

# DHA38

Dyes in History  
and Archaeology

Amsterdam,  
The Netherlands

6-9 November 2019

University of  
Amsterdam

Nieuwe Doelenstraat 16,  
1012 CP Amsterdam

## CALL FOR ABSTRACTS

Deadline **15 June 2019**

Submissions to [dha38@cultureelerfgoed.nl](mailto:dha38@cultureelerfgoed.nl)

More information and conference registration at

[www.dha38.nl](http://www.dha38.nl)



Cultural Heritage Agency  
Ministry of Education, Culture and Science



UNIVERSITY OF AMSTERDAM

RIJKS MUSEUM

erfgoedAcademie

## **FINAL PROGRAMME (6-8 November)**

*Wednesday, 6 November*

17h – 19h Welcome reception and registration,

Ateliergebouw,

Hobbemastraat 22

NL-1071 ZC

Amsterdam

## Thursday, 7 November

- 9:00-9:30 Arrivals at the **University of Amsterdam Theatre**  
Nieuwe Doelenstraat 16-18  
1012 CP Amsterdam
- 9:30-9:45 Welcome
- 9:45-11:00 Session 1 – Chair: Maarten van Bommel**
- 9:45-10:05 Tannins and the weighting of silk: the effects on pigments made from silk extracts  
David Peggie & Jo Kirby
- 10:05-10:25 What is “*bruzuljoks*”? or study on the dyewood discarded on the coast of the Baltic sea  
Anete Karlson & Valda Valkovska
- 10:25-10:45 The colorful Saxon flowers and their dye sources  
Irina Petroviciu, Iulia Teodorescu, Florin Albu, Marian Virgolici, Eugenia Nagoda & Andrei Medvedovici
- 10:45-11:00 Questions
- 11:00-11:30 Coffee break\*
- 11:30-12:45 Session 2 – Chair: Dominique Cardon**
- 11:30-11:50 The materials used to create the Tahitian chief mourner’s costume and other Pacific bark cloth objects in the British Museum collection  
Diego Tamburini & Caroline R. Cartwright
- 11:50-12:10 Studies on the Central American dyestuff *Justicia spicigera*.  
Joan M. Esson, Victor J. Chen & Gregory D. Smith
- 12:10-12:30 Città Paradiso: The Purples of Dura-Europos  
Zvi Koren
- 12:30-12:45 Questions
- 12:45-13:05 Poster pitch session 1**
- 13:05-14:15 Lunch + Poster session

\* Breaks, lunch and posters session will be at:

Vox Pop

Binnengasthuisstraat 9, 1012 ZA Amsterdam

**14:15-15:30 Session 3 – Chair: Suzan Meijer**

14:15-14:35 Dyeing with lac-dye in France and England in the 18th century  
Dominique Cardon & Anita Quye

14:35-14:55 Natural Dyes in Worth Carpets at the Victoria and Albert Museum  
Laura Maccarelli, Roisin Morris & Terry Schaeffer

14:55-15:15 Comparison of Archival Documents and Analysis Results in the Materials of  
Ottoman Palace Fabrics  
Recep Karadag & Emine Torgan Güzel

15:15-15:30 Questions

**15:30-15:50 Poster pitch session 2**

15:50-16:15 Coffee break + Poster session

**16:15-17:30 Session 4 – Chair: Ana Serrano**

16:15-16:35 Lac production in north east India: The history of its trade and current  
methods of production and marketing  
Cheryl Porter

16:35-16:55 Reconstruction of Persian dyes used in manuscripts based on traditional  
recipes and development of a spectral database by non-invasive analytical  
techniques

Mojtaba Mahmoudi Khorandi, Maurizio Aceto, Monica Gulmini, Oliver Hahn,  
Samanehalsadat Ehteram, Angela Benotto & Angelo Agostino

16:55-17:15 From India with love: a non-invasive method for the identification of lac dye in  
paintings and textiles  
Maurizio Aceto

17:15-17:30 Questions

**19h Conference dinner at restaurant de Kantjil & de Tijger**

**Spuistraat 291-293, 1012 VS Amsterdam**

## Friday, 8 November

- 9h00-9h30 Arrivals at the University of Amsterdam Theatre  
Nieuwe Doelenstraat16-18  
1012 CPAmsterdam
- 09:30-10:45 Session 5 – Chair: Art Ness Proaño Gaibor**
- 09:30-09:50 The Zötl family: a tradition of dyeing in Austria  
Regina Hofmann-de Keijzer, Matthijs de Keijzer & Alfred Atteneder
- 09:50-10:10 The Burgundian Black Collaboratory: a look behind the scenes of an interdisciplinary research on black dyes  
Natalia Ortega Saez, Jenny Boulboulé & Claudy Jongstra
- 10:10-10:30 From Brilliant to Fanal - Precipitation of Triphenylmethane dyes in the early 20th century  
Rika Pause & Klaas Jan van den Berg
- 10:30-10:45 Questions
- 10:45-11:15 Coffee break
- 11:15-12:30 Session 6 – Chair: David Peggie**
- 11:15-11:35 On the set of Fellini's movies: investigating and preserving multi-material stage costumes  
Francesca Sabatini, Jacopo La Nasa, Camilla Guerrini, Isetta Tosini, Sara Bonadio, Federica Ursino, Marta Cimò, Licia Triolo & Ilaria Degano
- 11:35-11:55 The coal tar chemistry of Vincent van Gogh's ink drawings  
Frank Ligterink, Art Ness Proaño Gaibor, Johan Neevel, Sanne Berbers, Inez van der Werf, Teio Meedendorp, Rob Erdmann & Birgit Reissland
- 11:55-12:15 Conserving the Rainbow – Preservation of the Dye Collection of the Hochschule Niederrhein  
Marc Holly, Christoph Herm & Jürgen Schram
- 12:15-12:30 Questions
- 12:30-13:00 Poster pitch session 3**
- 13:00-14:15 Lunch + Poster session

**14:15-15:30 Session 7 – Chair: Zvi Koren**

14:15-14:35 Development of a Toolbox for studying the Chemistry of light-induced degradation (TooCOLD)

Iris Groeneveld, Mimi den Uijl, Govert Somsen, Freek Ariese, Peter Schoenmakers & Maarten van Bommel

14:35-14:55 Visible-excited spectrofluorimetry as a non-invasive tool for the “in situ” identification of natural dyes in historical textiles

Silvia Bruni, Margherita Longoni, Silvia De Meo, Francesca Scalzo, Angela Dibenedetto & Vittoria Guglielmi

14:55-15:15 New approach for dyes extractions with gel application of ammonia-EDTA for microextraction from textiles

Ilaria Serafini, Giulia Germinario, Alessandro Ciccola, Ludovica Ruggiero, Marco Sbroscia, Flaminia Vicenti, Claudia Fasolato, Armida Sodo, Marcella Ioele, Fabio Talarico, Paolo Postorino & Roberta Curini

15:15-15:30 Questions

**15:30-15:50 Poster pitch session 4**

15:50-16:15 Coffee break + Poster session

**16:15-17:30 Session 8 – Chair: Jo Kirby Atkinson**

16:15-16:35 New method of natural indigo reduction using Baker’s Yeast as a biocatalyst  
Younsook Shin, Kyunghee Son & Dong Il Yoo

16:35-16:55 Investigation of wars dye on blue and brown Yemeni cotton ikats

Julie H. Wertz, Richard Newman, Mark Nesbitt, Meredith Montague, Robin Hanson, Elizabeth Dospěl Williams & Mary McWilliams

16:55-17:10 Questions

17:10-17:30 Closing remarks

### Poster pitch session 1

Aurélie Mounier	Materials identification of a 18th C. high quality tapestry of Aubusson (France) by UV-VIS-NIR in situ analyses. The case of the Verdure fine of the Brülh Count's coat of arms.
Ioannis Karapanagiotis	UV-induced degradation of silk dyed with madder, cochineal and shellfish purple
Magdalena Wróbel-Szypula	The application of ATR-FTIR spectrometer in analysis of synthetic dyes produced in The "Boruta" Factory in Zgierz at the beginning of 20th century
Recep Karadag	Characterization of 19th Century Istanbul Kandilli Yazmas (hand-painted textiles)
Sarah J. Schmidtke Sobeck	Comparative Study of the Photostability and Degradation of Anthraquinone-based Dyes
Terry T. Schaeffer	An American Purple: North Carolina Cudbear

### Poster pitch session 2

Jantiene van Elk	Textile printing and dyeing : collection and research by artists and designers in the TextielMuseum
Ilaria Degano	The colours of street art: the case of Blue's mural
Riikka Räisänen	BioColour: Bio-based Dyes and Pigments for Colour Palette - Combining Traditions with Innovations
Eva Eis	A late 19 <sup>th</sup> century recipe collection " <i>Farben-Recepte</i> " of the company Heinrich Wiesel
Marcella Stenbichler	Hidden secrets behind a folding screen
Younsook Shin	Microbial Indigo Reduction by using KDB1 strain separated from Traditional Fermentation Bath

### Poster pitch session 3

Yoshiko Sasaki	Study on sample books of textile fragments from Dutch ships in the 19th century, stored in KIT Museum
Sanne Berbers	Benzylated methyl violet dye compounds structurally elucidated through UHPLC-PDA-HRMS analysis
Václava Antušková	Synthetic organic colorants in the assessment of an artwork's authenticity
Jocelyn Alcántara-García	Using Norwich Pattern books to Accomplish Non-Destructive Analysis of Textiles
Edith Sandström	Understanding colour in Renaissance embroidery: new analytical approaches
Dominique Cardon	Reds of the bronze age "civilization of the red thread" from the north cemetery in the Taklamakan desert

### Poster pitch session 4

Julia Martínez García	The organic indigo vats: the magic blue of vegetable world
Yasmine Schulenburg	How Spectroscopy helps Synthetic Textile Dyes to tell their Story
Cristina Barrocas Dias	Analysis of the velvet fabric from the royal coach of King Philip II of Portugal (17th century)
Ana Serrano	Crimson, black, silver and gold and a lavish 17th-century finding off the coast of Texel, North Holland
Natércia Teixeira	Disclosing medieval Iberian iron-gall inks recipes through the use of historically accurate reconstructions



# Tannins and the weighting of silk: the effects on pigments made from silk extracts

David Peggie<sup>1\*</sup>, Jo Kirby<sup>2</sup>

<sup>1</sup>Scientific Department, National Gallery, London

<sup>2</sup>Scientific Department, National Gallery, London (retired)

\*david.peggie@ng-london.org.uk

### Abstract

Silk was commonly degummed during processing, making it soft and lustrous but reducing its weight. Treating it with a tannin solution, commonly from oak galls, replaced weight and improved draping qualities. [1] This procedure was generally forbidden in Italian Renaissance guild regulations, however, ellagic acid from a tannin treatment is often observed during the analysis of kermes- and cochineal-dyed silks and red lake pigments derived from them. Perhaps unsurprisingly, there are very few, if any, references in Italian Renaissance dyeing literature for the weighting of silk using oak galls, other than those to dye silk black. However, in later centuries and in other parts of Europe the practice became common and 18th-century recipes give some details on the oak gall treatment, suggesting amounts of oak galls of between 3 and 12.5% by weight of silk. [2, 3]

This paper aims to clarify the link between the pigments obtained from dyed silk shearings and the weighting of the original silk using results obtained by HPLC analysis from a series of reference samples. Silk yarns were treated with an alum mordant, with and without a treatment of oak galls equivalent to 5, 15 and 50 % by weight of silk. These were dyed with cochineal and a selection were chosen for pigment preparation using a standard recipe. [4] By varying the proportion of oak galls used and the order in which galling and mordanting took place, the effects on the colour of cochineal-dyed silk, and thus on the colour of pigments obtained from them, could be investigated. Furthermore, the experiment allowed the ellagic acid, detected by HPLC analysis of the fibres or pigments, to be correlated with the amount of oak galls used in the original recipe.

### References

1. J.H. Hofenk de Graaff, *The Colourful Past: Origins, Chemistry and Identification of Natural Dyestuffs*. London, Archetype Publications Ltd, 2004, particularly pp. 286–7.
2. P.J. Macquer, *L'Art de la teinture en soie*. Paris, 1808 (first published 1763), pp. 76–8.
3. G. Tallier, *Nuovo plico d'ogni sorte di tincture*. Bologna, per il Longhi, 1786, p. 67.
4. J. Kirby, M. van Bommel, A. Verhecken and others, *Natural Colorants for Dyeing and Lake Pigments: Practical Recipes and their Historical Sources*. London, Archetype Publications Ltd, 2014, pp. 62, 100.

### What is “*bruzuljoks*”? or study on the dyewood discarded on the coast of the Baltic Sea

Anete Karlson<sup>1</sup>, Valda Valkovska<sup>2</sup>,

<sup>1</sup>Dr.hist., University of Latvia, Institute of Latvian History, Latvia\* 1

<sup>2</sup>Mg.chem., University of Latvia, Faculty of Chemistry, Latvia\*\* 2

anete.karlson@gmail.com

#### Abstract

Not only local plants have previously been used to dye textiles in lands on the coast of the Baltic Sea, including in the territory of modern Latvia. As a result of economic activity (horticulture, trade, etc.), both park and garden plants were used here, which also could be as a source for dyeing, and several types of dyewood. This study focuses on wood of foreign origin used in dyeing.

Historical sources in Latvia [1] have repeatedly mentioned non-identified sources of natural colouring matter. Among them are names that could mean different types of dyewood. They were used for red and black color, suggesting that they could be brazilwood [2] and logwood [3].

In the 19th century and earlier dyewood were imported mainly by vessels. During storms, their cargo was sometimes rinsed off from the deck. The ethnographic records show that the peasants have also used these dyewoods discarded on the beach. In most cases it is mentioned that a red colour is obtained from them, indicating to brazilwood.

Even today, the so-called “*bruzuljoki*” are occasionally rinsed out from the Baltic Sea during autumn storms on the Latvian coast. When the dyeing experiments are performed, only a violet colour can be obtained from them. What is the dyewood found today?

Phytochemical screening of methanol extracts of the wood using liquid chromatography methods showed presence of neoflavonoids (haematoxylin), isoflavonoids, flavanols, chalcones (sappanchalcone), amino acids and primary amides. Obtained results are in accordance with the literature about *H. campechianum* [4,5].

#### References

1. In Latvian press publications from the 19th century, in the records of ethnographic expeditions from various periods in the 20th century and from today's interviews.
2. *Paubrasilia echinata* (Lam.) Gagnon, H.C.Lima & G.P.Lewis, syn. *Caesalpinia echinata* Lam.
3. *Haematoxylum campechianum* L.
4. Escobar-Ramos, A., Lobato-Garcia, C.E., Zamilpa, A., Gomez-Rivera, A., Tortoriello, J., Gonzales-Cortazar, M. Homoisoflavonoids and Chalcones Isolated from *Haematoxylum campechianum* L., with Spasmolytic Activity. *Molecules*. 2017, 22, 1405.
5. Kahr, B., Lovell, S., Subramony, J.A. The Progress of Logwood Extract. *Chirality*. 1998, 10, 66–77

### The colorful Saxon flowers and their dye sources

Irina Petroviciu <sup>1\*</sup>, Iulia Teodorescu <sup>2\*</sup>, Florin Albu <sup>3</sup>, Marian Virgolici <sup>4</sup>, Eugenia Nagoda <sup>5</sup>,  
Andrei Medvedovici <sup>6</sup>

<sup>1</sup> National Museum of Romanian History (MNIR), Calea Victoriei 12, 030026 Bucharest, Romania

<sup>2</sup> The ASTRA National Museum Complex, Piata Mica 11, 550182 Sibiu, Romania

<sup>3</sup> Agilrom Scientific SRL, Sos. Pipera-Tunari 1H, 077190 Voluntari, Ilfov, Romania

<sup>4</sup> "Horia Hulubei" National Research Institute for Physics and Nuclear Engineering, IRASM, Str.  
Reactorului 30, Magurele, Romania

<sup>5</sup> University of Bucharest, "Dimitrie Brândză" Botanical Garden, Bucharest, Romania

<sup>6</sup> University of Bucharest, Faculty of Chemistry, Department of Analytical Chemistry, Bucharest,  
Romania

petroviciu@yahoo.com

#### Abstract

Confirmed since the 12th century, the Saxon community in Transylvania established there the famous Seven Fortified Towns, SiebenBurgen. The community developed in a rigorous powerful society, with clear rules, revealed in legal, economic, religious and artistic aspects. Flowers, represented embroidered on textiles or painted on wood, are the fundamental expression of the rural artistic feelings of this rigorous society. ASTRA National Museum Complex, Sibiu, Transylvania preserves a large number of objects representative for the Saxon community, including over three thousand Saxon textiles, created by the local Saxon people from Transylvania.

