DHA 34

Dyes in History & Archaeology 34

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University Ecclesiastical Academy of Thessaloniki
Department of Management and Conservation of Ecclesiastical Cultural Heritage Objects
October 21-24, 2015

PROGRAMME AND BOOK OF ABSTRACTS

Organizing Committee

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PROGRAMME OF ORAL PRESENTATIONS

Location:
Conference Centre, University Ecclesiastical Academy of Thessaloniki, Department of Management and Conservation of Ecclesiastical Cultural Heritage Objects
N. Plastira 65, 542 50 Thessaloniki, Greece
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Wednesday 21st October 2015

Location: Conference Centre, University Ecclesiastical Academy of Thessaloniki

18:30 – 20:30 Reception

Thursday 22nd October 2015

Location: Conference Centre, University Ecclesiastical Academy of Thessaloniki

08:45-09:30 Registration and placement of posters

09:30-09:45 Opening remarks

Session 1. Chair: Dominique Cardon

09:45-10:05 A medieval illuminated manuscript "Ajuda Songbook": what the identification of organic dyes in the colour paints can tell us?
Maria J. Melo, Paula Nabais, Rita Castro, Tatiana Vitorino, Graça Videira Lopes

10:05-10:25 Natural dyes in seal threads from documents issued by Prince Stephan the Great (1457-1504)
Irina Petroviciu, Ileana Cretu, Florin Albu, Marian Virgolici, Andrei Medvedovici

10:25-10:45 Non-invasive characterization of dye-based paints in prehispanic Mesoamerica: The colors of the Codex Borbonicus
Fabien Pottier, Anne Michelin, Christine Andraud, Fabrice Goubard, Aymeric Histace, Bertrand Lavédrine

10:45-11:00 Questions

11:00-11:30 Coffee break and posters

Session 2. Chair: Ioannis Karapanagiotis

11:30-11:50 A new archaeometric method for the fast non-destructive identification of molluskan purple in textile dyeings
Zvi C. Koren

11:50-12:10 Shining a light on Turkey red: applying FTIR for non-invasive identification of heritage textiles
Julie H. Wertz, Anita Quye, David France, Pik Leung Tang, Lesley Richmond

12:10-12:30	**Degradation products of the glycosidic components in *Rubia tinctorum*** Lauren Ford, Richard S. Blackburn, Christopher M. Rayner
12:30-12:50	**Mass spectrometric study of protoberberine alkaloids in aged textiles dyed with amur cork tree (*Phellodendron* spp.)** Yoshiko Sasaki, Ken Sasaki
12:50-13:10	***Questions***
13:10-14:30	**Lunch break and posters**

Session 3. Chair: Anita Quye

14:30-14:50	**The early synthetic organic dyes: the sulphur or sulphide dyes** Matthijs de Keijzer, Regina Hofmann-de Keijzer
14:50-15:10	**A study of dye colour charts of the 1860s and 70s and their adoption by fashion of the period** Susan Kay-Williams
15:10-15:30	**The activity of dyers in Thrace during the 19th and 20th century** Ifigeneia Papakonstandinou
15:30-15:45	***Questions***
15:45-16:15	**Coffee break and posters**

Session 4. Chair: Recep Karadag

16:15-16:35	**Textile dyes in pre-Columbian northern Chile** Hans Barnard, Ran Boytner
16:35-16:55	**Identification of dyestuffs used in Peruvian ancient textiles** Kirti Patel, Candy Ruiz, David Condori, Camilo Díaz, Geraldine Espinoza, Jenny Figari, Rosario Rojas
16:55-17:15	**Dyes in Italy during the first millennium BC** Margarita Gleba, Ina Vanden Berghe
17:15-17:30	***Questions***
17:30-17:45	**Announcements**
	Gala dinner (optional)

Friday 23rd October 2015

Location: Conference Centre, University Ecclesiastical Academy of Thessaloniki

09:30-09:45 **Opening remarks**

Session 5. Chair: Jo Kirby

09:45-10:05 **Typically variable? A chemical study of commercial aniline dyes in a 19th C sample book**
Anita Quye, Jing Han

10:05-10:25 **Dye and metal thread analyses of some tomb covers in Istanbul Fatih Mosque Complex**
Recep Karadag, Emine Torgan

10:25-10:45 **Timeline of colours in Dutch fashion Rijksmuseum costume collection, 17th to 20th century**
Art Néss Proaño Gaibor, Suzan Meijer, Bianca du Mortier

10:45-11:00 ***Questions***

11:00-11:30 **Coffee break and posters**

Session 6. Chair: André Verhecken

11:30-11:50 **Yellow dyes of historical importance IV. Sawwort (*Serratula tinctoria* L.) and weld (*Reseda luteola* L.) in the Florentine Dye company "Francesco di Giuliano Salviati e Comp., tintori d'arte Maggiore", 1483-149**
Dominique Cardon, Ingrid Houssaye-Michienzi

