of ionization radiation is undeniable. Working at DNA level, its efficiency and efficacy indicate it for the disinfection of Cultural Heritage objects, but its application is limited to a maximum dose and dose rate effect on some biopolymers, already naturally degraded by natural, physical-chemical or biological factors. Regarding the effect of gamma irradiation on dyed textiles, there is very little data in literature, some of them referring to the effect of ionizing radiation on different type of textiles' mechanical properties [1].

The present study describes the effect of gamma radiation on different dyed textiles' experimental models, prepared according to traditional recipes. Irradiation experiments were carried out at about 3.5 kGy/h, target doses being between 10 and 25 kGy. This approach was tested on silk and wool yarns dyed with flavonoids, anthraquinones and indigoid dyes, being afterwards extracted by acid hydrolysis. These dyes extracted substrates were then analysed using reversed phase liquid chromatography and diode-array detection (RPLC-DAD), their identification and characterization providing significant insights on the disinfection operation.

This work will allow us to bring a significant contribution in understanding the required degree of gamma sterilization and identification of dyes, by achieving a new comprehension of the effect and changes induced by gamma irradiation decontamination processes on dyed historical textiles.

Keywords: gamma irradiation, historical textiles, natural dyes, RPLC-DAD

Reference: [1] W. Machnowski, B. Gutarowska, J. Perkowski, H. Wrzosek, *Text. Res. J.*, **2012**, 83, 44-55

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## Comparative study of the extraction of natural pigments from dyed woollen yarn using different acids

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Natural dyes from plants, fungi and insects have been used since prehistoric times until the mid-nineteenth century when the earliest synthetic chemical dyes began to be used. Identification of pigments and dyes for historical textiles is usually based on comparison with references of plant or animal origin dyes. Practical dyeing experiments using written sources provides an opportunity to obtain reference materials. The most commonly used method for identification of pigments and dyes is HPLC with UV-Vis and MS detection. The HPLC analysis requires the extraction of the dyes from textile fibres. The traditional extraction method is hydrolysis with 37% HCl/MeOH/H<sub>2</sub>O/ (2:1:1, v/v/v) [1]. The disadvantage of method is decomposition of flavonoids (aglycon + sugar derivatives), the most widespread used as source of yellow colour [2]. For this reason, a method with milder extraction conditions is required.

In the present study, dyed samples of woollen yarn were used as models to find suitable extraction conditions for flavonoids. Yarn was treated with potassium aluminium sulphate mordant and dyed with fresh, crushed and dried leaves of *Malus domestica*. A traditional extraction method was modified replacing concentrated hydrochloric acid (37%) by diluted hydrochloric acid (c=1M) and weak organic acids solutions (c=1M): formic acid and acetic acid. Samples were hydrolysed in compliance with the method described by Wouters and Verhecken (1989) with some modifications [1]. Extracts were analysed by liquid chromatography coupled with diode array detector and mass spectrometry (LC-DAD-MS) for identification of pigments.

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## **"If These Walls Could Talk". The Advent of Synthetic Dyes and Their Highly-Debated Toxicity**

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The present work<sup>7</sup> describes an artistic project aiming to offer a brief retelling on the emergence of synthetic dyes and the subsequent poisoning affecting those bearing exposure to them, pertaining to the Victorian era (1837-1901). Additionally, by evoking this well-documented chapter of world history, it hopes to bring to public attention the imminent dangers which lie in lax regulation, corporate greed and irresponsible shopping habits in the textile industry.

The supply and demand cycle accelerated by the Industrial Revolution called for a better managing of funds and fast-paced production methods to suit all tastes. Natural dyes were costly to make; they could not accommodate the ever-changing preferences of the Victorians, nor keep up with on-growing requests. Thus emerged synthetic dyes, which belonged to three main classes: triphenylmethane dyes, azo dyes and sulphur dyes. The dangerous nature of these findings was not yet visible: chemistry was in its infancy and hardly regarded as relevant. Therefore, Victorians were not as inclined to turn to it for answers concerning a shocking wave of symptoms ranging from a state of general sickness to imminent death. When they finally did, they referred to arsenic, either an oxidizing agent or one of the main components of the dye itself, as the culprit in an assortment of poisoning cases related to its use as dyestuff. The most ill-reputed shade was Scheele's Green. Its extensive use could be ascribed to the growing need of being close to nature. Furthermore, shades of green had been quite hard to obtain by employing natural dyestuffs, making them all the more appealing.