In the last years, dyes in textiles from Romanian collections have been studied by liquid chromatography with UV-Vis and mass spectrometric detection (LC-DAD-MS) [1]. The analytical protocol associates the information provided by the two detectors and allows distinguishing between major and minor dyes; furthermore, it facilitates a clear attribution of the dyes and biological source/sources used.

In the present study, about 60 samples from 15 objects, vestments, head dresses and interior decoration textiles, among the oldest in the Saxon collection - dated from the second half of the 19th to the beginning of the 20th century, are studied based on the above-mentioned analytical protocol. The rich color palette, the embroidery technique and the date (embroided on the object) were the main criteria for selection. Results are compared with those in previous studies, which were focused on Romanian textiles from Transylvania, also preserved in ASTRA museum. Dyes in ethnographical textiles from the other Romanian provinces, Wallachia and Moldavia, as well as literature data provided by a collection of dyeing recipes edited by the Romanian Academy in 1914, are also considered [2]. Local dye sources, such as dyer's broom, sawwort, young fustic, *Rhamnus* berries, emodin based dyes, madder and woad, are discussed together with imported colorants (carminic acid containing insects and redwood type) and early synthetic dyes.

The results obtained document the mixt rural society in Transylvania in the second half of the 19th - beginning of the 20th century and place ethnographic and other textiles in Romanian collections, in a European context.

#### References

1. I. Petroviciu, F. Albu and A. Medvedovici (2010), LC/MS and LC/MS/MS based protocol for identification of dyes in historic textiles, *Microchemical Journal* 95, 247-254
2. T. Pamfile, M. Lupescu, (1914), *Cromatica poporului român*, Socec & C. Sfetea, Bucureșt

### The materials used to create the Tahitian chief mourner's costume and other Pacific barkcloth objects in the British Museum collection

Diego Tamburini<sup>1\*</sup> and Caroline R Cartwright<sup>1</sup>

<sup>1</sup>Department of Scientific Research, The British Museum, Great Russell Street, London WC1B 3DG, UK

\* DTamburini@britishmuseum.org

#### Abstract

The British Museum houses one of the few examples of complete Tahitian chief mourner's costumes in the world. For the 250<sup>th</sup> anniversary of Captain Cook's first voyage, the costume was displayed after over 40 years in the storage. The conservation assessment of the numerous parts that compose the costume provided a unique opportunity to undertake scientific analyses of the materials used to create the costume, in particular the plant materials (wood and fibres), the natural dyes and the pigments.

Non-invasive investigations, including observations using UV light and spectral acquisitions using fibre optic reflectance spectroscopy (FORS) suggested the presence of turmeric (*Curcuma longa*) and red ochre, respectively. Several samples were then taken. Scanning electron microscopy (SEM) was used to identify the plant materials, such as paper mulberry (*Broussonetia papyrifera*) for the various barkcloth components, coconut (*Cocos nucifera*) fibres for the cordage, *Pandanus* sp. leaves for a woven hat and Pacific rosewood – or *milo* – (*Thespesia populnea*) for a wooden figurine found inside the head cape. High performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) was also used to confirm the presence of turmeric, identify the noni (*Morinda citrifolia*) dye in some red areas and an unknown red dye was also found. Raman spectroscopy finally enabled carbon black to be identified in the black areas.

The materials identified were consistent with the local sources expected to be used. However, this work reports the first scientific confirmation of the use of these materials in such a unique and precious object. These results will be complemented by a summary of the main findings obtained during a separate investigation of 36 barkcloth-related objects [1], in which both similar and different colour and fibre sources were identified, thus giving a comprehensive overview of the decorative materials used in Pacific barkcloth tradition.

#### References

1. Tamburini, D., Cartwright, C.R., Melchiorre Di Crescenzo, M., Rayner, G. Archaeol Anthropol Sci (2018). <https://doi.org/10.1007/s12520-018-0745-0>

## Studies on the Central American dyestuff *Justicia spicigera*

Joan M. Esson<sup>1\*</sup>, Victor J. Chen<sup>2</sup>, Gregory D. Smith<sup>2</sup>

<sup>1</sup> Otterbein University, Chemistry Department, 1 South Grove St, Westerville OH 43081, USA

<sup>2</sup> Indianapolis Museum of Art, Conservation Science Laboratory, 4000 Michigan Road, Indianapolis IN 46208, USA

\* jesson@otterbein.edu

### Abstract

In Central America and Mexico, natural blue dyes are obtained from the indigenous plants *Indigofera suffruticosa* and *Justicia spicigera*. While compounds in the former have been characterized, questions remain about those in *J. spicigera*. Known as *muitle* in Mexico and *sacatinta* in Guatemala, it was used in pre-Hispanic times as a dye and medicine. Some inks in the 16<sup>th</sup> century Aztec Codex Borbonicus were likely made with *muitle*, and 18th century reports describe pigments obtained from the plant at the Academy of San Carlos [1, 2]. *Muitle* extracts result in purple to bluish grey colors, but they are prone to rapid fading [3, 4].

Although previous reports identify the dye in *muitle* as indigo, more recent studies show that this is not the case. No indigotin is identified by surface-enhanced Raman spectroscopy (SERS) and high performance liquid chromatography-diode array detector (HPLC-DAD) studies [5-7]. The identities of the dye compounds have yet to be confidently determined, although suggestions include an unspecified anthocyanin or up to twelve specific anthocyanins, despite the fact that monomeric anthocyanins were not found in a study of leaf extracts [2, 9, 10].

Conclusively identifying the colorant from *muitle* may help in recognizing its use in art and artifacts, and aid in understanding why materials made using its dye are prone to fading. This study involved dyeing fabric samples with *muitle* under different conditions and analyzing the plant material, dyebath, and fabric using a variety of methods. Results from liquid chromatography-diode array detector-mass spectrometry (LC-DAD-MS), collision induced dissociation (CID), and 2-D NMR studies to characterize the components of *Justicia spicigera* will be described as well as the effects of pH and light on the colorant. Furthermore, the unique fluorescence of swatches dyed with *muitle* is proposed as a possible screening tool to identify garments containing the dye.

### References

1. Pottier, F. (2017). Etude des matières picturales du Codex Borbonicus - Apport de spectroscopies non-invasives à la codicologie, PhD Thesis, Université de Cergy-Pontoise.
2. Baquero-Pena, I. and Guerrero-Beltran, J. A. (2016). Physicochemical and antioxidant characterization of *Justicia spicigera*. Food Chemistry, 218, 305-312.
3. Klein, K. (1997). The Unbroken Thread: Conserving the textile traditions of Oaxaca. Los Angeles. The Getty Conservation Institute.
4. De Ávila A. (2009). Tejer el Arcoíris: Colorantes en el mundo. Museo Textil de Oaxaca. Mexico. Retrieved from [http://www.museotextildeoaxaca.org.mx/admin/media/images/expo\\_pdf\\_6.pdf](http://www.museotextildeoaxaca.org.mx/admin/media/images/expo_pdf_6.pdf)
5. Cardon, D. (2007). Natural Dyes. Oxford: Archetype Books.
6. Casanova-Gonzalez, E., Garcia-Bucio, A., Ruvalcaba-Sil, J. L., Santos-Vazquez, V., Esquivel, B., Falcom, T., Arroyo, E., Zetina, S., Roldan, M. L., Domingo, C. (2012). Surface-enhanced Raman spectroscopy spectra of Mexican dyestuffs. Journal of Raman Spectroscopy, 43, 1551-1559.
7. Ushida, S., Terada, T., Fukumoto, T., Kohama, Y. (2005). Properties of the colorant obtained from *sacatinta* and its behavior to dyeing. Journal of Home Economics of Japan, 56(12), 899-902.
8. Chan-Bacab, M. J., Sanmartin, P., Camacho-Chab, J. C., Palomo-Ascanio, K. B., Huitz-Quime, H. E., Ortega-Morales, B. O. (2014). Characterization and dyeing potential of colorant-bearing plants of the Mayan area in Yucatan Peninsula, Mexico. Journal of Cleaner Production, 1-10. <http://dx.doi.org/10.1016/j.jclepro.2014.12.004>.
9. Espinosa-Morales, Y., Reyes, J., Hermosin, B., Azamar-Barrios, J. A. (2012). Characterization of a Natural Dye by Spectroscopic and Chromatographic Techniques. Materials Research Society Symposium Proceedings, 1374. Doi: 10.1557/opl.2012.1377.
10. Awad, N. E., Abdelkawy, M. A., Hamed, M. A., Souleman, A. M. A., Abdelrahman, E. H., Ramadan, N. S. (2015). Antioxidant and hepatoprotective effects of *Justicia spicigera* ethyl acetate fraction and characterization of its anthocyanin content. International Journal of Pharmacy and Pharmaceutical Sciences, 7(8), 91-96.

### **Città Paradiso: The Purples of Dura-Europos**

Zvi C. Koren

The Edelstein Center for the Analysis of Ancient Artifacts,

Department of Chemical Engineering, Shenkar College of Engineering, Design and Art

12 Anna Frank St. Ramat-Gan, Israel

[zvi@shenkar.ac.il](mailto:zvi@shenkar.ac.il)

#### **Abstract**

The ancient Roman-Period site of Dura-Europos, situated near the Euphrates River in today's Syria, was a multi-ethnic and multi-religious city with coexisting pagan temple, Christian church, and Jewish synagogue – a virtual multi-cultural paradise. Though originally founded at about 300 BCE, various foreign armies have succeeded in capturing this settlement, including the Romans who conquered it in the mid-2<sup>nd</sup> century CE and occupied it for about a century, until it was finally captured by the Persian Sasanians, which led to the abrupt abandonment of this town. That last century of Roman rule over Dura-Europos yielded many archaeological artifacts, such as remains of parchment, papyrus, carved inscriptions, wall paintings of biblical scenes, and the most personal items of all – textiles.

The various extant textile fragments exhibit the typical fashions of the Roman Period, including the ever-popular clavi. These textiles were studied in detail and the results published in the famous 1945 book authored by Pfister and Bellinger. Especially noteworthy for those aficionados of purple is that a number of textile dyeings were reported to contain molluscan purple. These non-instrumental analyses were performed almost a century ago by using Pfister's famous protocol for the analysis of dyes by treating the dyeings with a series of different solvents and comparing the resulting reactions and colors with those performed on known standard dyes.

The Dura-Europos artifacts are now housed in three different international museums, in Damascus, Paris, and at Yale University (USA). In order to determine the dyestuff sources of various purple dyeings, and especially of all of those in which real molluscan purple was reported, I analyzed representative samples via HPLC. These dye analyses showed interesting results regarding the constitution of these beautiful purple dyeings, and the answer as to whether real purple is actually present in these textiles will be revealed in my talk.

### Dyeing with lac-dye in France and England in the 18th century

Dominique Cardon<sup>1\*</sup>, Anita Quye<sup>2</sup>

<sup>1</sup> CIHAM/UMR 5648/CNRS/ ISH - 14 av. Berthelot - 69363 Lyon Cédex 07, France

<sup>2</sup> Centre for Textile Conservation and Technical Art History, History of Art, 8 University Garden, University of Glasgow, Glasgow, Scotland, G12 8QH

cardon.dominique@wanadoo.fr

#### Abstract

Lac-dye was used for large scale dyeing of wool broadcloth in 18th century South of France and England. This presentation is based on our studies of French and English broadcloth dyers' books with textile sample 'patterns' and other unpublished archives. Our investigations by colorimetric measurements of patterns along with textual analysis of associated dyeing instructions show how dyers used lac dye on a large scale and the resulting color shades. Dye analysis of the patterns may reveal chemical compositional differences relating to the species of lac supplied to the dyers [1,2], but before samples are taken from this precious material evidence of historical practice, a review of analytical and dyeing literature is being undertaken to inform ethical sampling decisions [3].

#### References

1. J. Han, J. Wanrooij, M. van Bommel, A. Quye, *J. Chromatogr. A.* 2017, 1479, 87-96. doi: <http://dx.doi.org/10.1016/j.chroma.2016.11.044>.
2. R. J. Santos, Hallett, M. Conceição Oliveira, M. M. Sousa, J. Sarraguça, M. S. J. Simmonds, M. Nesbitt. *Dyes and Pigments*, 2015, 118:129-136. doi: 10.1016/j.dyepig.2015.02.024.
3. A. Quye, M. Strlič. Icon Heritage Science Group Ethical Sampling Guidance. Institute of Conservation, January 2019. Open access download from: [https://icon.org.uk/system/files/documents/icon\\_hsg\\_ethical\\_sampling\\_guidance\\_-\\_jan\\_2019.pdf](https://icon.org.uk/system/files/documents/icon_hsg_ethical_sampling_guidance_-_jan_2019.pdf)

### Natural Dyes in Worth Carpets at the Victoria and Albert Museum

Laura Maccarelli,<sup>1</sup> Roisin Morris<sup>2</sup> and Terry Schaeffer<sup>1\*</sup>

<sup>1</sup>Conservation Center, Los Angeles County Museum of Art

<sup>2</sup>Victoria & Albert Museum

lmaccarelli@lacma.org

#### Abstract

The Victoria & Albert Museum (V&A) collections include six carpet samples manufactured in the mid nineteenth century by Worth & Company of Kidderminster. All of them are Brussels weave of worsted wool with bast fibre warps. They have looped uncut wool pile and bright, multi-coloured floral patterns, cartouches inspired by jewelry motifs, or stylised fleur-de-lys designs. Most major colour groups, except blues, are represented.

The Los Angeles County Museum of Art (LACMA) owns a dyed-yarn sample book assembled by William Henry Worth - a partner in the Worth company. Recipes accompany a majority of the samples in this book, which was begun in 1842. Many samples have been characterised at LACMA by fibre optic reflectance spectroscopy, fluorescence spectroscopy and high performance liquid chromatography with a diode array detector.

Thirty-six small yarn samples from the six V&A carpets were collected and analysed using these techniques. The results have permitted comparisons to the information in the Worth book. Several similarities and some noteworthy differences have been revealed.

Most carpet colours were created with two or more dyestuffs. The majority of the book recipes also use mixtures of dyes. Cochineal, probably the only dye used alone in the carpets, was found in many reds and pinks, as it is in the book. About one-fifth of the carpet samples contained cudbear; a similar number of the book recipes also list this lichen dye.

Sandalwood and indigo were each identified in some carpet samples; these dyes are not mentioned in the book at all. Some green carpet samples contained indigo and yellow dye(s), others had indigo carmine and yellow(s). In comparison, all green recipes in the book call for indigo carmine and fustic.