11:50-12:10 **The failed experiment. An attempt at reviving the Polish cochineal dyeing in eighteenth-century Poland**
Ewa Orlińska-Mianowska, Monika Janisz

12:10-12:30 **How much scientific information could be preserved in an embroidery thread?**
Ileana Cretu, Irina Petroviciu, Zizi Ileana Balta, Ina Vanden Berghe, Mihai Lupu

12:30-12:50 **The politics of colour – recovering the dye producing lichens of the Scottish highlands in June 1916**
Vanessa Habib

12:50-13:10 ***Questions***

13:10-14:30 **Lunch break and posters**

Session 7. Chair: Prokopios Magiatis

14:30-14:50 **Dye analysis of historical textiles from Okinawa and Indonesia. Was there any exchange of dyeing techniques between these regions?**
Chika Mouri

14:50-15:10 **A Study of Dyeing in the Ming and Qing Dynasties (1368-1912) from multiple perspectives**
Jing Han, Anita Quye

15:10-15:30 **Comparison of Malaysian and Indian ikat technique. Color and design analysis**
Katarzyna Schmidt-Przewozna

15:30-15:45 ***Questions***

15:45-16:15 **Coffee break and posters**

Session 8. Chair: Irina Petroviciu

16:15-16:35 **The problematic of bleeding of indigo dyed threads of a group of central Asian silk samites dated from the 7-8th century**
Hélène Dubuis

16:35-16:55 **Characterization of Madder compounds present in lake and textile, throw ammonia extraction and micro-sampling with Ag-gel matrix associated with SERS analysis**
Livia Lombardi, Ilaria Serafini, Marcella Guiso, Fabio Sciubba, Armandodoriano Bianco

16:55-17:15 **The quest for folium**
Maurizio Aceto, Aldo Arrais, Elisa Calà, Claudio Cassino, Marco Clericuzio, Francesco Marsano, Angelo Agostino, Gaia Fenoglio, Monica Gulmini, Ambra Idone, Luigi Menghini, Lidia Leporini, Nicola Di Matteo, Cheryl Porter

17:15-17:30 ***Questions***

17:30-17:45 **Closing remarms**

Saturday 24th October 2015

Optional: **Bus excursion to the archaeological site of Agai, Vergina and nearby area.**
The schedule will be announced soon.

POSTER PRESENTATIONS

Red dyes used for Kalamkari textiles
Ina Vanden Berghe, Lynda Hillyer

Degradation of glycosylated aglycons of natural dyes
David Kohout, Helena Brezinova, Ivan Viden, Josef Chudoba

Identification of natural dyestuffs of four historical naval ensigns in the Istanbul Naval Museum with high pressure liquid chromatography (HPLC)
Sevim Karabulut, Türkan Yurdun, Gülbin Erdoğan, Emre Dölen

Examination of dyed silk fabrics with dyer's sumac (*Cotinus coggygria* Scop.) according to different mordants
Emine Torgan

Eco-friendly indigo dyeing using extract from orange peel waste
Younsook Shin, Min Choi, Young-Mee Yeo, Dong-Il Yoo

Effect of cryoprotectant on bacterial reduction in indigo dyeing
Younsook Shin, Kyunghee Son, Eun-Sil Choi, Dong-Il Yoo

Hair-dyeing by using *Rubus coreanus Miquel* sludge
Dong Il Yoo, Min Choi, Younsook Shin

Cosolvent effect on micellar solubilization of indigo
Neşe Çakir, Çağlar Demirbağ, Sinem Göktürk

The analysis findings that will form the basis of textile conservation process in the Ankara Ethnography Museum
D. Gizem Özkan, Halide Sarıoğlu

Inorganic substrates of lake pigments: data from post-byzantine Greek icons
George P. Mastrotheodoros, Konstantinos G. Beltsios, Yannis Bassiakos

Turmeric: to eat or to dye? A natural historical dye
Ekaterini Tsatse, Elvira Kotali, Ioannis Karapanagiotis, Antigoni Kotali

The Byzantine *Epitaphioi* of Mount Athos: historical and technological context
Christos Karydis, Dimitrios Mantzouris, Ioannis Karapanagiotis

HPLC-DAD-MS and LDI-MS strategies for anthraquinoid lakes identification in paint samples
Francesca Sabatini, Anna Lluveras-Tenorio, Ilaria Degano, Stepanka Kuckova, Maria Perla Colombini