As antagonised as these shades were, colour was not a direct pointer to the arsenic nature of the dyestuff. Organic and inorganic compounds alike proved to be hazardous. Other than arsenic, inorganic poisoners included mercury, chromium and lead. Organic compounds could similarly be responsible for

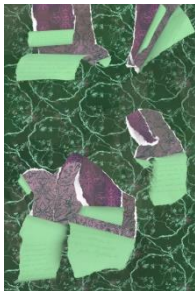
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<sup>7</sup> The work is part of the bachelor's thesis presented at the National University of Arts, Bucharest (UNArte), Faculty of Decorative Arts and Design, Department of Textile Arts and Design (2020)

poisoning cases - dyes containing anilines or triphenylmethane backbones posed a threat to both individuals and the environment. Although poisoning could occur in anyone, it is undeniable that those belonging to the working class were more likely to suffer from acute poisoning, especially those employed in flower-making or factory work, as the laissez-faire economic system of the time paid no attention to them.

I acknowledged the need for an artistic project that would require the viewer to play along, in order to gain insight into the subject and not just dismiss it as baseless fearmongering. The artworks, forming a group of five layered textile panels, would display personas denoting various social classes of the time, all falling prey to the threat that wallpaper dyes were thought to be: Queen Victoria (representing royalty itself), the wallpaper designer, the nobleman, the doctor and the working-man.

Over time, new threats in the textile industry have started to surface, such as pollution, global warming and exploitation of labour. In some cases, corporations have resorted to lesser known chemical compounds that can be just as damaging to both human health and the environment. Before making a purchase, one should document themselves every so often by consulting verified, science-backed sources, and empathise with people belonging to different social strata.



Digital simulation for the textile panel depicting Queen Victoria



Digital simulation for the textile panel depicting the wallpaper designer



Digital simulation for the textile panel depicting the nobleman



Digital simulation for the textile panel depicting the doctor



Digital simulation for the textile panel depicting the working-man

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## **Sharing colour – Sharing knowledge. A new database for synthetic dyes and related materials.**

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The research project „Weltbunt – Colourful World“ focussed on the investigation of the Dye Collection at the Niederrhein University of Applied Sciences in Krefeld, the Historic Dye Collection at the TU Dresden and the Collection of Historical Artistic Materials at the CICS, TH Köln.

Together the Dresden and Krefeld Collection represent nearly all dyes invented and developed by the chemical industry until end of the 20<sup>th</sup> century and thus broadly documents the development of this industry. Additional sample books and teaching materials are also preserved.

One of the main aims of the project was to create a database linking the two largest collections of synthetic dyes in Germany with material collections and textile artefacts and to make them available to the scientific community for the first time.

The sample books and textile materials, e.g. sample cards, dresses and accessories in the database were provided by the German Textile Museum in Krefeld, the TextileTechnikum of the Rheydt Castle Museum in Mönchengladbach and the CICS, Cologne. Other collections will be implemented in the future.

In addition to the object information, the results of the chemical analyses, e.g. FTIR and RAMAN Analyses are included in the database. With this function the database also offers a tool for the exchange of research data relating to synthetic dyes. For this implementation, new tools had to be developed to add the data in an open format, which allow the data to be stored and processed independently of the instrument software. Existing storage formats, such as JCAMP-DX, which were developed for the exchange of infrared spectra and related chemical and physical information between spectrometer Data Systems of different manufactures, did not prove to be practical.

The database system used is Faust (Land Software Development, Germany) and will be hosted by the Cologne Institute of Conservation Sciences (CICS), TH Köln. All partners will add more parts of their collections over time. But also other institutions and laboratories are welcome to share their data and research expertise in the database. This includes analytical data as well as historical information on trade names, chemical compounds or contexts of production. With this poster we would like to share the database and its unique features with you and discuss several problems of this project.

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