# Comparison of Archival Documents and Analysis Results in the Materials of Ottoman Palace Fabrics

Recep Karadag<sup>1,2\*</sup> and Emine Torgan Güzel<sup>2</sup>

<sup>1</sup>Istanbul Aydin University, Faculty of Fine Arts, Department of Fashion and Textile Design Florya Campus, Istanbul, Turkey

<sup>2</sup>Turkish Cultural Foundation (TCF), Cultural Heritage Preservation and Natural Dyes Laboratory, Istanbul, Turkey

\*recepkaradag@aydin.edu.tr

### Abstract

Ottoman palace fabrics are very rich fabrics belonging to the sultan family and members of the palace [1]. The archival documents which contain information about the properties of the materials used or produced for the Ottoman palace from the 15-19th centuries and other materials are investigated in this study. In the archive documents, the contents of the materials in the fabrics woven in the Ottoman dynasty of these periods and the other materials, which are used for the wire, metal threads and the dyes, have been recorded and reached to the present day. The palace fabrics studied are the artifacts of the Topkapi Palace Museum which has the richest textile collection of the Ottoman Empire. The archive documents related to this in the palace were examined.

The main purpose of this study is to compare the woven textile materials in archival documents and the materials in palace fabrics which are examined by different analytical techniques. According to the results of the analysis, it was determined that the changes in the vetch and auxiliary materials used in the past. For example, 16th century was the most important period of Ottoman Empire. In the 16th century, precious metals such as gold and silver used in textile materials were replaced by materials such as zinc and copper in the 19th and 20th centuries. Again, such a change manifests itself in pattern quality. That is to say, there is a clear difference between the materials used during the rise of the Ottoman period and the materials used in the period of regression and pause. As a result of this study, a database was created for all materials used in the palace fabrics according to the archive documents and the results of the analysis.

### Reference

1. Nurhan Atasoy, Walter B. Denny, Louise W.Mackie, Hülya Tezcan, İPEK: Imperial Ottoman Silks and Velvets, TEB Publications, London, 2001.

**Lac production in north east India:  
The history of its trade and current methods of production and marketing**

Cheryl Porter

The Montefiascone Project

Venice Lodge, 55 Maida Vale, London W9 1SD, England

**Abstract**

The recent identification of lac as the main, and often the only organic red, used to paint in a large number of manuscripts and albums, for more than 500 years and over a wide geographical range, has been surprising.

This paper will give a brief history – based on records from the Cairo Geniza, the oldest synagogue in Egypt - of the trade in lac from India, via Yemen to Cairo, and from there, to al-Andalus, and later, via Constantinople to Europe.

It will also outline the fundamental changes made by the British East India Company, to its production and marketing in the 17<sup>th</sup> century. From that time (and as a result of the coming of cochineal from the newly discovered Americas) lac was no longer used to produce the dye, except for small amounts for local (Indian) dyeing and painting.

The lac dye production began again in northern India, in 1954, with a commercial proposition from the Japanese.

The main part of the paper will show details of my visit to the area in January-February this year, and explain the way that lac is produced and harvested by the hill-tribes in northeast India (Jharkhand), as well as the way it is processed and brought to market. It will also examine the way that the lac dye is produced in the Jharkhand factories.

### Reconstruction of Persian dyes used in manuscripts based on traditional recipes and development of a spectral database by non-invasive analytical techniques

Mojtaba Mahmoudi Khorandi<sup>1\*</sup>, Maurizio Aceto<sup>2</sup>, Monica Gulmini<sup>3</sup>, Oliver Hahn<sup>1</sup>, Samanehalsadat Ehteram<sup>4</sup>, Angela Benotto<sup>5</sup>, Angelo Agostino<sup>3</sup>

<sup>1</sup>Centre for the Study of Manuscript Cultures (CSMC), University of Hamburg (Germany),  
Warburgstraße 26, D-20354 Hamburg

<sup>2</sup>Dipartimento di Scienze e Innovazione Tecnologica (DISIT), Università degli Studi del Piemonte Orientale, viale T. Michel, 11 - 15121 Alessandria, Italy

<sup>3</sup>Dipartimento di Chimica, Università degli Studi di Torino, via Giuria, 7 - 10125 Torino, Italy

<sup>4</sup>University of Bologna, Italy "Alma Mater Studiorum Università di Bologna Campus di Ravenna"

<sup>5</sup>Museo di Arte Orientale (MAO), via San Domenico, 11 - 10122 Torino, Italy

\* mojt.mahmoudi@gmail.com

#### Abstract

According to the antique Persian book resources which include information about different stages of making manuscripts, it is quite obvious that a large number of dyes were used to decorate the Persian manuscripts: for example, to colour sheets of paper, dyes were applied on the paper to create the favourite tonality of colour; pigments were mixed with dyes to render a shining surface or sometimes the dyes were separately used to create the tonality for a particular colour [1].

The lack of non-invasive effective methods to recognize the dyes in the manuscripts, the faded dyes due to their organic nature, and the lack of spectral databases of the dyes have led to the fact that there have been a few studies examining precisely dyes in Persian manuscripts. In this research, in order to build up a spectral data-base devoted to dyes possibly employed in Persian manuscripts that were not studied before, a set of mock-up samples was prepared by considering natural dyestuffs indicated in the comprehensive book of "Gulistan-i Hunar (Rose Garden of Art)" written by Qadi Ahmad at early XVII century, which collects articles dealing with penmanship, ink making, papers, gilding and book binding [4]. The paper employed as a support was obtained from hemp by miming historical procedures whereas Mallow (*Althea officinalis*), Anemone (*Anemone coronaria*), Henna (*Lawsonia inermis*), Barberry (*Berberis vulgaris*), Rhubarb (*Rheum undulatum*), Turmeric (*Curcuma longa*), Red onion skin, Indigo (*Indigofera tinctorial*), and Saffron (*Crocus sativus*) [2] were considered as sources of dyes. The plants were treated according to ancient recipes to extract the dyes and used to dye or paint the paper substrate. Fiber Optics Reflectance Spectroscopy (FORS) [3] and Fiber Optics Molecular Fluorimetry (FOMF) were then employed to record the spectral features of the mock-up samples. The information obtained on mock-ups were then considered for the interpretation of reflectance and fluorescence spectra obtained after analyzing the dyes in some Persian manuscripts.

#### References

1. Nadjib Mayil Harawi, 1993, Art of bibliopegy in Islamic civilization, Printing and publishing department of Astan Quds Razavi, Mashhad, Iran.
2. D. Cardon, *Natural Dyes, sources, tradition, technology and science*, Archetype Publications Ltd, London (2007).
3. M. Aceto, A. Agostino, G. Fenoglio, A. Idone, M. Gulmini, M. Picollo, P. Ricciardi, J.K. Delane, 2014, Characterisation of colourants on illuminated manuscripts by portable fibre optic UV-visible-NIR reflectance spectrophotometry, *Analytical methods*, DOI: 10.1039/c3ay41904e
4. M. BARKESHLI, 2009. Historical and scientific analysis of Iranian illuminated manuscripts and miniature painting. *Golestan-e Honar. Quarterly on the History of Iranian Art and Architecture*, 5 (2(16)).

### From India with love: a non-invasive method for the identification of lac dye in paintings and textiles

Maurizio Aceto<sup>1\*</sup>, Elisa Calà<sup>1</sup>, Fabio Gosetti<sup>1</sup>, Mojtaba Mahmoudi Khorandi<sup>2</sup>, Monica Gulmini<sup>3</sup>, Patrizia Davit<sup>3</sup>, Elaine Sheldon<sup>4</sup>, Cheryl Porter<sup>5</sup>

<sup>1</sup> 1Dipartimento di Scienze e Innovazione Tecnologica (DISIT), Università del Piemonte Orientale, viale T. Michel, 11 - 15121 Alessandria, Italy

<sup>2</sup> Centre for the Study of Manuscript Cultures (CSMC), University of Hamburg (Germany)

<sup>3</sup> Dipartimento di Chimica, Università degli Studi di Torino, via Giuria, 7 - 10125 Torino, Italy

<sup>4</sup> The John Rylands Library, The University of Manchester, 150 Deansgate, Manchester M3 3EH, UK

<sup>5</sup> Montefiascone Conservation Project, Montefiascone (VT)

\* maurizio.aceto@uniupo.it

#### Abstract

*Lac dye* or *Indian lac* is the name given to the dye extracted from *Kerria lacca* scale insects. Its colour is a beautiful red that was used for painting, from at least the 3rd century BC [1] and for dyeing, since at least the Vedic period (1500-500BC) [2]. In the past, it has been difficult to date and locate the use of *lac dye*, since it is not easy to identify, except by means of HPLC - which can identify the main components, i.e. laccaic acids A, B, C and D [3]. Microspectrofluorimetry is another powerful and selective technique that has recently been used to identify lac [4]. Unfortunately, neither of these techniques is appropriate for analysing illuminated manuscripts if/when a non-invasive system is required. In addition, FT-IR, Raman, and XRF spectrometry are unable to distinguish among the various dyes from scale insects.

In this research we examine the possibilities of using UV-Visible diffuse reflectance spectrophotometry with fibre optics (FORS), a totally non-invasive technique, to distinguish between lac dye and the other scale insect dyes. The research examines the position of two absorption bands in the reflectance spectrum, and notes that such bands occur at ca. 520/560 nm in most scale insect dyes, whilst lac dye exhibits a bathochromic shift, so that the absorption bands occur at 530-535/565-575 nm. The analysis has been confirmed with HPLC-MS/MS on a number of samples previously analysed using FORS: in all cases, working from samples of diameter < 1mm taken from miniatures or from textiles, we obtained the selective identification of laccaic acids A, B, and C. The method is particularly suited for the analysis of textiles, easel paintings, and especially painted miniatures in manuscripts. Real cases concerning Mughal miniatures are presented.

#### References

1. J. Dyer, D. Tamburini, S. Sotiropoulou, The identification of lac as a pigment in ancient Greek polychromy - the case of a Hellenistic oinochoe from Canosa di Puglia, *Dyes and Pigments*, 149 (2017), pp. 122-132.
2. D. Cardon, *Natural Dyes, sources, tradition, technology and science*, Archetype Publications Ltd, London (2007).
3. S.V.J. Berbers, D. Tamburini, M.R. van Bommel, J. Dyer, Historical formulations of lake pigments and dyes derived from lac: A study of compositional variability, *Dyes and Pigments*, 170 (2019), <https://doi.org/10.1016/j.dyepig.2019.107579>.
4. M. Vieira, P. Nabais, E.M. Angelin, R. Araújo, J.A. Lopes, L. Martín, M. Sameño, M.J. Melo, Organic red colorants in Islamic manuscripts (12th-15th c.) produced in al-Andalus, part 1, *Dyes and Pigments*, 166 (2019), pp. 451-459.

### The Zötl family: a tradition of dyeing in Austria

Regina Hofmann-de Keijzer<sup>1</sup>, Matthijs de Keijzer<sup>1</sup>, Alfred Atteneder<sup>2</sup>

<sup>1</sup> Robert Lachgasse 2, 1210 Vienna, Austria

<sup>2</sup> Färbermuseum Gutau, St. Leonharderstraße 3, 4293 Gutau, Austria

\* r.hofmann-de.keijzer@a1.net

#### Abstract

The Mühlviertel, a region north of the Danube and south of the Bohemian Forest was known for its flax cultivation since the 13<sup>th</sup> century [1]. After the annexation of Lombardy and Venetia to Austria in 1815, Milanese merchants opened textile factories in Haslach and Helfenberg.

From the 16<sup>th</sup> century many generations of the Zötl family were master-dyers. In 1825 and 1826 Josef Zötl (1806-1871) had his journeyman years. Travelling through Austria-Hungary, Italy, Switzerland, Germany and England he sent 23 letters to his parents and returned home to the Mühlviertel with many dyeing recipes. In 1827, he wrote his recipe book containing 215 recipes dealing with the dyeing of wool, silk, linen and cotton and with printing. In these recipes 24 natural dyestuffs are mentioned, such as weld, Persian berries, young fustic, old fustic, quercitron, cochineal, dyer's madder, brazilwood, woad, indigo, logwood and galls. He also came in contact with more modern dyeing methods using indigo carmine for dyeing blue and Prussian blue for printing.

His son Josef Zötl (1836-1925) had his journeyman years in Austria-Hungary in 1858 and 1859 and wrote also a recipe book. While his father collected as many recipes as possible, he focused on dyeing of wool and textile printing. The majority of his 48 recipes concerns printing pastes. He mentions eleven natural dyestuffs, among them weld, old fustic, quercitron, cochineal, dyer's madder, brazilwood, indigo, logwood and catechu. In 1868 he bought the dyer's house in Gutau, which came later in the hands of his daughter Chlotilde Zötl (1877-1962), the first female master-dyer in Austria. Her daughter Margarethe Krennbauer, born Zötl (1904-1995) was the last master-dyer in the dyer's house of Gutau specializing in blue printing and later in dyeing with synthetic dyes. In 1968 the dyer's house closed and since 1982 a dyer's museum is located in this building.

#### References

1. Bernhard Heindl (Ed.), Textile-Landschaft Mühlviertel, Fidelis Druck GmbH, 4020 Linz, ISBN 03-901100-17-2, 1992.

### **The Burgundian Black Collaboratory: a look behind the scenes of an interdisciplinary research on black dyes**

Natalia Ortega Saez <sup>1\*</sup>, Jenny Boulboulé<sup>2</sup>, Claudy Jongstra<sup>3</sup>

<sup>1</sup> University of Antwerp, Faculty of Design Sciences, Heritage Department, Campus Mutsaard, Blindestraat 9, 2000 Antwerp, BE

<sup>2</sup> Utrecht University, Department of History and Art History, Drift 15, 3512 B5 Utrecht, NL

\* natalia.ortegasaez@uantwerpen.be

#### **Abstract**

This presentation will take a look behind the scenes of a collaborative research between 1) a museum, Hof van Busleyden, 2) academic research groups: Artechne (University Utrecht & University of Amsterdam), the Rijksmuseum, Cultural Heritage Agency of the Netherlands, the Heritage Department of the University of Antwerp, and 3) a contemporary artist, Studio Claudy Jongstra.

During this research on black dyes different initiatives with a focus on re-making or re-enacting of black dye recipes were undertaken. The University of Antwerp held a summer school on Burgundian Blacks in July 2019. During this week participants focused on black colored art materials such as dyes inks and pigments [1]. In January 2019 a three-day workshop hosted by Studio Claudy Jongstra on a Frisian farm was organized [2]. An international team of experts and scholars worked on the colour black and made a series of reconstruction experiments based on a selection from a corpus of black dyeing recipes that were collected prior to the workshop. The aim of this workshop was to substantially contribute to the preparatory research for the exhibition project 'Back to Black at the museum Hof van Busleyden (Malines, Belgium) [3].

This interdisciplinary project resulted in the re-making or re-enacting of black dye recipes found in premodern manuscripts and printed books in order to better understand the practical dyeing, the feasibility of the recipe and to assess broader information on historical techniques, methodology and used ingredients of Burgundian black dyes. This project also inspired master dyers from studio Claudy Jongstra who reinterprets the centuries-old recipes in contemporary textile art work as a dialogue between the past and the present [4].

#### **References**

1. <https://www.uantwerpen.be/en/summer-schools/roohts/>
2. <https://artechne.wp.hum.uu.nl/workshops/burgundian-black/>
3. <https://www.hofvanbusleyden.be/back-to-black>
4. <https://www.e-flux.com/announcements/228484/back-to-black/>

# From Brilliant to Fanal - Precipitation of Triphenylmethane dyes in the early 20<sup>th</sup> century

Rika Pause<sup>1\*</sup>, Klaas Jan van den Berg<sup>1</sup>

<sup>1</sup> Rijksdienst voor het Cultureel Erfgoed/ Cultural Heritage Agency of the Netherlands

\*rika\_pause@web.de

### Abstract

In 1958, Fuch sine was the second organic dye that was discovered and produced industrially.[1] It was the first representative of the class of Triphenylmethane dyes, that became very popular for their brilliant shades and high tinting strength, not only in the field of textile and paper dyeing, but also for the pigment industry.