Red pigments of Boraginaceae family: A historical overview
Antigoni E. Koletti, Eleni G. Karapanagioti, Alexandros Nakas, Vassilios P. Papageorgiou, Andreana N. Assimopoulou

Non-destructive analysis of pigments in Byzantine paintings.
Thomas Katsaros, Theodore Ghanetsos

Partial Solvation Parameters: An holistic approach in solubility prediction –Application in anthraquinone dye.
Dimitra Aslanidou, Costas Panayiotou

Chemical analysis for coloring materials used for “Guanyin with Rainbow Halo” stored in Scripps College, USA
Yoshiko Sasaki, Masaaki Naka, Ken Sasaki

Storing grains during Ninevite 5 Period in the Khabour basin: ways and methods used
Nancy Badra

Dye extraction from *Dialium guinense*, characterization and application on cellulose fabric.
Adeola V. Popoola

Colorimetric study of Chinese traditional dyeing and ageing silk textiles
Jinjin Xu, Decai Gong

Proposal of a new mild extraction technique for organic dyes in historical artworks
Ilaria Serafini, Livia Lombardi, Marcella Guiso, Fabio Sciubba, Armandodoriano Bianco

Raman spectroscopy pigment identification in a painting from J. F. Mücke
Theodore Ghanetsos, Igor Lukačević, Thomas Katsaros, Ante Matanić

Reviving the ancient indigo cultivation and industry in southern Jordan as a source of income for the local community: from historical and archaeological evidence to a modern trial
Valentina Gamba, Konstantinos D. Politis, Mohammed I. Al-Qinna

Antimicrobial activity of dyed silk fabrics with madder and gall oak
Rezan Alkan, Emine Torgan, Recep Karadag

Traditional use of saffron, safflower and celidonia for yellow-gold dye in the Ancient Mediterranean World: references from written sources.
Carmen Alfaro Giner, M Julia Martínez García, Jónatan Ortiz García

Dyes from Boraginaceae species: from ancient codes to modern medicine
Vassilios P. Papageorgiou, Andreana N. Assimopoulou

Dyeing camel wool with acetic acid extract of *Hibiscus rosa sinensis* flower for Sadu House of Kuwait
Lamya Hayat

ABSTRACTS OF ORAL PRESENTATIONS
(Listed in programme order)

A medieval illuminated manuscript "Ajuda Songbook": what the identification of organic dyes in the colour paints can tell us?

Maria J. Melo[1*], Paula Nabais[1], Rita Castro[1], Tatiana Vitorino[1], Graça Videira Lopes[2]

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The Galician-Portuguese medieval songs, one of the most valuable cultural assets of the Iberian Middle Ages, continue to raise all kinds of questions today. One of the biggest problems faced by researchers concerns its manuscript tradition, that is, the collective compilations that have transmitted the songs to us, the songbooks. Only three songbooks have survived, and of these only one, the "Ajuda Songbook" (*Cancioneiro da Ajuda*), is a medieval manuscript [1]. It is a rich illuminated manuscript, of great artistic and patrimonial value that was left unfinished, and on whose workmanship and posterior course we know almost nothing.

In this presentation we will reveal the molecular palette of "Ajuda Songbook" and how the organic dyes that were used contribute for establishing a chronology [2]. Integrating materials and their processing in cultural history, within specific contexts, will shed new light on the "Ajuda Songbook", and its cultural and artistic importance within an Iberian as well as European context.

ACKNOWLEDGMENTS
This work has been financially supported by FCT-MCTES under grant UID/QUI/50006/2013. Paula Nabais, Rita Castro and Tatiana Vitorino would like to thank FCT-MCTES for their PhD grants. This research has been made possible by the generous support of the director of Palácio Nacional da Ajuda (PNA), José Alberto Ribeiro, and the director of the PNA Library, Cristina Pinto Basto.

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1. http://cantigas.fcsh.unl.pt/manuscritos.asp?ling=eng
2. M. J. Melo, R. Castro, A. Miranda, "Colour in Medieval Portuguese Manuscripts: between Beauty and Meaning", in *Science and Art: the painting surface*, A. Sgamellotti, B. G. Brunetti, C. Miliani (Eds), RSC 2014, pp. 170-192.