However, their low lightfastness, both in laked and in dye form, prompted ongoing developments and continued search for new precipitation methods. Trying to achieve a high level of lightfastness, while maintaining the intense and bright hue was complex. Several techniques of precipitation were developed, resulting in varying characteristics of the final product, but never merging the desired properties of lightfastness and brilliance.[2] In 1913, two chemists succeeded in developing a new method for the precipitation of triphenylmethane dyes at the laboratories of the German pigment producer BASF, resulting in the 'Fanal' pigments.[3] Finally, this precipitation method improved lightfastness, while keeping the pigment's brilliant hue and tinting strength.[4]

It is therefore not surprising that these pigments were considered by artists' paint producers, such as the Dutch manufacturer Talens, where the Fanal pigments build a frequent part within various paint production recipes. This research aims to link these pigments with the corresponding Talens artists' paints and clarify the pigments' general significance for artists' paint production in the early 20<sup>th</sup> century. In addition, their fastness and ageing properties will be examined, measured by current standards.

This paper will focus on the examination of historical pigment and paint recipes from the Talens and BASF archives, combining them with results from technical analysis from archival samples. The production steps and development of pigment precipitation processes and paint manufacturing will be outlined, to address possibilities of reconstruction.

### References

1. Weyer, Jost: *Geschichte der Chemie Band II – 19. und 20. Jahrhundert*, Springer Spektrum, 2018.
2. Jennison, Francis H.: *The manufacture of lake pigments from artificial colours*, London, Scott Greenwood & Son, 1900.
3. Friedländer, Paul: *Fortschritte der Teerfarbenfabrikation und verwandter Industriezweige*, Berlin, Springer, 1877-1921.
4. Wagner, Hans: *Die Körperfarben in Chemie in Einzeldarstellungen, Band XIII, wissenschaftliche Verlagsgesellschaft m. b. H., Stuttgart, 1928.*

### On the set of Fellini's movies: investigating and preserving multimaterial stage costumes

Francesca Sabatini\*<sup>1</sup>, Jacopo La Nasa<sup>1</sup>, Camilla Guerrini<sup>1</sup>, Isetta Tosini<sup>2</sup>, Sara Bonadio<sup>3</sup>,  
Federica Ursino<sup>3</sup>, Marta Cimò<sup>2</sup>, Licia Triolo<sup>2</sup>, Ilaria Degano<sup>1</sup>

<sup>1</sup> Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Pisa, Italy

<sup>2</sup> MiBAC, Opificio delle Pietre Dure, Firenze, Italy

<sup>3</sup> Restorers (graduated from OPD)

\* f.sabatin4@gmail.com

#### Abstract

Since the second half of 19th century, textiles production was changed both from the aesthetic point of view and from the performances and durability of the materials. New fabrics were introduced, characterised by lower production costs and tailored features, while bright synthetic organic molecules were adopted for dyeing the new textiles. This wave of innovation led to industrial products whose chemical proprieties were unknown and unexplored.

This work aims at characterizing the composition of two stage costumes used in Fellini's movies, recently restored in the framework of two diagnostic and conservation thesis projects at the Opificio delle Pietre Dure. One is a bishop's tunic worn in the movie "Roma" (1972) and the other is the beautiful dress of "the golden lady" in "Il Casanova di Federico Fellini" (1976). The project was undertaken in view of the opening in Rimini of a Museum dedicated to the famous Italian director.

To identify the fibers used for the manufacturing, a reference database was created analyzing several synthetic fibers by Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Pyrolysis Gas Chromatography with Mass Spectrometry (Py-GC/MS). Liquid Chromatography coupled with Diode Array Detector and high-resolution mass spectrometry (HPLC-DAD-ESI-Q-ToF) was employed for dyes characterization. The analytical approach allowed us to disclose the composition of the costumes constituted by synthetic and artificial fibers dyed with last generation synthetic dyes. Different fabrics and various formulations were employed for different elements and hues in the dresses. The simultaneous study of both the fibers and the dyes points out the importance of their mutual compatibility and possible interactions especially after ageing.

The results collected on these multi-material objects were fundamental to fine-tune an effective restoration aimed at removing or minimizing the damages due to ageing or poor conservation conditions, and to inform preventive conservation and exhibition strategies.



### The coal tar chemistry of Vincent van Gogh's ink drawings

Frank Ligterink<sup>1\*</sup>, Art Ness Proaño Gaibor<sup>1</sup>, Johan Neevel<sup>1</sup>, Sanne Berbers<sup>1</sup>, Inez van der Werf<sup>1</sup>, Teio Meedendorp<sup>2</sup>, Rob Erdmann<sup>3</sup>, Birgit Reissland<sup>1</sup>

<sup>1</sup> Rijkserfgoedlaboratorium, Cultural Heritage Agency of the Netherlands / Amsterdam, The Netherlands

<sup>2</sup> Van Gogh Museum / Amsterdam, The Netherlands

<sup>3</sup> University of Amsterdam, The Netherlands

\* f.ligterink@cultureelerfgoed.nl

#### Abstract

Essentially all ink drawings made by Van Gogh no longer show their original vivid colors. They have faded or turned to brown, making it difficult to appreciate the full qualities of Van Gogh as a draftsman. Several years ago, the NWO-Science4Arts project ReViGo therefore set out to digitally reconstruct the original color appearance of these important drawings, based on interdisciplinary scientific modeling. This research goal turned out more difficult and more interesting than anticipated.

Our team has reported earlier [1] about a specially developed micro sampling and monitored extraction technique that can be used in combination with UHPLC-PDA. It is now possible to take ink samples, albeit small, from drawings without causing visible damage. The ink sample chromatograms make apparent that Van Gogh was using inks that contain complex mixtures of many red to blue aniline dye components. These violet coal tar dyes with their unprecedented bright colors must have been attractive to the color-minded artist. Similarly complex compositions are typical for early synthetic industrially produced coal tar dyes due to use of non-pure substances and multiple reaction pathways.

Our analytical results thus invoke exciting new questions and further technical challenges. Do varying ratios of chromatographic distinct dye components in the ink samples indicate that Van Gogh was using several inks, perhaps even within single drawings? Can we infer which specific dyes are present?

Answering these questions requires intricate understanding of the rapidly evolving, and now partly obsolete, technology of late 19<sup>th</sup> century coal tar dye synthesis and ink production [2,3,4]. Recently our laboratory acquired a high resolution mass-spectrometry Orbitrap system which allows molecular structure elucidation of chromatographic components [5,6]. How a comprehensive UHPLC-PDA-MS analysis of approximately sixty early twentieth century historic blue-red aniline dyes helps to answer our burning questions is reported in this presentation.

#### References

- [1] Proaño Gaibor A, Neevel H, Ligterink F, Reissland B, Geldof M. Use of a new sampling technique for identification of 19th century inks for drawing and writing. In: Dyes in history and archaeology 35, 2016.
- [2] Reissland B, Proaño Gaibor A, Ligterink F, Neevel H. Exploring the late 19th-century landscape of ink manufacturing via a collection of 90 bottles. In: Proceedings of ICOM-CC 18th Triennial Conference, Copenhagen: 2017.
- [3] Schultz G. Die Chemie des Steinkohlentheers mit besonderer Berücksichtigung der künstlichen organischen Farbstoffe - Zweiter Band: Die Farbstoffe. Dritte vollständig umgearbeitete Auflage. Friedrich Vieweg und Sohn; 1901.
- [4] Travis AS. The rainbow makers: The origins of the synthetic dyestuffs industry in western Europe. Lehigh University Press; Associated University Presses; 1993.
- [5] Degano I, Sabatini F, Braccini C, Colombini MP. Triarylmethine dyes: Characterization of isomers using integrated mass spectrometry. Dyes and Pigments 2019;160:587–96.
- [6] Berbers S., Werf I van der, Proaño Gaibor A, Reissland B, Ligterink F, Neevel J. Decoding historical methy violet reference samples with UHPLC-DAD-MS/MS and XRF analysis. In: Technart 2019 - book of abstracts, 2019, p. 103.

### Conserving the Rainbow – Preservation of the Dye Collection of the Hochschule Niederrhein

Marc Holly <sup>1,2\*</sup>, Christoph Herm <sup>2</sup>, Jürgen Schram <sup>1</sup>

<sup>1</sup> Hochschule Niederrhein- Niederrhein University of Applied Sciences Faculty of Chemistry -  
Instrumental Analysis, Frankenring 20, D-47798 Krefeld

<sup>2</sup> Hochschule der bildenden Künste Dresden – Dresden University of Fine Arts

\* marc.holly@hs-niederrhein.de

#### Abstract

Subject of this ongoing research is the historical Dye Collection at the Niederrhein University of Applied Sciences at Krefeld, Germany which is one of the biggest and oldest collections of this type. It was established already in the 1860s and today comprises about 10,600 colorants. The collection was gathered in the precursor institution, the School for Dyeing and Finishing, Krefeld (1883 – 1947). It represents nearly all dyes invented by the (German) chemical industry until end of the 20th century and thus broadly documents the development of this industry. Additional sample books and teaching materials are also preserved.

One aim of the ongoing research project “Weltbunt” (Colourful World) is to develop a collection based conservation concept. Due to their unique character dye collections do not fit into established conservation genres. All factors of deterioration must be identified carefully to preserve the dye powders in their original state. The dye powders, liquids or crystals are stored in their original and unique glass bottles, metal or plastic containers, which also needs to be conserved. Traditional conservation methods have to be extended or modified to fit all needs of the collection. Generally, best practice approaches for the conservation of dye collections are being developed of which first results are presented here.

The condition of the dyes after more than 100 years cannot be defined easily. Of those dyes that are not produced until today the original state only can be assumed and their degradation must be classified carefully. The question of authenticity and originality often plays an important role when dealing with historic objects, but is most important when we look at the collection as a reference for analytical chemistry. For this reason the dye collection in Krefeld will be compared to other dye collections, e.g. the Historic Dye Collection of the Dresden Technical University.

### Development of a Toolbox for studying the Chemistry of light-induced degradation (TooCOLD)

Iris Groeneveld<sup>1</sup>, Mimi den Uijl<sup>2</sup>, Govert Somsen<sup>1</sup>, Freek Ariese<sup>1</sup>, Peter Schoenmakers<sup>2</sup>, Maarten van Bommel<sup>2,3</sup>

<sup>1</sup>Bioanalytical Chemistry, Vrije Universiteit Amsterdam, The Netherlands, i.groeneveld@vu.nl;

<sup>2</sup>Faculty of Science, University of Amsterdam, The Netherlands;

<sup>3</sup>Faculty of Humanities, University of Amsterdam, The Netherlands

#### Abstract

Many organic compounds change under the influence of (UV) light. Sometimes this is beneficial, for example in water purification, but in many other cases this is undesirable, for example when cultural-heritage objects fade, affecting their esthetical value, or when healthy food ingredients (e.g. vitamins) degrade or when undesirable flavours are formed. Studying photochemical conversion is challenging and can be very time consuming. Often it is difficult to establish a strong link between the degradation products and the starting materials which results in poor degradation-prediction models.

An innovative, high-resolution and fully orthogonal system is developed to study degradation of a wide range of mixture components under the influence of light. Complex mixtures can be separated on a High Performance Liquid Chromatography (HPLC) system after which components can selectively be trapped, either separately or simultaneously in a light-induced degradation (LID) cell. For this cell we will make use of a Liquid Core Waveguide (LCW) which is typically a small inner diameter tubing made of Teflon. When the tubing is filled with a liquid having a higher refractive index than the tubing material, it will start to act as a fiber, thus guiding the incoming light through the tubing into the direction of the detector which is placed at the end of the LCW tubing. Using this technique, trapped analytes can be illuminated continuously by means of lasers or LED's at any desired wavelength(range). Other detection methods such as Raman or absorption spectroscopy will be implemented as well to observe the degradation process on a molecular level in a real-time fashion.

Eventually, when the photo-degradation is satisfactory, the sample is sent to a second HPLC-MS system to separate and identify the degradation products that were created in the LID cell. This fully on-line set-up will make it possible to determine existing links between starting compounds and degradation products faster and more easily. The TooCOLD application will be applied on samples from cultural heritage, food and food packaging materials, and on drinking water.

### Visible-excited spectrofluorimetry as a non-invasive tool for the “in situ” identification of natural dyes in historical textiles

Margherita Longoni<sup>1</sup>, Silvia De Meo<sup>1</sup>, Francesca Scalzo<sup>1</sup>, Angela Dibenedetto<sup>1</sup>, Vittoria Guglielmi<sup>1</sup>,  
Silvia Bruni<sup>1\*</sup>

<sup>1</sup> Università degli Studi di Milano, Dipartimento di Chimica, via C. Golgi 19, 20133 Milano (Italy)

\* silvia.bruni@unimi.it

#### Abstract

For the identification of natural dyes in ancient textiles laboratory analyses are usually employed requiring the extraction of the dyes from small samples of the textile fibre. On the other hand, the non-invasive techniques commonly applied to artworks allow to recognise easily most inorganic pigments, but are of less use for organic dyes.

Therefore, a method based on the use of visible-excited fluorescence spectra has been developed in our research group for the “in situ” identification of such dyes in ancient textiles. While spectrofluorimetry has already been exploited to such aim, very few examples are reported of its application on artefacts in the museums. Moreover, the wavelength of the emission maximum is commonly considered for identification purposes, while we could demonstrate that the use of the whole spectral information is much more effective to this goal [1].

A previous study was performed on red dyes by using laser exciting radiation [2]. The present one is based instead on the application of a more versatile light source, allowing the analysis of colorants of different tints.

First of all, the method was tested on mock samples of wool and silk threads dyed with a wide number of natural dyes of different hues. Multivariate analysis of spectral data allowed to obtain a satisfying differentiation of the various dyes.

Finally, the analytical protocol was employed for the investigation of dyes in historical textiles belonging to Milanese museums, including several tapestries dating to the 16<sup>th</sup>-17<sup>th</sup> century, silk and velvet fabrics. The choice of the artefacts was partly based on the availability of literature data [3] concerning previous laboratory analyses of dyes on the same textiles, in order to provide a cross-validation of the assignments put forward by means of the non-invasive technique.

#### References

1. Zaffino C., Bertagna M., Guglielmi V., Dozzi M.V., Bruni S., In-situ spectrofluorimetric identification of natural red dyestuffs in ancient tapestries, *Microchemical Journal*, 132, 77-87 (2017).
2. Clementi C., Miliani C., Romani A., Favaro G., Santamaria U., Morresi F., Mlynarska K., Favaro G., In-situ fluorimetry: a powerful non-invasive diagnostic technique for natural dyes used in artefacts. Part II. Identification of orcein and indigo in Renaissance tapestries, *Spectrochimica Acta Part A*, 71, 2057-2062 (2019).
3. Pertegato F., *Il restauro degli arazzi*, Nardini, Fiesole (1996).

### New approach for dyes extractions with gel application of ammonia-EDTA for microextraction from textiles

Ilaria Serafini<sup>1\*</sup>, Giulia Germinario<sup>2</sup>, Alessandro Ciccola<sup>1</sup>, Ludovica Ruggiero<sup>3</sup>, Marco Sbroscia<sup>3</sup>, Flaminia Vicenti<sup>1</sup>, Claudia Fasolato<sup>4</sup>, Armida Sodo<sup>3</sup>, Marcella Ioele<sup>2</sup>, Fabio Talarico<sup>2</sup>, Paolo Postorino<sup>5</sup>, Roberta Curini<sup>1</sup>

<sup>1</sup>Dept. Chemistry, <sup>5</sup>Dept. Physics, University of Rome "Sapienza", Piazzale Aldo Moro 5, 00185, Rome (Italy)

<sup>2</sup>Istituto Superiore per la Conservazione e il Restauro, via di San Michele 25, 00153, Rome (Italy)

<sup>3</sup>Dept. Science, University "Roma Tre", via della Vasca Navale, 84, 00146, Roma (Italy)

<sup>5</sup>Dept. Physics and Geology, University of Perugia, via Alessandro Pascoli, 06123, Perugia (Italy)

\* ilaria.serafini@uniroma1.it

#### Abstract

Cultural heritage represents one of the most stimulating and challenging field in scientific research, due to the complexity of the matrices and the multi-technical approach that they require. A clear example of this approach is represented by natural dyes analysis.