Natural dyes in seal threads from documents issued by Prince Stephan the Great (1457-1504)

Irina Petroviciu[1,2*], Ileana Cretu[3], Florin Albu[4], Marian Virgolici[5], Andrei Medvedovici[6]

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Prince Stephan the Great was the ruler of Moldavia[i] between 1457-1504. From his long reign a large number of monuments and movable objects were preserved, the latter including textiles, metalwork, manuscripts and documents. These objects have kept the attention of historians and art historians for many years and, more recently, several items from the large collection of Putna Monastery (Stephan's the Great first foundation, situated in North-eastern Romania) have been studied in terms of materials and techniques [1-3]. Analysis of dyes from liturgical embroideries and brocaded velvets showed that, for red dyes, the combination of lac dye and madder was used in most cases while kermes was reserved for the more precious ones. Weld, young fustic and dyer's broom were the most frequently used sources for yellow and, in combination with indigo, for green. Other sources, such as redwood, bastard hemp and emodin containing dyes (rhubarb/ buckthorn) were also identified [2]. A significant number of historical documents issued by Prince Stephan the Great between 1459-1503 have been preserved, many of them being now part of the Romanian Academy Library (Bucharest, Romania) collection. Such documents contain the Prince's seal, bounded to the document by a thread, which in most cases is red.
In the present study, 50 thread samples from 42 documents, dated between 1459-1503, were analysed by LC-DAD-MS/MS in order to achieve a larger view on the biological sources used in the time of Stephan the Great. The contribution will discuss these results as compared with those obtained on liturgical embroideries and brocaded velvets from the same period as well as, on a larger scale, with those obtained on various textiles in Romanian and European collections [4,5]. Detection of biological sources mainly used in Oriental textiles, such as lac dye, together with others, particularly detected in Europe (kermes), confirm the position of Moldavia at the confluence of the major trade routes that connected the Oriental Empire to Europe.

ACKNOWLEDGEMENTS
The authors are grateful to the Romanian Academy Library for providing access to their collections. They also express their gratitude to Agilrom Scientific SRL (Romania) and the IRASM Centre in "Horia Hulubei" National Research Institute for Physics and Engineering (Romania), the former offering access to the analytical instrumentation and the latter to the sample preparation laboratory.

REFERENCES
1. I.Z. Balta, G. Niculescu, I. Petroviciu, B. Brunetti, L. Cartechini, F. Rosi, B. Doherty, A. Sassolini, M. Lupu and I. Cretu). *Study of materials and techniques used in a Romanian Illuminated medieval manuscript*, Sources and Serendipity: Testimonies of Artists' Practice, 2009
2. I. Petroviciu, I. Cretu, I. Vanden Berghe, J. Wouters, *Analysis of Dyes in 15th-17th Century Byzantine Embroideries from Putna Monastery, Romania*, in DHA 24/25, Archetype, in print
3. Z.I. Balta, L. Csedreki, E. Furu, I. Cretu, R. Huszánk, M. Lupu, Z. Török, Z. Kertész, Z. Szikszai, *Ion beam analysis of golden threads from Romanian medieval textiles,* in Nuclear Instruments and Methods in Physics Research B 348, 2015, 285–290
4. I. Petroviciu, I. Vanden Berghe, I. Cretu, F. Albu and A. Medvedovici, *Identification of natural dyes in historical textiles from Romanian collections by LC-DAD and LC-MS (single stage and tandem MS),* Journal of Cultural Heritage, 13, 2012, 89-97
5. I. Petroviciu, I. Cretu, M. Lupu "*Dyes in textiles from Romanian collections in a European context (EURODYE) a CHARISMA/ ARCHLAB project developed at the Cultural Heritage Agency of the Netherlands (OCW-RCE)*", poster, Dyes in History and Archaeology 32, La Rochelle, France, 2013.

[1] Moldavia included NE part of Romania and the area between Prut and Nistru rivers, today belonging to the Republic of Moldavia

Non-invasive characterization of dye-based paints in prehispanic Mesoamerica: The colors of the Codex Borbonicus

Fabien Pottier[1*], Anne Michelin[1], Christine Andraud[1], Fabrice Goubard[2], Aymeric Histace[3], Bertrand Lavédrine[1]

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The library of the French national parliament holds a colorful XVIth century Aztec manuscript, the Codex Borbonicus. In this codex, two stylistically different parts can be distinguished, likely painted by at least two different scribes, possibly at different times (as can be seen in the photographs of page 14 and 24 of the document). The goal of our study is to characterize the coloring matters in order to determine similarities or differences in the paints composition of those parts. To perform such analyses we applied non-invasive (no sampling, no contact) techniques such as X-ray fluorescence, diffuse reflectance, specular FTIR and Raman spectroscopies. While they provide easily interpretable data when the coloring matters are not organic, they are often more challenging for dye-based paints. Our analyses suggest that every single color that has been used to paint the two parts of the document is based on a dye preparation. Some of them are very common and already well-understood by scholars (indigo and cochineal), while others have never been characterized as paints in the other codices recently studied. Extracts from two local plants, *Commelina Coelestis* and *Justicia Spicigera* are suspected, and fit what can be found in colonial XVIth century historical records such as the famous Florentine Codex. Clues regarding the characterization and the specific preparation of all these dyes along the two parts of the document will be discussed, and it will be demonstrated that the complete palette was obtained from a limited number of these dyes, through mixes and superimpositions. A comparison with the historical records and the results of the analyses of other Mesoamerican codices will be developed during the discussion of the results.

Pages 14 (left) and 24 (right) (details) of the Codex Borbonicus

A New Archaeometric Method for the Fast Non-Destructive Identification of Molluskan Purple in Textile Dyeings

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A simple and quantitative breakthrough method is described for the determination of the presence of the molluskan pigment in archaeological and modern textile dyeings. This methodology is fast, non-destructive, requires no sample preparation, and utilizes well-known scientific principles and instrumentation that is normally available in an analytical laboratory. Relative quantification of the trademark dyes in molluskan pigments is obtained, and these results are normalized and independent of the amount or size of sample analyzed. Comparative analyses were performed on a total of 18 samples – modern and archaeological (from Masada, Israel) – consisting of different textures and surface densities – fabric weaves, string, single yarns, loose yarn fibers, and fleece – clean and soiled, and with and without molluskan purple as determined via HPLC analyses. The colors of the samples examined were the various ones that can be obtained from the malacological pigment via natural and artificial processing, and included light blue, blue, dark blue, dark blue-purple/violet, to red-purple. In all of the cases examined, this method consistently produced clear results for the unmistakable presence, or lack of, the molluskan purple pigment. A good correlation is obtained between the new method’s results and the HPLC-measured molluskan dye content. This revolutionary method can serve as a very rapid and reliable diagnostic tool for the detection of the molluskan pigment in purple dyeings, which can then be followed by a detailed multicomponent analysis via the micro-destructive HPLC method. The ramifications of this new archaeometric technique for museum collections are enormous.

The talk will showcase the new methodology and correlate the results with those from HPLC analyses.

Shining a light on Turkey red: Applying FTIR for non-invasive identification of heritage textiles

Julie H. Wertz[1,2*], Anita Quye[1], David France[2], Pik Leung Tang[3], Lesley Richmond[4]

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[2]School of Chemistry, University of Glasgow
[3]Department of Pure and Applied Chemistry, University of Strathclyde
[4]Scottish Business Archive, University of Glasgow

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Once a major part of the Scottish textile industry and a globally-traded product in the 1800s, the production of Turkey red dyed cotton went into decline in the early 20th-century and was abandoned before there was a true understanding of the chemistry of this exceptionally fade-resistant textile.[1] One of the most persistent questions about the process is the exact role of the oil, documented in the literature as a vital part of the lengthy process.[2] Previous research on the role of the oil involved extractive processes, typical for dyestuff analysis.[3] A study of Turkey red methods reveals there is no single-application method to dye it and the final product is only obtained by a series of steps 'building' it on the fibres. Given this, it is unlikely an extractive process is the ideal analytical approach.

This paper outlines the preparation of cloth for Turkey red dyeing by the application of oil and the proposed chemistry of this process. It describes the use of two forms of infrared spectroscopy, diffuse (DRIFTS) and attenuated total reflectance (ATR), for identifying key characteristics of calico oiled according to Turkey red methods as well as historical textile samples. The ATR technique operates with a fixed grazing angle and penetrates the sample about 3µm, while DRIFTS collects scattered reflectance and penetrates about 7µm. Both techniques have applications in heritage textile conservation, each with strengths and weaknesses depending on the object and the bonds in question. In this case, the ATR is more sensitive to the surface formation of bonds between oil and fibre in the 1800cm^{-1} to 1600cm^{-1} region for these samples, but the physical limitations of the objects require the use of DRIFTS, providing an opportunity to compare how both methods can be used to answer the same question.

This research is part of a project studying historical methods for Turkey red dyeing to better inform conservation and display practices, emphasizing non-invasive analysis. Replica samples created according to the methods and following principles of modern chemistry are compared to authentic 19th-century Turkey red from the Scottish Business Archive.

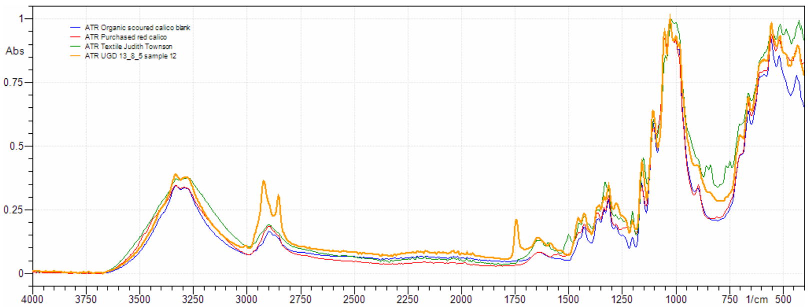

Figure 1. ATR spectral comparison of red textiles compared to historical Turkey red

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2. Knecht, Edmund, Christopher Rawson, and Richard Loewenthal. 1893. *A Manual of Dyeing*. London: Charles Griffin & Company, Limited.
3. Parks, Lytle Raymond. 1930. "The Chemistry of Turkey Red Dyeing." *Journal of Physical Chemistry* 35 (2): 488–510. doi:10.1021/j150320a008.