Their identification requires an analytical protocol that includes, as first step, non-invasive or micro-invasive techniques (such as FORS, SERS, FTIR) for discriminating between different matrices. Then, validation and implementation of chemical information are achieved with chromatographic techniques, coupled with high resolution mass spectrometry or PDA [1]. Recently, it has been tried to overcome the step of microsampling, thanks to the potentiality of chemical gels, loading with extraction solution [2].

We describe the test of two gel substrates and a mild basic solution for the extraction of dyes from historical textiles, in terms of efficiency/efficacy and versatility. This approach was tested on wool yarns dyed with madder, cochineal and indigoids. For what concerns gel substrates, considering their widespread use in this field, Agar and Nanorestore<sup>®</sup> gel have been evaluated. These were soaked in the ammonia-EDTA solution as proposed in [3]. The ammonia method guarantees a good yield and the maximization of the information concerning the chemical pattern [3]. The dyes-extracting substrates were then analyzed with Raman and Surface-Enhanced Raman spectroscopy (SERS), while the fraction re-extracted from them were examined with (U)HPLC-HRMS.

For this latter, an improvement will be proposed, revising the extraction steps, improving the clean-up working on reducing volumes of extraction and the sample needed, but ensuring enrichment factor from 20 to 60 times. This clean-up will be performed through the DLLME technique [4]. Finally, the procedure was tested on a real case, dyed in red: an ancient textiles in wool in restoration at the "Istituto Superiore per la Conservazione e il Restauro".

#### References

1. M. Aceto, A. Agostino, G. Fenoglio, A. Idone, M. Gulmini, M. Picollo, P. Ricciardi, J. K. Delaney, *Analytical Methods*, 2014, DOI: 10.1039/c3ay41904e
2. C. Lofrumento, M. Ricci, E. Platania, M. Becucci, E. Castellucci, *Journal of Raman Spectroscopy*, 2013, 44 (1), 47-54
3. I. Serafini, L. Lombardi, G. Vannutelli, C. Montesano, F. Sciubba, M. Guiso, R. Curini, A. Bianco, *Microchemical Journal* 134 (2017) 237–245.

### New method of natural indigo reduction using Baker's Yeast as a biocatalyst

Kyunghee Son<sup>1</sup>, Dong Il Yoo<sup>2</sup>, Younsook Shin<sup>1\*</sup>

<sup>1</sup>Clothing and Textiles, <sup>2</sup>Polymer Science and Engineering, Chonnam National University, Yongbong-dong, Buk-gu, Gwangju 61186, Korea

E-mail: yshin@jnu.ac.kr

#### Abstract

The yeast strain (*Saccharomyces cerevisiae*) is known to produce aldo-keto reductase that promotes the reduction of carbonyl groups, and is widely used as a biocatalyst for the reduction of organic synthesis[1]. In the traditional indigo dyeing of Korea, makgeolli(Korean fermented rice wine) or sikhye(Korean rice beverage) was added to activate fermentation. With interest in this, in a previous research, yeast strains were separated from makgeoll and the baker's yeast powder, cultured, and used for indigo reduction. The possibility of indigo reduction with yeast strain was confirmed. And it was found that pH among the reduction conditions was the most important factor in obtaining maximum color strength[2].

In this study, we explored baker's yeast for a biocatalyst in indigo fermentation dyeing. The pH of the indigo dye bath was controlled to maintain the high reducing power. In addition, repeated dyeing was carried out at optimum pH condition to obtain the fabric samples with various strength of blue color. The reduction power was evaluated as color yield(K/S value) of the dyed fabrics and oxidation/reduction potential(ORP) of dye bath. When the pH of dye bath was controlled constant at 10.5, the maximum dye uptake was obtained on 10th day(K/S 17.8) and the reduction power was maintained for more than 70 days. Various strength of blue colors in the range of K/S 17.6~28.4 for cotton, ramie, wool, and nylon fabric were successfully achieved by repeated dyeing. According to microscopic observation, the viability of yeast was maintained at pH 10.5 for more than 70 days. From the obtained results, baker's yeast can be used as a biocatalyst in natural indigo reduction.

#### Acknowledgements

This work was supported by the National Research Foundation of Korea(NRF) grant funded by the Korea government (Ministry of Science, ICT and Future Planning) in 2019 (No. 2017R1A2B400955).

#### References

1. Y. Lee and K. Kim, J. Life Science, **16**, 375 (2006).
2. Y. Shin, K. Son, and D. I. Yoo, Textile Coloration and Finishing, **26**, 237-241(2014).

## Investigation of *wars* dye on blue and brown Yemeni cotton ikats

Julie H. Wertz<sup>1\*</sup>, Richard Newman<sup>2</sup>, Mark Nesbitt<sup>3</sup>, Meredith Montague<sup>2</sup>, Robin Hanson<sup>4</sup>, Elizabeth Dospěl Williams<sup>5</sup>, Mary McWilliams<sup>1</sup>

<sup>1</sup>Straus Center for Conservation and Technical Studies, Harvard Art Museums

<sup>2</sup>Museum of Fine Arts, Boston MA

<sup>3</sup>Royal Botanic Gardens, Kew UK

<sup>4</sup>Cleveland Museum of Art, Cleveland OH

<sup>5</sup>Dumbarton Oaks, Washington D.C.

\* julie\_wertz@harvard.edu

### Abstract

During the Abbasid caliphate, Yemeni weavers produced distinctive plain-woven cotton *ikat* textiles in blue, brown, and natural white shades, sometimes with gilt inscriptions [1]. While it is fairly straightforward to identify the blue dye as indigo, very little attention has been paid to complementary brown dye named *wars*. *Wars*, also called *waras* or *warrus*, is the English transliteration of the Arabic name for a dye harvested and used primarily around the Gulf of Aden region [2]. Inconsistencies persist in the literature [3] and in general knowledge [4] about the precise botanical identity of *wars*. In art historical literature, the plant source named is *Memecylon tinctorium*, a likely misattribution probably originating from Pfister in 1936. More recent research has determined *wars* is *Flemingia grahamiana* or *F. rhodocarpa* [5]–[7]. Compounds from *Flemingia* have been characterised in the context of natural products [8]–[12], but no analytical study of textiles said to be dyed with *wars* has confirmed the identity of the dye and whether it comes from *Flemingia*. This research investigates the dyes on blue and brown fibres from ikats in the collections of the Museum of Fine Arts, Boston the Cleveland Museum of Art, and Dumbarton Oaks using high-performance liquid chromatography with mass spectrometry (HPLC-MS). Botanical reference materials from Kew Gardens are analysed for comparison to establish the identity and composition of *wars* dye.

### References

- [1] C. Bier, *A Calligrapher's Art: Inscribed Cotton Ikat from Yemen*. Washington DC: The Textile Museum, 2001.
- [2] C. Bier, "Inscribed Cotton Ikat from Yemen in the Tenth Century Ce," in 9th International Shibori Symposium, 2014.
- [3] R. Pfister, "Matériaux pour servir au classement des Textiles Égyptiens postérieurs à la Conquête Arabe (suite)," *Rev. des arts Asiat.*, vol. 10, no. 2, pp. 73–85, 1936.
- [4] M. S. Shamsi, "Lesson No. 32 Warss," *Dr Shakeel's Tib-e-nabi*, 2015. [Online]. Available: <http://www.tib-e-nabi-for-you.com/warss.html>.
- [5] J. Balfour-Paul, *Indigo in the Arab World*. Surrey: Curzon Press, 1997.
- [6] D. Cardon, *Natural Dyes: Sources, Tradition, Technology, and Science*. London: Archetype Publications, 2007.
- [7] M. Nesbitt, "Indian dyes and textiles at the Royal Botanic Gardens, Kew," *MARG: a Magazine of the Arts*, vol. 65, no. 2, pp. 100–105, 2014.
- [8] G. Cardillo, L. Merlini, and R. Mondelli, "Natural Chromenes-III. Coloring matters of wars: The structure of Flemingins A, B, C and Homoflemingin," *Tetrahedron*, vol. 24, pp. 497–510, 1968.
- [9] B. Cardillo, A. Gennaro, L. Merlini, G. Nasini, and S. Servi, "New chromenochalcones from Flemingia," *Phytochemistry*, vol. 12, no. 8, pp. 2027–2031, 1973.
- [10] K. Nageswara Rao and G. Srimannarayana, "Fleminone, A Flavanone from the Stems of Flemingia Macrophylla," *Phytochemistry*, vol. 22, no. 10, pp. 2287–2290, 1983.
- [11] K. Nageswara Rao and G. Srimannarayana, "Flemiphyllin, an Isoflavone from Stems of Flemingia macrophylla," *Phytochemistry*, vol. 23, no. 4, pp. 927–929, 1984.
- [12] Y. R. Lee and L. Xia, "An Efficient and Concise Synthesis of Biologically Interesting Natural Flemichapparin A, Flemingins A, Flemingins D, and Their Non-Natural Analogues," *Bull. Korean Chem. Soc.*, vol. 28, no. 9, pp. 1579–1584, 2007.

### Materials identification of a 18th C. high quality tapestry of Aubusson (France) by UV-VIS-NIR *in situ* analyses.

The case of the *Verdure fine* of the Brühl Count's coat of arms.

A. Mounier,<sup>1\*</sup> F. Daniel,<sup>1</sup> C. Biron,<sup>1</sup> and P. F. Bertrand<sup>2</sup>

<sup>1</sup>IRAMAT-CRPAA (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.

<sup>2</sup>Centre François-Georges Pariset (EA 538 / Université Bordeaux Montaigne). Esplanade des Antilles 33607 Pessac – France.

\* aurelie.mounier@u-bordeaux-montaigne.fr

#### Abstract

Aubusson located in the South of France is on the List of Intangible Cultural Heritage of Humanity by UNESCO (since 2009). This quality label rewards a centuries-old tradition for the art of tapestry. The "Verdures" (landscape tapestries), a specialty of Aubusson, are of very high quality and fine weaving, dyeing made mainly for abroad.

The Cité Internationale of Aubusson has recently acquired a tapestry with the count of Brühl's coat of arms. It is a good example of the representation of the landscapes in the mid-18th century. Red, blue, green & yellow are the main colours. The restoration in progress gave the rare opportunity to study it both faces. The lining of the back was removed and analyses were done on each side of the tapestry after dusting and before and after cleaning. So, the study offers the possibility to measure the alteration of dyes, through colour measurements, comparing the results obtained on each side and appreciating the original colours.

The study of the tapestry's materials (fibres, dyes,...) has been done by *in situ* analyses (hyperspectral imaging, near-infrared reflectance spectroscopy (FORS-NIR) and portable fluorimetry (LED $\mu$ SF) [1, 2]. The complementarity of these techniques makes possible the identification of the dyes (weld, indigo, madder, ...). From these dyes, 5-6 shades are achieved by the soaking time of wool or silk in the bath or by successive baths in different colours. For example, to get a green, the fibres are first soaked in a blue bath and then, once dry, in a yellow bath for a few minutes by regularly checking the colour obtained. These combinations of dyes were also highlighted by the analyses. Colour measurements showed a fading and a fouling of them. Infrared analyses distinguished the wool to the silk fibres.

#### References

1. A. Mounier et al., *Microchemical Journal*, 140 (2018) 129 – 141.
2. A. Mounier et al., *Heritage Science*, 2:24 (2014).



### UV-induced degradation of silk dyed with madder, cochineal and shellfish purple

Athina Vasileiadou<sup>1</sup>, Ioannis Karapanagiotis<sup>2\*</sup>, Anastasia Zotou<sup>1</sup>

<sup>1</sup>Laboratory of Analytical Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

<sup>2</sup>Department of Management and Conservation of Ecclesiastical Cultural Heritage Objects, University Ecclesiastical Academy of Thessaloniki, 54250 Thessaloniki, Greece

\* y.karapanagiotis@aeath.gr

#### Abstract

The effects of harsh UV radiation ( $\lambda=254$  nm) on silk dyed with madder (*Rubia tinctorum* L.), cochineal (*Dactylopius coccus* L.) and shellfish purple (*Hexaplex trunculus* L.) were investigated. In particular, the changes of the (i) chemical compositions of the dyes and (ii) colours of the dyed silk samples were measured.

The changes of the relative compositions of the dyes as a function of accelerated ageing time were monitored using HPLC-DAD. Attention focused on alizarin, purpurin, carminic acid, indigotin, 6-bromoindigotin, 6,6'-dibromoindigotin and 6,6'-dibromoindirubin which were quantified by an efficient HPLC-DAD method. The latter was validated in terms of linearity, detection and quantification limits, precision and accuracy. Dyes were extracted from the silk samples and were analysed by an established HPLC method [1,2], using the standards addition approach. To evaluate the matrix effect, the matrix-induced signal suppression/enhancement was determined. The accuracy was evaluated by recovery experiments. The effect of the UV light was initially dramatic, leading to a rapid decrease in the amounts of the colouring compounds, attached on silk. After extensive exposure in harsh UV light, only slight changes in the dye compositions were observed.

The colour changes ( $\Delta E^*$ ) of the aged dyed silk with respect to the fresh samples were measured as a function of the artificially accelerated ageing time. The colours of the dyed silk specimens faded rapidly within the first days of ageing treatment and became unaltered after prolonged ageing i.e. the visual effect of the UV radiation on the textiles became saturated. Overall, the effect of the artificially accelerated ageing conditions on the aesthetic appearance of the dyed silk was dramatic corresponding to colour changes ( $\Delta E^* > 3$ ) which were easily perceived by the human eye.

#### References

1. A. Vasileiadou, I. Karapanagiotis and A. Zotou, UV-Induced Degradation of Wool and Silk Dyed with Shellfish Purple, *Dyes and Pigments* 2019, 168, 317-326.
2. A. Vasileiadou, I. Karapanagiotis and A. Zotou, Determination of Tyrian purple by High Performance Liquid Chromatography with Diode Array Detection, *Journal of Chromatography A* 2016, 1448, 67-72.

### The application of ATR-FTIR spectrometer in analysis of synthetic dyes produced in The “Boruta” Factory in Zgierz at the beginning of 20<sup>th</sup> century

Magdalena Wróbel-Szypula

Laboratory, Department of Conservation, National Museum in Warsaw, Poland

mwrobel@mnw.art.pl

#### Abstract

From the middle of 19<sup>th</sup> century synthetic chemistry has been developing in dynamic mode and obviously affected production of dyes. In Poland the milestone for synthetic dyes industry was set up of The “Boruta” Factory in 1894 by Jan Śniechowski and Ignacy Hordliczka in Zgierz (Łódź district) [1] where a strong tradition of the production of textiles had already been established. After regaining the independence of Poland in 1918, the production of dyes in Zgierz expanded rapidly. Compounds synthesized in The “Boruta” Factory were used for dyeing many different types of materials, such as wool, paper, wood etc. Hence most of artifacts created between 1920 – 1940 in Poland contain dyes coming from The Factory in Zgierz. Although there is a number of publications [2 – 4] concerning analysis of early synthetic dyes present in museum objects from different parts of the world, neither the catalogues that remained from the archives of The “Boruta” company nor the Polish historical objects dyed with colorants from Zgierz have ever been investigated by analytical chemistry instruments.

In this study both the documentation of example samples from The “Boruta” Factory as well as identification of chemical components of inks used in historical textiles or illustrations on paper (i. e. posters) coming from the first half of 20<sup>th</sup> century was performed by Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectrometer. Additionally the advantages and challenges of analysis of the artificial dyes, which were ultimately prepared in different ways of processing (i.e. dissolution in different binders) in order to be applied on miscellaneous kinds of materials, made by the ATR-FTIR spectrometer are discussed.