Degradation Products of the Glycosidic Components in *Rubia tinctorum*

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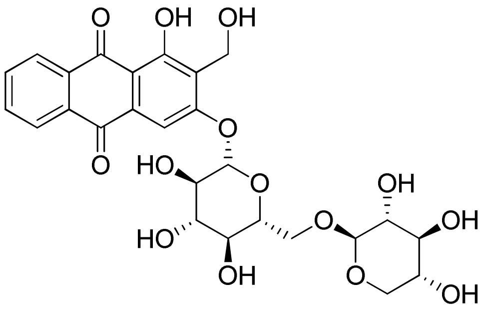
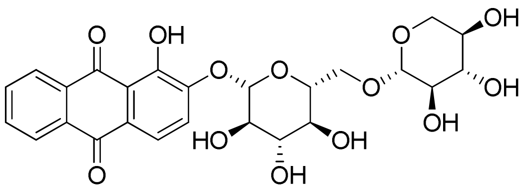
Red coloration of textiles from extracts of various madder species (*Rubia spp*) is a longstanding tradition. The colouring components of these natural plant extracts belong to the chemical family of anthraquinones compounds. By extracting and analysing the solutions obtained in traditional dye recipes it can be seen that the most abundant colouring components present in the plant are glycoside-containing moieties, lucidin primeveroside (1) and ruberythric acid (2), along with smaller amounts of aglycons including alizarin and purpurin (Henderson *et al*., 2013). It has long been apparent that these glycoside-containing moieties are easily broken down into their aglycons when under acidic conditions, hence the drive for more gentle ‘soft’ extraction methods.



(1)



(2)

The aglycons of these glycosides are alizarin and lucidin however the only products usually reported in the literature after acid hydrolysis are alizarin and small amounts of purpurin. The breakdown products of lucidin are usually thought of as the oxidation to nordamnacanthal (Derksen *et al*., 2003) and throughout the literature the breakdown that occurs under acidic back extraction conditions is not described or is stated as being unknown (Boldizsar *et al*., 2006).

Using synthetic models of these molecules a degradation pathway has been established to better understand the reactivity and stability of these compounds under analysis conditions. The retro-aldol reaction of the lucidin forms xanthopurpurin under acidic and neutral aqueous conditions at high temperatures; the reaction was followed by HPLC-DAD, and NMR data of the standards were obtained. This also provides insights into why lucidin is often missed in back extraction analysis of historical textiles due to similarities between xanthopurpurin and alizarin in analysis.

References

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2. DERKSEN, G., NAAYER, M., VAN BEEK, T., CAPELLE, A., HAAKSMAN, I., VAN DOREN, H. & DE GROOT, A. 2003. Chemical and enzymatic hydrolysis of anthraquinone glycosides from madder roots. *Phytochem Anal,* 14**,** 137-44.
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Mass spectrometric Study of Protoberberine Alkaloids in Aged Textiles dyed with Amur Cork Tree (*Phellodendron* spp.)

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Amur cork tree (*Phellondendron amurense*) *and* related species have been sources of herbal medicines and natural cationic yellow dyes used widely in East Asia since ancient times. Its major ingredients are protoberberine alkaloids, which are ingredients with the efficacy, and are easily and non-destructively detectable by their characteristic fluorescence. We have previously reported a method to determine the provenance between Japan and China of traditional textiles based on high-pressure liquid chromatography (HPLC) analysis of relative amount of jatrorrhizine and palmatine to berberine in the dye [1,2,3]. In this report, application of electrospray ionization (ESI) mass spectrometry (MS) to micro-level analysis of traditional textiles and determination of the characteristic aging products of protoberberines in traditional samples are described. At least two chemical ingredients with spectroscopic characteristics of protoberberines (X1 and X2) were detected by HPLC analysis for traditional textiles. ESI-MS showed that X1 had m/z 324 and two H-D exchangeable hydrogen atoms and that X2 had m/z 352 and one exchangeable hydrogen atom. HPLC ESI-MS and MS/MS revealed that X1 was derived from elimination of a CH_2 group from a methylene dioxy group on the berberine A ring and that X2 was from hydroxylation of the benzyl position on the berberine B ring. Total amounts of X1 and X2 increased with increasing damage and age, and could be used as an index for time-related deterioration of traditional textiles.