#### References

1. Przygucki T., Sto lat koloru, Pryzmat, Łódź, 2004
2. F. Casadio, K. Mauck, M. Chefitz, R. Freeman, 2010, Appl Phys A, 885 – 899
3. C. Zaffino, A. Passaretti, G. Poldi, M. Fratelli, A. Tibiletti, R. Bestetti, I. Saccani, V. Guglielmi, S. Bruni, 2017, J Cult Her, 87 – 97
4. S. Steger, H. Stege, S. Bretz, O. Hahn, 2019, J Cult Herit, in press

### Characterization of 19th Century Istanbul Kandilli Yazmas (hand-painted textiles)

Recep Karadag<sup>1,2\*</sup> and Emine Torgan Güzel<sup>2</sup>

<sup>1</sup>Istanbul Aydin University Faculty of Fine Arts, Department of Fashion and Textile Design Florya  
Campus, Istanbul, Turkey

<sup>2</sup>Turkish Cultural Foundation (TCF), Cultural Heritage Preservation and Natural Dyes Laboratory,  
Istanbul, Turkey

\*recepkaradag@aydin.edu.tr

#### Abstract

'*Yazma*' is the name given to the application of designs to textiles either directly with a brush called "*kalem*", or using a wooden mold carved in relief. The major centers for this art in the Ottoman period were many regions in Anatolia but the most valuable *yazma* was Kandilli yazmas. The specimens from Istanbul rose to prominence with its hand-painted 'Kandilli' textiles, were highly prized for their artistry, in the 17-19th centuries [1].

Production of such hand-printed textiles commences with the application of designs previously drawn on paper to a piece of cloth stretched over a frame. The outlines are first traced using only a brush, and the areas to be coloured are then filled in, exactly as if making a painting. The prints of this type are also known as 'hand-prints'. In the combined technique, the outlines are first printed on the cloth with a wooden mold, and the colours then filled in with a brush. In block-printing both the black outlines and the coloured areas are applied to the cloth using appropriate molds [1].

In this study, technical, dyestuffs, weaving, yarn, mordant analyses and colour measurements of the 19<sup>th</sup> century *Kandilli yazmas* (hand-painted textiles) from the *Armaggan* collection (Fig. 1) were carried out. According to the analysis results, natural dyes and mordant materials used were determined by High Pressure Liquid Chromatography (HPLC) and Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy (SEM-EDX).

#### Reference

1. Reyhan Kaya, Türk Yazmacılık Sanatı (Tahta Kalıpla Kumaş Baskısı), Akbank, Ak İktisat Ansiklopedisi.

# Comparative Study of the Photostability and Degradation of Anthraquinone-based Dyes

Yukin Jin<sup>1</sup>, Leah Bowers<sup>1</sup>, Meg Heller<sup>1</sup>, Elliott Detrich<sup>1</sup>, Sarah J. Schmidtke Sobeck<sup>\*,1</sup>

<sup>1</sup>The College of Wooster Department of Chemistry, 943 College Mall, Wooster, OH 44691, USA

\* e-mail: ssobeck@wooster.edu

### Abstract

Anthraquinone-based organic dyes and pigments have been used since pre-historic times and have been identified in textiles dating to the 4th century [1]. The light stability can vary significantly across this chemical class of dyes and depending upon the dye preparation or environment [2]. Our studies focus on understanding the impact of structural variations and environment on the photo-stability and degradation mechanisms for anthraquinone-based dyes. A comparative study of the photo-induced degradation of purpurin, alizarin, and carminic acid is presented. The dyes are assessed in different pH environments to compare the lightfastness for different preparations and hues. Alizarin and purpurin provide a model set to evaluate how substituents on the anthraquinone core impact photostability. The color loss, traced spectroscopically throughout UV-irradiation, is fit to unique kinetic models for alizarin and purpurin indicating that the dyes follow different degradation mechanisms and rates vary with pH. The experimentally determined fluorescence lifetimes and computationally modeled excited state energetics for alizarin are consistent with an excited state proton transfer process, but not for purpurin. This process is thought to provide an efficient means for alizarin to return to its stable ground state following UV-excitation and results in better lightfastness relative to purpurin. The results are considered in the context of our investigations of the photo-degradation of carminic acid [3]. The degradation of carminic acid and formation of photoproducts are traced using HPLC, and resulting kinetic fits are combined with LC-MS and NMR characterization to propose a breakdown mechanism. The investigations allow a broader understanding of the impact of structural modifications and environment on the photochemistry of anthraquinone dyes. This can inform preservation methods, analysis of objects for original composition, and potential new applications for this class of dye materials.

### References

1. M.J. Melo in Handbook of Natural Colorants, T. Bechtold and R. Mussak (Eds.), Chichester: Wiley, 2009, 3-20.
2. C. Miliani, L. Monico, M.J. Melo, S. Fantacci, E.M. Angelin, A. Romani, K. Janssens, *Angew. Chem. Int. Ed.* **2018**, 57 (25), 7324-7334.
3. L.M. Radar Bowers, S.J. Schmidtke Sobeck, *Dyes Pigments*, **2016**, 127, 18-24.

### An American Purple: North Carolina Cudbear

Terry T. Schaeffer<sup>1</sup>, Laura Maccarelli<sup>1</sup>, Victor J. Chen<sup>2</sup> and Gregory D. Smith<sup>2</sup>

<sup>1</sup>Conservation Center, Los Angeles County Museum of Art

<sup>2</sup>Conservation Science Laboratory, Indianapolis Museum of Art at Newfields

terrys@lacma.org

#### Abstract

A gift from a colleague of a small tin, labeled “1 oz. Cudbear, No. 1 N. F. Powdered” which contained a dark purple powder, has led us to extend our investigations of cudbear dyes. The undated tin is from S. B. Penick & Company, “Manufacturers of fine drugs and chemicals”, which was founded in Ashville, North Carolina in 1914. Penick was a major supplier of botanicals and drugs until the mid-1960s. Label information and National Formulary listings suggest our tin may date from the 1940s.

The Penick Company was well known for purchasing plant materials from local residents experienced in identifying and gathering indigenous flora from the North Carolina countryside. Penick processed, compounded as appropriate, packaged and sold these materials as botanical drugs or chemicals. For example, in an early company advertisement cudbear is listed as a minor ingredient in “White Pine Compound”.

The powder in the Penick tin has been examined by reflectance and fluorescence spectroscopy and by high performance liquid chromatography - mass spectrometry (HPLC-MS). In addition, a sample was used to dye contemporary woollen yarn following a mid-19<sup>th</sup> century recipe, and the dyed yarn was analysed. The results were compared to data obtained for woollen yarn similarly dyed with cudbear prepared from British *Ochrolechia* lichens by Robert Hill, and to data for wool yarns dyed with archil from *Rocella tinctoria* by Schweppe.

HPLC-MS results indicated that the molecular composition of the cudbear from Penick is more like the Hill cudbear than the archil on the Schweppe sample. In this regard, it may be noteworthy that several species of *Ochrolechia* lichens native to North Carolina are known as cudbear lichens [1]. Spectral and MS data suggest that the highly fluorescent colourants in the cudbears may be  $\beta$ -orcein imine components absorbing maximally at ~588 nm [2, 3].

#### References

1. Brodo, I. M., Sharnoff, S.D. and Sharnoff, S. 2001, Lichens of North America, Yale University Press, p. 81 and pp.372-90.
2. Witkowski, B., Ganeczko, M., Hryszko, H., Stachurska, M., Gierczak, T. and Biesaga, M. (2017), ‘Identification of orcein and selected natural dyes in 14<sup>th</sup> and 15<sup>th</sup> century liturgical paraments with high-performance liquid chromatography coupled to the electrospray ionization tandem mass spectrometry (HPLC-ESI/MS/MS)’, *Microchemical Journal*, 133, pp. 370–9.
3. Melo, M.J., Nabais, P., Guimarães M., Araújo, R., Castro, R., Oliveira, M.C. and Whitworth, I. (2016), ‘Organic dyes in illuminated manuscripts: a unique cultural and historic record’, *Philosophical Transactions of the Royal Society A* 374, doi: 10/1098/rsta.2016.0050.

### Textile printing and dyeing : collection and research by artists and designers in the TextielMuseum

Jantiene van Elk<sup>1</sup>

<sup>1</sup>TextielMuseum

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

#### Abstract

The TextielMuseum in Tilburg is a working museum with a collection and exhibitions on textile technique, industrial culture, design and art. The TextielLab, part of the TextielMuseum, is a unique workshop for producing experimental knits and woven fabrics with national and international designers, architects, artists and promising students.

In this poster the TextielMuseum will present three collections of manuscripts from the museum's library on textile dyes and printing. The museum also presents two projects by artists/designers based on these collections. The TextielMuseum wants to keep textile heritage alive by stimulating collection research and by collection assignments to artist and designers.

The Driessen collection (obtained from the Driessen family, owners of the Leidsche Katoen Maatschappij) holds textiles and books on textile dyeing and printing. The collection also holds sample and recipe books from the laboratory of the company. Studio Formafantasma was intrigued by the story of Turkish red dyeing, a technique which travelled around the world. Formafantasma found Turkish red recipes in the Driessen collection and created an installation with printed silks[1].

The second collection consists of more than 30 manuscripts with dye recipes from Dutch companies. In the collection you can find hand written recipes from companies from the early 19th century till the 1970s. The two manuscripts called *Memorie voor de ververij* from Pollet & Co (Tilburg, 1811 and 1822) were an inspiration to artist Nan Groot Antink. She used natural dye plants and urine to create an art work [2]. Urine (*emmers pis* in Dutch) is used in many of the recipes in the two Pollet manuscripts.

In the third collection textile the TextielMuseum keeps more than 100 sample books with textile dyes from Dutch chemical companies (Franken-Donders, Vondelingenplaat, Twernerij en Ververij Broekhoven, Servo and other companies) [3].

#### References

1. <https://www.textielmuseum.nl/nl/collectie/BK1068a=q>
2. <https://www.textielmuseum.nl/nl/collectie/BK1197a=n>
3. <https://www.textielmuseum.nl/en/news/how-chemical-companies-became-trendwatchers>

### The colours of street art: the case of Blue's mural

Francesca Sabatini<sup>1</sup>, Jacopo La Nasa<sup>1</sup>, Lorenzo Cantini<sup>1</sup>, Daphne De Luca<sup>2</sup>, Ilaria Degano<sup>1\*</sup>, Francesca Modugno<sup>1</sup>

<sup>1</sup>Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Pisa, Italy

<sup>2</sup>Dipartimento di Studi Umanistici, Università di Roma Tre, Rome

\*ilaria.degano@unipi.it

#### Abstract

It is unknown where Street Art was born; nevertheless it started to be popular in the ill-famed ghettos of New York in the 70's under the positive influence of Pop Art. Since then, Street Art has grown becoming an affirmed and acknowledged form of art diffused all around the world.

Contemporary outdoor mural paintings present specific conservative issues not only due to the direct interaction with the physical and social environment, but also to the modern paint formulations, tools, techniques (such as stencils, stickers, spray cans) chosen by the artists. Thus, the characterization of these paint materials and their stability is fundamental to the debate on preservation strategies over time.

The present work is settled in the frame of a study of Street Art paint materials, a field poorly investigated up to now. The contribution describes the chemical characterization of the paint materials and techniques of the prominent Italian contemporary artist Blue (1980?, his identity is unrevealed) in the preparation of the mural on an ex airforce barrack (via del Porto Fluviale, Rome, 2014).

A multi-analytical approach based on Raman and Infrared spectroscopies (ATR-FTIR), Pyrolysis Gas Chromatography coupled with Mass Spectrometry (Py-GC/MS) and Liquid Chromatography coupled with Diode Array Detector and high-resolution mass spectrometry (HPLC-DAD, HPLC-ESI-Q-ToF) was chosen. The results collected by the complementary techniques highlighted as the brilliant hues are constituted by synthetic organic pigments, belonging to different chemical classes, while the black and white areas were achieved using inorganic pigments. Different synthetic binders were used in the paint formulations such as acryl, alkyd and vinyl resins.

The acquired knowledge on the paint technique and the palette of the most important Italian street artist is relevant not only for supporting conservators in planning a future cleaning and stabilization intervention, but also for collecting new information on urban art materials.

### BioColour: Bio-based Dyes and Pigments for Colour Palette

#### - Combining Traditions with Innovations

Riikka Räisänen<sup>1\*</sup>

<sup>1</sup>Craft Studies, University of Helsinki, Finland

\* riikka.raisanen@helsinki.fi

#### Abstract

*BioColour: Bio-based Dyes and Pigments for Colour Palette* is a newly funded (Academy of Finland, 2019–2025) project which aims to advance the usage of natural colourants in different applications.

Sustainable bio- and circular economy calls for alternatives for the one-sided production and consumption culture based on mass markets. The aim of the BioColour project is to initiate a renewal of current coloration principles and consumer preferences to include a wider adaptation of sustainability in businesses and consumer lifestyles. Therefore, studies of new biocolorant production methods, structure – property relationship, toxicology and dye-substrate interactions with scale-up, co-creation and investigation of cultural, social and ethical aspects associated with producing and using biocolourants will be carried out. The achieved understanding and results will enable the buildup of novel processes, leading to a variety of sustainable products and gaining the societal acceptance needed for successful implementation. Due to the inherent properties of many biocolorants, like UV-resistance, antimicrobial and antioxidant, water resistance and electrical conductivity, multifunctional products are possible.

Past traditions have saved tremendous amounts of knowledge and skills concerning natural dyes and coloration methods. Therefore, the BioColour project wishes cooperation with the researchers of history, archaeology and conservation science to understand more deeply the effect of time on the stability of natural dyes, and interactions between material and a dye. Further, collecting the data in an open database would be the goal.

The BioColour consortium is multidisciplinary, representing expertise of agriculture, applied plant science, chemistry, biosciences, toxicology, material science and technology, design research, information and communications technology, data science and consumer studies, and combining scientists from the University of Helsinki, University of Eastern Finland, Aalto University, Häme University of Applied Sciences, Luke Natural Resources Institute Finland, VTT Technical Research Centre of Finland Ltd, North Carolina State University, USA and University of Campinas, Brazil.



### A late 19<sup>th</sup> century recipe collection

#### *“Farben-Recepte”* of the company Heinrich Wiesel

Eva Eis<sup>1\*</sup>

<sup>1</sup> Kremer Pigmente, Aichstetten, Germany

\* eis@kremer-pigmente.de

#### **Abstract**

The Wiesel collection is an extensive recipe collection, compiled in the late 19<sup>th</sup> century by Hermann and Otto Wiesel. The brothers owned a paint factory in Gehren in Thuringia. *“Farben-Recepte”* is a compilation of letters, notes and recipes. While some of the recipes were written by the Wiesel brothers themselves, others were bought from various external sources.

The recipe collection has been the focus of the authors doctoral thesis at the Technical University of Munich [1]. During the last years the manuscripts have been transcribed, sorted and edited. The recipes have been evaluated and will soon be available for further research [2]. Experiments with selected recipes have shown that these recipes can be reproduced and can provide valuable information about 19<sup>th</sup> century paint manufacture.

Some of these reproductions have already been the focus of two presentations at DHA conferences. However, with more than 1500 recipes the Wiesel collection still offers many production secrets. The poster will give an overview about the contents of the collection, focusing on the recipes using natural and synthetic dyes. The collection contains 150 recipes with natural dyes as well as 512 recipes with synthetic dyes. These recipes include instructions for the production of lake pigments from natural and/or synthetic dyes as well as various pigment mixtures, inks and varnishes.

The author would like to invite participants to have a look at the collection and discuss recipes which may be of interest for further research.

#### **References**

1. Eva Eis: Die *“Farben-Recepte”* der Firma Heinrich Wiesel. Transkription und Auswertung der Rezeptsammlung eines Farbenfabrikanten aus dem ausgehenden 19. Jahrhundert.
2. A publication of the recipe collection is planned.