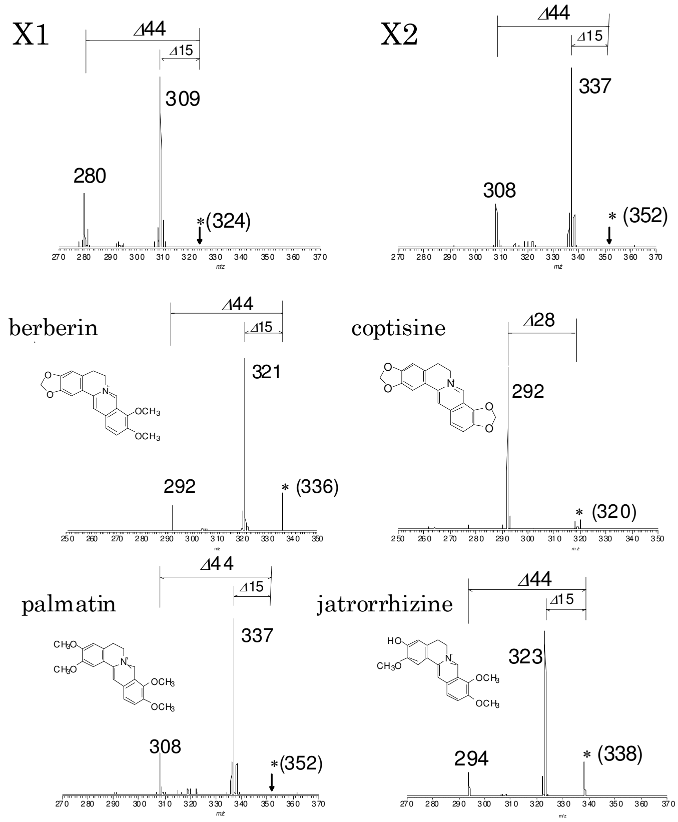

Fig. 8 MS/MS analyses of X1, X2, and four typical protoberberine alkaloids. Target ions were indicated by * and the mass numbers were shown in parentheses

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The early synthetic organic dyes: the sulphur or sulphide dyes

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The presentation will discuss the history, the chemical constitution, the production, the properties and the names of the sulphur or sulphide dyes. These early synthetics were widely used for dyeing cotton and were obtained by heating various organic materials with sulphur and sodium sulphide. Sulphur dyes are water-insoluble. When acted upon by sodium sulphide they form water-soluble leuco compounds and can be absorbed by the fabric. After the fabric is removed from the dye solution these compounds are oxidised by oxygen in the air and are reconverted on the fibre into insoluble sulphur dyes.

The forerunner of the sulphur dyes was prepared by the French chemists Croissant and Bretonnière in 1873. They heated various organic materials, such as sawdust, starch, straw, bran, etc., with sodium sulphide and sulphur and named their product Cachou de Laval (*Sulphur Brown 1, 53000*). This impure and unstable substance dyes cotton greenish-yellow shades, which change to brown on the exposure to air. The colour is fast to washing, but moderately fast to light. The fastness to light is improved by after treatment with iron, copper and chromium mordanting salts. Cachou de Laval was manufactured by several firms for many years.

In 1893 the French chemist Raymond Henri Vidal prepared the first black sulphur dye Vidal Black / Noir Vidal (*Sulphur Black 3, 53180*), obtained by fusing p-aminophenol with sulphur and sodium sulphide and by after treatment with oxidation substances. Its light-fastness and fastness to washing is good.

Some later (in 1897) a better black sulphur dye, which did not require any after treatment, was manufactured by heating 4-hydroxy-2,4-dinitrodiphenylamine with sodium sulphide, discovered by the German chemist Georg Kalischer and marketed by Cassella as Immedial Black V (*Sulphur Black 9, 53230*). Immedial Black V was the first sulphur dye which gave a true black shade and was the opening of the sulphide era. During the next ten years almost every organic substance was subjected to sulphide condensation.

In 1899 the German chemists Bernhard Priebs and Oskar Kaltwasser achieved a great improvement by reacting 2,4-dinitrophenol with sodium sulphide in hot water. The resulting dye was produced as Sulphur Black T (*Sulphur Black 1, 53185*) by AGFA. It is the most important member of this dye class and many equivalent products were made by other firms. It gives blacks with very good fastness properties.

The discovery of the blacks led between 1898 and 1904 to a rapid development of this dye class. By further research, especially by German and Swiss factories, many different coloured sulphur dyes were invented. Blue, brown and green dyes have the greatest importance; yellow and orange dyes have a limited use and red dyes are hardly known (*see table*). Sulphur dyes are cheap, have good wash-fastness and are easy to apply.