### Hidden secrets behind a folding screen

Marcella Steinbichler<sup>1</sup>, Art Néss Proaño Gaibor<sup>2</sup>, Luc Megens<sup>2</sup>, Henk van Keulen<sup>2</sup>, Sigrid Eyb-Green<sup>1</sup>,

Florian Thaddäus Bayer<sup>3</sup>, Matthijs de Keijzer<sup>2</sup>

<sup>1</sup>Academy of Fine Arts Vienna, Department Conservation and Restoration, Vienna, Austria

<sup>2</sup>Cultural Heritage Agency of the Netherlands, Cultural Heritage Laboratory, Amsterdam, the Netherlands

<sup>3</sup>Sammlung Privatstiftung Esterházy, Privatstiftung Esterházy, Eisenstadt, Austria

\* marcella.steinbichler@hotmail.com

#### Abstract

The three-part folding screen is part of a 'Chinese Room' in the Esterházy Palace in Eisenstadt, Austria. The painting is executed on machine made paper, which is an indication that the object dates to the second half of the 19<sup>th</sup> century.

The condition of the folding screen is poor. The front and back papers were originally coloured deep red, but the colour has faded and is only visible on the back of the panels; in areas previously covered by nails. The red is extremely water-sensitive, and very strong tidelines have formed recto and verso in areas damaged by water.

To know more about the creation, the artistic intention and to understand the damage phenomena in order to be able to interpret the object and its biography and to develop and implement conservation and preservation strategies the folding screen was analysed.

By SEM-EDX lead white, minium, a green copper pigment, Kessler brown and the 19<sup>th</sup> century paints lead chromate and synthetic ultramarine blue were identified. By UHPLC-PDA the red organic dye carminic acid was analysed together with other characteristic components, which points to the dye insect American cochineal (*Dactylopius coccus* Costa). SEM-EDX analysis showed in the red dye the element tin. American cochineal mordanted with tin is known as Drebbel's Scarlet. This method was developed in the beginning of the 17<sup>th</sup> century by the Dutch inventor Cornelis Jacobszoon Drebbel (1572-1633) in England. By detecting tin it is possible to find out that the discoloured backgrounds had originally a red colour dyed with cochineal.

By GC-MS a carbohydrate, most likely starch, a protein, probably an animal glue, and some colophony, were identified and showed that the paint layers were applied in a gouache technique.

Based on the scientific examination the restoration and conservation of the folding screen was successfully completed last year.

### Microbial Indigo Reduction by using KDB1 strain separated from Traditional Fermentation Bath

Chanhee Jung<sup>1</sup>, Dong Il Yoo<sup>1</sup>, Jong Il Rhee<sup>2</sup>, Younsook Shin<sup>3\*</sup>

<sup>1</sup>School of Polymer Science and Engineering, Chonnam National University, 61186, Korea

<sup>2</sup>School of Chemical Engineering, Chonnam National University, 61186, Korea

<sup>3</sup>Dept. of Clothing and Textiles, Chonnam National University, 61186, Korea

\* yshin@jnu.ac.kr

#### Abstract

Microbial reduction is one of the environmentally friendly methods applied for indigo dyeing. However, to be a practical method, it should be improved in view of low reproducibility or slow reduction time [1]. Establishing optimum pH condition may be referred to as another one. Among reaction variables, controlling pH was the most critical to get maximum color strength (K/S value) when bacterial strain was involved [2].

In this study, we isolated gram-positive, aerobic moderate and alkaliphile bacteria (*Dietzia sp.* KDB1) capable of reducing indigo dye from traditional indigo fermentation dye-bath at Naju, Korea [3]. The reducing power of KDB1 was compared between the alkaline baths which were adjusted by lye (pH 10.7), buffer solution (NaHCO<sub>3</sub>/NaOH) or Na<sub>2</sub>CO<sub>3</sub> in this study. The color strength of dyed ramie sample was measured along with pH, oxidation/ reduction potential (ORP) for evaluating reducing power. The elapsed times required to start reduction and maximum reduction were also measured. We obtained the K/S value of more than 2 at pH 9.5-10.4 when 0.66g/L of KDB1 whole cells was added to the buffer solution at day 2. In particular, the ORP of less than -600mV and the K/S value of 5 or more were shown at day 3, and ORP of less than -650mV and K/S value of 7-9 were obtained at day 4-5. Through repeated dyeing, we obtained the color strength of ramie sample more than 20.

#### Acknowledgement

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (Ministry of Science, ICT and Future Planning) in 2019 (No. 2017R1A2B4009555).

#### References

1. M.Bozic, V. Kokol, Ecological alternatives to the reduction and oxidation processes in dyeing with vat and sulphur dyes, *Dyes and Pigments*, **76**, 299(2008).
2. Y. Shin, K. Son, D.I. Yoo, Using, Using *Saccharomyces cerevisiae* Strains as Biocatalyst for Indigo Reduction. *Fibers and Polymers*, **20**(1), 80(2019).
3. E. Choi, E. Lee, H. Choi, K. Son, G. Kim, Y. Shin, Analysis and Enrichment of Microbial Community Showing Reducing Ability towards indigo in the Natural Fermentation of Indio-Plant. *Korean Soc. For Biotech. And Bioeng. J.*, **28**(5) 295(2013)

### Study on sample books of textile fragments from Dutch ships in the 19<sup>th</sup> century, stored in KIT Museum

Yoshiko SASAKI <sup>\*1,2</sup>, Riichi HAGIHARA<sup>2</sup>, Tadataka SATO<sup>2</sup>, Ken SASAKI<sup>2,3</sup>

<sup>1</sup> Kyoto Saga University of Arts

<sup>2</sup> Textile Research Investigation Committee, Museum and Archives, Kyoto Institute of Technology

<sup>3</sup> Kyoto Institute of Technology

\* yasaki@kit.ac.jp

#### Abstract

Japan had a secular policy from the 17th century to the 19th century, but only China (Qing) and the Netherlands were allowed to trade with exceptions. Trade was allowed only in Nagasaki. Imported goods were purchased in bulk at the government's Nagasaki branch office and sold to domestic merchants by public tender. And exported goods were delivered to merchants designated by the Nagasaki branch office and sold to foreign merchants.

The sample books of the textile fragments, imported from Netherlands in 19<sup>th</sup> C, which are stored at Museum and Archives, Kyoto Institute of Technology, were surveyed. Acquired number (AN.) 71 consists of eight sample books made by merchants from 1850 to 1854. On the other hand, AN. 90 consists of 19 volumes from 1849 to 1860, and was created by Mr. Shinozaki whose family had worked as a textile appraiser for generations at the Nagasaki branch office [1].

At that time, spinning machines, power weaving machines, and roller printing machines were developed and considered to be used in these textile samples, but synthetic dyes had just been put into development and it is hard to believe that they had been used in these samples.

This time, the dyes used for printed textile were investigated by nondestructive analysis. The results showed the use of cochineal, indigo and Prussian blue.

#### References

1. Y.SASAKI et al., Study of sample fragments from Nederland ships (KIT Collection AN.71) (Investigation of textiles stored in Kyoto Institute of Technology (10)), SENNI, 69, 2016 pp.39-46 (Japanese).

## Benzylated methyl violet dye compounds structurally elucidated through UHPLC-PDA-HRMS analysis

S. V. J. Berbers<sup>1\*</sup>, I. D. van der Werf<sup>1</sup>, A. N. Proaño Gaibor<sup>1</sup>,

F. Ligterink<sup>1</sup>, J.G. Neevel<sup>1</sup>, B. Reissland<sup>1</sup>

<sup>1</sup>Cultural Heritage Laboratory, Cultural Heritage Agency of The Netherlands, Hobbemastraat 22, 1071 ZC Amsterdam, The Netherlands

s.berbers@cultureelerfgoed.nl

### Abstract

Triarylmethanes belong to one of the earliest synthetic dye classes that were mass-produced for trade and are commonly used for inks and dyeing textiles. Among these, methyl violet (C.I 42535) was first synthesised in 1860.[1] Late 19<sup>th</sup> century artists such as Vincent van Gogh used inks that contain these dyes in drawings and letters.[2] Today, they show colour shifts or/and fading due to degradation of the colourant molecules.[3]

Methyl violet is defined as being a mixture of tetra-, penta-, and hexapararosaniline.[3] To better understand early synthesis methods of methyl violet and related dyes 40 historical reference samples (Reference collections of TU Dresden and RCE Amsterdam), dating from the late 19<sup>th</sup> century until the 1930ies, originating from leading dye producers in Europe, were analysed with UHPLC-PDA-HRMS. A considerable amount of the references contained, besides methyl violet, higher molecular weight compounds. This study focusses on the structural elucidation of these compounds with UHPLC-PDA-HRMS.

They were identified as a range of ethylated and benzylated pararosanilins. These types of molecules can be found in late 19<sup>th</sup> century synthesis and patent literature, but are not described in modern publications on triarylmethanes.[5] The structural elucidation provides a starting point for the characterisation of these compounds and important insights into historical patented synthesis procedures and applied production methods across Europe, and provide better understanding of the composition and decay of the many artworks where these dyes have been used.

### References

1. C. Lauth, On the New Aniline Dye "Violet de Paris", Laboratory: A Weekly Record of Scientific Research, Vol. 1 (1867) 138–139
2. J. G. Neevel, in Van Gogh's Studio Practice, M. Vellekoop, M. Geldof, E. Hendriks, L. Jansen, A. De Tagle editors, (2013), 420-433
3. Confortin, Daria, J.G. Neevel, Maarten Bommel, and Birgit Reissland. 2010. 'Study of the Degradation of an Early Synthetic Dye (Crystal Violet) on Cotton Linters, Lignin and Printing Paper by the Action of UV-Vis and Vis Light and Evaluation of the Effect of Gum Arabic on Degradation Products and on Colour Change'. In The CREATE 2010 Conference Proceedings - 'Colour Coded', 81–85. Editors: G. Simone, J. Y. Hardeberg, I. Farup, A. Davis and C. Parraman.
4. I. Degano, F. Sabatini, C. Braccini, M. Perla Colombini, Dyes and Pigments, 160 (2019), 587-596
5. G. Van Schultz, Farbstofftabellen, Akademische verlagsgesellschaft M.B.H. Leipzig, 7<sup>th</sup> edition (1931), entry 786 edited and improved by Dr Ludwig Lehmann

### Synthetic organic colorants in the assessment of an artwork's authenticity

Václava Antušková<sup>1\*</sup>, Radka Šefců<sup>1</sup>, Martina Bajoux Kmoníčková<sup>1</sup>

<sup>1</sup> National Gallery Prague, Staroměstské náměstí 12, 110 00, Prague, Czech Republic

\* vaclava.antuskova@ngprague.cz

#### Abstract

Scientific analysis, including identification of pigments and dyes, is an integral part of the assessment of an artwork's authenticity. The presence of materials produced after expected time of origin gives a sign that the artwork is suspicious at least. For synthetic organic colorants, the time of their discovery and production is usually well documented and could be easily found in specialized literature [1, 2]. First organic pigments were synthesized in the late 19th century and more commercially important classes were discovered throughout the 20th century. Patented manufacturing processes uniquely determine their chemical composition and structure. In the identification of an artwork's counterfeits dated to the first half of the 20th century, the presence of these materials is often the key.

Raman and infrared spectroscopy are suitable methods for identification of most organic colorants. Both methods can be used not only for analysis on micro-samples but also non-invasively allowing analysis of paintings and drawings where sampling is not possible. Phtalocyanine pigments (both blues and greens) are quite often found on fake artworks however other pigments like quinacridone reds and arylide yellows were identified as well. Nevertheless, sample analysis showed wide range of organic colorants applied on the original artworks from the first half of the 20th century too. Therefore, unambiguous identification is necessary for correct assessment of the authenticity.

This work has been financially supported by the project of the Ministry of the Interior of the Czech Republic: Comprehensive Instrumental Methods for the Assessment of an Artwork's Authenticity, a Material Database of the 20th century (VI20172020050).

#### References

1. Herbst, W.; Hunger, K. Industrial organic pigments, 3rd ed.; Wiley-VCH: Weinheim, 2004.
2. Craddock, P. Scientific investigation of copies, fakes and forgeries, 1st ed.; Butterworth-Heinemann: Oxford, 2009.

## Using Norwich Patternbooks to Accomplish Non-Destructive Analysis of Textiles

Jocelyn Alcántara-García<sup>1\*</sup>, Amelia M. Speed<sup>2</sup>, Karl S. Booksh<sup>2</sup>

<sup>1</sup>University of Delaware – Department of Art Conservation / Department of Chemistry and Biochemistry

<sup>2</sup>University of Delaware – Department of Chemistry and Biochemistry

\* joceag@udel.edu

### Abstract

Cross-disciplinary, multi-instrumental research into the Norwich textile industry revealed a remarkable consistency across the use of dyes, mordants, and dye combinations/recipes used in the case study of a Norwich textile pattern book dated c. 1790–1793.[1, 2] These critical findings further strengthened the views of 18th-century manufacturing processes in Norwich as part of an advanced and organized industry. Interested in further advancing the knowledge of this industry in par with advancing the non-destructive analysis of textiles, we continued our work with other Norwich fabrics of the same time period. Spectroscopic and chromatographic analysis of ca. 200 swatches followed by statistical analysis, showed promise in using naturally aged samples to build a database that, in the near-future, can accomplish a reliable 100% non-destructive analysis for other textiles.

### References

1. Alcántara-García J. The 'Industrial Patent' of Norwich Dyers in the late 18th century revealed through science. *Miscellany Costume and Textile Association*. 2018;5:6.
2. Alcántara-García J, Nix M. Multi-instrumental approach with archival research to study the Norwich textile industry in the late eighteenth and early nineteenth centuries: the example of a Norwich pattern book dated c. 1790–1793. *Heritage Science*. 2018;6(76).

### Understanding colour in Renaissance embroidery: new analytical approaches

Edith Sandström<sup>1,2\*</sup>, Helen Wyld<sup>2</sup>, Logan Mackay<sup>1</sup>, Lore Troalen<sup>2</sup>, Alison Hulme<sup>1</sup>

<sup>1</sup>EaStCHEM School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh, EH9 3FJ, UK

<sup>2</sup>National Museums Scotland, Chambers Street, Edinburgh, EH1 1JF, UK

\* e.sandstroem@nms.ac.uk

#### Abstract

The large European textile and dress collection at National Museums Scotland (NMS) includes over 30 Scottish and English embroideries from the 16th and 17th centuries. The collection showcases a variety of embroidered objects, such as clothing items, book covers and pictures, made with various techniques and materials. Despite the richness and diversity of the objects, little research on the material used in their production has been undertaken. Such an analysis would allow interesting questions relating to British vs Continental, professional vs amateur and workshop specificity to be asked and potentially answered.

The science lab at NMS has a long history of dyestuff analysis using ultra-high-performance liquid chromatography with photodiode array detection (UPLC-PDA). This project is building on previous research conducted at NMS on natural dyestuffs in historical tapestries [1, 2]. A new UPLC-PDA method was developed, allowing a 14 min gradient separation of 9 flavonoid dyes and achieving resolution factors of > 1.17 for regio-isomeric flavonoid compounds. This new method will allow faster analysis, resulting in a larger volume of samples to be investigated.

Concurrently, micro-destructive mass spectrometry platforms for dye analysis are under development, focussing on direct-desorptive techniques, such as MALDESI. The introduction of techniques under ambient conditions for dye analysis would allow the analysis of objects that are too fragile or significant for sampling. The application of both advanced chromatography techniques and ambient mass spectrometry on the Renaissance embroidery collection hosted at NMS will give a greater understanding of these objects; how they were made and how we might care for them.

#### References

1. L. G. Troalen, A. S. Phillips, D. A. Peggie, P. E. Perdita, A. N. Hulme, Historical textile dyeing with *Genista tinctoria* L.: a comprehensive study by UPLC-MS/MS analysis, *Analytical Methods*, 6, 2014, 8915–8923
2. L. G. Troalen, PhD Thesis, the University of Edinburgh, 2013



### Reds of the bronze age “civilization of the red thread” from the north cemetery in the Taklamakan desert

Dominique Cardon<sup>1\*</sup>, Corinne Debaine-Francfort<sup>2</sup>, Lore Troalen<sup>3</sup>, Clarisse Chavanne<sup>3</sup>, Pao Lei Kang<sup>3</sup>, Witold Nowik<sup>4</sup>

<sup>1</sup> CIHAM/UMR 5648/CNRS/ ISH - 14 av. Berthelot - 69363 Lyon Cédex 07, France

<sup>2</sup> CNRS - UMR7041 - ArScAn-Asie centrale/ Maison de l'Archéologie et Ethnologie René Ginouvès/ 21 allée de l'Université, 92023 Nanterre cedex, France

<sup>3</sup> National Museums Scotland, Chambers Street, EH1 1JF, Edinburgh, UK

<sup>4</sup> Laboratoire de Recherche des Monuments Historiques, 29, rue de Paris, 77420 Champs-sur-Marne, France

\* cardon.dominique@wanadoo.fr

#### Abstract

The Bronze Age site of the North Cemetery in the Taklamakan desert of Xinjiang (China) is composed of a number of tombs, only some of which have not been looted. Nearly all preserved pieces of clothing and adornment are decorated with red wool thread [1].

In order to yield a maximum of information from these important textiles, the red yarns were extracted using a combination of oxalic acid and hydrochloric acid solvents [2]. The samples were then investigated using ultra-high-performance liquid chromatography (UPLC-PDA) following established protocol at National Museums Scotland [3]. Alizarin was detected in all the samples, but in variable amount, resulting in difficulties to suggest a precise identification of the red dye(s) sources.

In order to further explore some hypotheses concerning the Rubiaceae species and the dye process that might have been used, we recurred to experimental archaeology, producing a number of red dye samples obtained with *Rubia tinctorum* L. and *Galium boreale* L. They will be exhibited and the results of their dye analyses and colorimetric characterization will be presented at DHA 38.

Our poster will present the site, the types of textiles discovered, the problems met in our research into these early red dyes and its current results.

#### References:

1. D. Cardon, C. Debaine-Francfort, A. Idriss, K. Anwar & X. Hu, “Bronze Age textiles of the North Cemetery: discoveries made by the Franco-Chinese Archaeological Mission in the Taklamakan Desert, Xinjiang, China”, *Archaeological Textiles Review*, **55**, pp. 68-85.
2. J. Wouters, C. M. Grzywacz, A. Claro, “A Comparative Investigation of Hydrolysis Methods to Analyze Natural Organic Dyes by HPLC-PDA - Nine Methods, Twelve Biological Sources, Ten Dye Classes, Dyed Yarns, Pigments and Paints”, *Studies in Conservation*, **56**(3), 2011, pp. 231–249.
3. L. G. Troalen, A. S. Phillips, D. A. Peggie, P. E. Perdita, A. N. Hulme, “Historical textile dyeing with *Genista tinctoria* L.: a comprehensive study by UPLC-MS/MS analysis”, *Analytical Methods*, **6**, 2014, pp. 8915–8923.

### The organic indigo vats: the magic blue of vegetable world

Dra. M<sup>a</sup> Julia Martínez García<sup>1\*</sup>, Dra. M<sup>a</sup> Luisa Vázquez de Ágredos Pascual<sup>1</sup>

<sup>1</sup> University of Valencia

\* m.julia.martinez@uv.es

#### Abstract

Maybe we are not aware of all that nature offers us and what it has given us over the centuries, particularly in the world of textile production. A paradigmatic example is the organic indigo vats made only with vegetable reducers such as palm date, roots of madder, etc. and calcium carbonate, urine or ash to alkalize these. We are aware of the production of this type of products on neo Babylonian tablets from VII century BC., but possibly its origin is much older. Pliny pointed out that the Egyptians were sorcerers who took out from their indigo vats, the white textiles and when exposing them to the air they turned blue [1].

In South America the Mayans obtained the blue color of their textiles from *Indigofera sufrutticosa* L. [2]; among the Celts, Germans and Britons the blue was prepared from a plant that the Romans called *Vitrum (De bello Gallico)*; In India *Indigofera tinctoria* L. is the tree from which the blues are obtained and which is already reflected in the Vedic texts, but is not the only source of blue, since it can also be obtained from *Indigofera argentea* L. and other vegetal sources; Southeast Asia as well as China and Japan have used to make blue vats of *Persicaria tinctoria* L.

In this work, we carry out the experimental production of several indigo vats reduced with raisins, dates, henna, pomegranate and other vegetable raw materials without the addition of hydrosulfites or other chemical compounds. We applied a colorimetric analysis to the samples obtained on different textile fibers, initiating the creation of a small database.

The purpose of this study is to verify the feasibility of these blue vats for their possible application in different areas, in order to help make a sustainable blue dyes that respects the environment.

#### References

1. M. Julia Martínez García (2011): "Aspectos técnicos de la fabricación de colorantes en la vestimenta femenina de época romana; fuentes escritas y experimentación" en *Mujer y Vestimenta. Aspectos de la identidad femenina en la Antigüedad*, Valencia, pp. 215 – 228; M. Julia Martínez García (2019): "Alchemist of dyer? Dyeing in Roman Egypt" in M. E. Busana; M. Gleba; A. Tricomi; F. Meo (Eds.), *Textile and dyes in Mediterranean Economy and Society, Purpureae Vestes VI*, Valencia, pp. 471 – 481.
2. M<sup>a</sup> Luisa Vázquez de Ágredos; Cristina Vidal Lorenzo; Gaspar Muñoz Cosme (2014): "Archaeometrical Studies of Classic Mayan Mural Painting at Peten: La Blanca and Chilonche". *MRS Proceedings*, 1618, pp. 45 – 62; Teresa Domènech; Laura Osete; Antonio Domènech; M<sup>a</sup> Lusía Vázquez de Ágredos; Cristina Vidal Lorenzo (2014): "Identification of indigoid compounds present in archaeological Maya blue by pyrolysis-silylation-gas chromatography mass spectrometry". *Journal of Analytical and Applied Pyrolysis* (105), pp. 355 - 362

### How Spectroscopy helps Synthetic Textile Dyes to tell their Story

Yasmine Schulenburg<sup>1\*</sup>, Jochen S. Gutmann<sup>2</sup>, Jürgen Schram<sup>1</sup>

<sup>1</sup> Hochschule Niederrhein, University of Applied Sciences: Faculty of Chemistry - Instrumental Analysis, Frankenring 20, D-47798 Krefeld

<sup>2</sup> University of Duisburg-Essen: Faculty of Chemistry - Physical Chemistry,

Universitätsstraße 5, D-45141 Essen

\*yasmine.schulenburg@hs-niederrhein.de

#### Abstract

With the discovery of Mauveine by *William Perkin* in 1856 a colourful development commenced. During the second half of the 19<sup>th</sup> century, a multitude of dye producing companies was founded. More and more synthetic textile dyes were synthesized, e.g. aniline red or indigo to name but a few.

The Historical Collection of Dyes at the Hochschule Niederrhein, University of Applied Sciences, fortunately has preserved more than 10,600 dyes dating from the 1860s to the middle of the 20<sup>th</sup> century in their original flasks and containers. They can now serve as contemporary witnesses of this astonishing development and are part of the analysis in the presented research project.

By the use of infrared spectroscopy, the following exemplary questions to the colourful witnesses are to be answered: Are two dyes with the same name also chemically identical? Which deviations or similarities can be found between the products from two manufacturers? What do the suffixes in the names of the dyes indicate?

One sample group that has been investigated is a group of triphenylmethane blue dyes named water blue, navy blue or spirit blue. Historical and modern literature show inconsistencies in the definitions of those dyes: sometimes one hue described is as a mixture, in other cases as a discrete blue dye. The spectroscopic analysis helps to unravel the mystery and to show the true colours of the blue hues. As a part of this, the research aims for findings about the trading of patents by comparing the spectra of dyes which have been marketed under different trade names but are chemically identical. Thereby, information about the raw material deployed, the synthesis processes and possible contamination can be gathered, too. In addition to infrared spectroscopy, also other techniques such as TXRF and UV/Vis have been applied and the corresponding results will be presented.

**Analysis of the velvet fabric from the royal coach  
of King Philip II of Portugal (17<sup>th</sup> century)**

Cristina Barrocas Dias<sup>1,2,\*</sup>, Ana Manhita<sup>1</sup>, Ana Carolina Assis<sup>1</sup>, Madalena Serro<sup>3</sup>, Rita Dargent<sup>4</sup>, Paula Monteiro<sup>5</sup>

<sup>1</sup>HERCULES Laboratory, Évora University, Évora, Portugal

<sup>2</sup>Chemistry Department, School of Sciences and Technology, Évora University, Évora, Portugal

<sup>3</sup>Freelance textile conservator, Lisbon, Portugal

<sup>4</sup>National Coach Museum, Lisbon, Portugal

<sup>5</sup>José Figueiredo Laboratory, Directorate General for Cultural Heritage, Lisboa, Portugal

\* cmbd@uevora.pt

**Abstract**

King Philip II is the oldest coach in the collection of the Portuguese National Coach Museum, and it is presumed to have been brought from Madrid and left in Lisbon when, in 1619, the monarch came to Lisbon to watch his son's oath as his successor to the crown [1,2].

The inside of the coach is lavishly decorated in velvet [2]. A piece of the textile was available for analysis, and 7 samples were analysed, including silk colored fibers (white, carmine, and yellow) and metallic thread. The dyes were identified by liquid chromatography coupled with diode array detector and mass spectrometry (LC-DAD-MS), while the fibers, mordants, and metallic thread were analyzed by Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS).

The silk fibers were dyed with cochineal and weld using aluminum as mordant. The metallic thread was made of gilded silver, but the loss of the gold in some areas led to the corrosion of the silver base with the formation of silver chlorides and sulfides.

**References**

1. Pereira Botto, JM (1909) *Prontuário Analítico dos Carros Nobres da Casa Real Portuguesa e das Carruagens de Gala*, Tomo I. Lisboa: Imprensa Nacional .
2. <http://www.matriznet.dgpc.pt/MatrizNet/Objectos/ObjectosConsultar.aspx?IdReg=148079> (accessed in June 14<sup>th</sup> 2019)

### **Crimson, black, silver and gold and a lavish 17th-century finding off the coast of Texel, North Holland**

Ana Serrano <sup>1\*</sup>, Maarten van Bommel <sup>2</sup>, Ineke Joosten <sup>1</sup>

<sup>1</sup> Cultural Heritage Laboratory, Cultural Heritage Agency of the Netherlands (RCE), P.O. Box 1600, 3800 BP, Amersfoort, The Netherlands

<sup>2</sup> Programme Conservation and Restoration of Cultural Heritage & Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Johannes Vermeerplein 1, 1071 DV, Amsterdam, The Netherlands

\* afaserrano13@gmail.com

#### **Abstract**

An exceptional group of silk fragments was unearthed in 2014 from a shipwreck that sank in the mid-17th century, in the Wadden Sea, The Netherlands. A unique example of early modern fashion and artistry, it comprises about 300 textile fragments from costumes, parts of costumes and interior textiles, almost entirely made of silk and embroidered or woven with metal thread. Although buried for centuries, this finding is in very good condition, which might be related to the archaeological environment and the high quality of the fabrics.

To assess the quality and historical background of these textiles, as well as their state of conservation for future preservation strategies, their materials have been characterized. A total of 218 textile yarns and metal threads were sampled from 34 fragments to 1) characterize the dyestuffs and mordants used, 2) to identify and evaluate the condition of the textile fibres, and 3) to assess the composition and condition of the metal threads.

With ultra-high performance liquid chromatography coupled to diode array detector (UHPLC-PDA), it was verified that most fragments were coloured with insect dyes, and in some cases, madder and tannins as well. With research microscopy and scanning electron microscopy - energy dispersive x-ray spectrometer (SEM-EDX), silk fibres were mostly identified and these appeared clean, smooth and flexible; although those from more fragile fragments were evidently more friable and dirty, presenting pitting from biodegradation and contaminations from the archaeological environment. Silver sulphide crystals from the corrosion of silver were mostly observed on the metal threads, and gold was often detected, indicating that these were gilded [1]. Even though the historical background of these fragments is still under investigation, it is undoubtedly clear that this is quite a lavish, unique finding that deserves to be fully appreciated and preserved for generations to come.

#### **References**

1. Bommel, M. V., Serrano, A., Joosten, I., 2016, "De textielcollectie BZN17 chemisch ontsloten, het eerste onderzoek naar de gebruikte materialen in het textiel", *Archeologisch Kroniek van Noord Holland*, pp. 177-185.

### Disclosing medieval Iberian iron-gall inks recipes through the use of historically accurate reconstructions

Natércia Teixeira<sup>1\*</sup>, Alexandra Silva<sup>1</sup>, Catarina Henriques<sup>1</sup>, Filipa Silva Campos<sup>1</sup>, Inês Costa<sup>1</sup>, Paula Nabais<sup>2</sup>, Nuno Mateus<sup>1</sup>, Fernando Pina<sup>2</sup>, Maria João Melo<sup>2</sup>, Victor de Freitas<sup>1</sup>

<sup>1</sup> LAQV-REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal

<sup>2</sup> Department of Conservation and Restoration and LAQV-REQUIMTE, Faculty of Sciences and Technology, Universidade NOVA de Lisboa, 2829-516 Monte da Caparica, Portugal

\* natercia.teixeira@fc.up.pt

#### Abstract

Iron gall ink is one of the most important inks in the history of western civilization and it was in widespread use from the middle ages until the beginning of the 20th century. The degradation of manuscripts, catalyzed by iron-gall inks, is a major conservation issue and a serious threat to the world written heritage [1].

We have prepared five medieval inks using the same ingredients and similar methodologies. They are the result of research into Iberian written sources of medieval techniques and three basic ingredients are constantly described in these recipes: Fe<sup>2+</sup> obtained from an iron sulphate salt, a phenolic extract (tannins), usually from gall nuts, and a binder, gum arabic [1,2]. Other metal ions and different additives such as pigments, as well as different extraction conditions, were tested. These variations were studied and its contribution to the specific ink recipe was revealed [3].

All the extracts and inks were analyzed in threefold by HPLC-ESI-MS and HPLC-DAD. The first allowed the identification of the phenolic compounds present both in extracts and inks, while the second allowed the quantification of these compounds [3]. Therefore, this work allowed for the identification and quantification of the major phenolic compounds present in the gall extracts, while evaluating its variation by the addition of an iron sulphate salt and gum arabic when producing the iron-gall inks. Moreover, it was also possible to identify and quantify the effect of each additive on each tested recipe.

#### Acknowledgements:

We thank the Fundação para a Ciência e Tecnologia for financial support: FCT-MCTES project PTDC/QUI-OUT/29925/2017 for the contract REQUIMTE/EEC2018/PTDC/QUI-OUT/29925/2017 and UID/QUI/50006/2019 with funding from FCT/MCTES through national funds.

#### References

1. Neevel H. In: Kolar J.; Strlič M., editors. Ljubljana: National and University Library, **2006**, 147-172.
2. Zerdoun-Bat Yehounda M., Les encres noires au Moyen Âge (jusqu'à 1600). 1st ed. Paris: CNRS Éditions, **2003**.
3. Díaz Hidalgo, R.J.; Córdoba, R.; Nabais, P.; Silva, V.; Melo, M.J.; Pina, F.; Teixeira, N.; Freitas, V. Heritage Science, **2018**, 6(1), 63.