The best known brands and producers of the sulphide dyes are: **Auronal** (Weiler ter Meer), **Cross Dye** (Read Holliday), **Eclipse** (Geigy), **Immedial** (Cassella), **Katigen** (Bayer), **Kryogene** (BASF), **Pyrogene** (CIBA), **Sulphur** (AGFA), **Thiogene** (Farbwerke), **Thion** (Kalle), **Thional** (Sandoz), **Thionol** (Levinstein), **Thiophor** (Jäger), **Thioxine** (Griesheim-Elektron) and **Vidal** (Poirrier).

Name	C.I. Name	C.I. Number	Discoverer(s)	Discovery
Kryogengelb G	Sulphur Yellow 3	53125	BASF	1903
Immedialgelb GG	Sulphur Yellow 4	53160	Schmidt	1906
Immedialorange C	Sulphur Orange 1	53050	Weinberg, Lange	1902
Immedialorange N	Sulphur Yellow 6	53105	Weinberg, Lange	1903
Immedialmarron B	Sulphur Red 3	53710	Weinberg / Schmidt	1900 / 1905
Immedialbraun B	Sulphur Brown 5	53245	Hoffmann, Kalischer	1899
Immedialreinblau	Sulphur Blue 9	53430	Weinberg, Herz	1900
Immedialoliv GN	Sulphur Green 11	53165	Lepetit	1895
Immedialgrün GG	Sulphur Green 3	53570	Böniger	1904

A study of dye colour charts of the 1860s and 70s and their adoption by fashion of the period.

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In quick succession to Perkin's Mauve chemists and dyers developed a number of new colours. To differentiate and promote these they produced shade cards. This presentation follows a study of shade cards of the 1860s and 70s and how the colours they feature were taken up by fashion.

The research has been undertaken on colour charts from the UK and US markets including those produced by Brooke Spiller and Simpson, Corticelli and Seavey Foster Bowman; through a variety of naming and numbering systems these show the growth of the new colours and how they were incorporated into the existing colour ranges of the suppliers. They also show the internationalism of the trade in synthetic dyes from an early period.

Investigating the adoption by fashion is not as easy as might be imagined. Often the principal sources are magazines where the colour nomenclature used by the journalists tended to remain the commonly understood words their readers would recognize, rather than the new names the colours were being given, a notable exception being reference in the first edition of Harper's Bazaar to Bismarck Brown being the prevailing colour of the season[i].

The coloured plates found in some of the ladies magazines of the day, such as *Godey's Lady's Book,* are similarly misleading, as the choice of colour by the illustrator/printer may differ widely from the textile colours named. For example, on one illustrated page the caption describes a girl's dress as magenta and black but the colour on the page is much more of a pink[ii]. Of the dresses of this period in museums, few have been analysed for the actual dyes used and so curator's, even with guidance have sometimes suggested a particular new colour when further investigation shows this to be unlikely[iii]. This presentation will feature an update on this work.

[i] Harper's Bazaar 2 November 1867 Vol 1 No 1 p3

[ii] Godey's Lady's Book 1864

[iii] Personal correspondence with Chertsey Museum and the Science Museum about colour descriptions of a particular dress at Chertsey Museum 2014

The Activity of Dyers in Thrace during the 19th and 20th century

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The present study attempts a sociological and historical approach to the activity of dyers in the post-Byzantine Thrace.

It describes the form that the profession of dyers took and their activity in the historical and socio-economic environment of a region where during the early 20th century ethnic unrest was/conflicts were intensified.
In particular, it refers to:

a. Their geographical movements
b. Their expertise, techniques and working methods applied
c. To the form of economic and social transactions, to the transmission of knowledge to younger dyers.

Moreover, it attempts to connect the dyeing activity with the development of sericulture and the silk industry in the wider region of the former sanjak of Edirne. The presentation of the evolution of the profession is completed with a reference to the factors that contributed to the weakening of the traditional form of the dyeing art.

Textile dyes in pre-Columbian northern Chile

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As in most ancient and modern cultures, clothing and textiles carried great psycho-social meaning to the peoples in pre-Columbian South America [1]. In order to understand the importance of colours and dyestuffs in these ancient societies we analysed 765 samples from 256 textiles [2], currently kept in the Museo San Miguel de Azapa of the Universidad de Tarapacá in northern Chile. The samples ranged in date from the Chinchorro to the Inca cultures (ca. 8000 BCE–1500 CE). A wider range of dyes was used in the region than expected. Annatto, cochineal and relbunium, red dyes well known from textiles elsewhere in the Andes [2-6], were used next to three unidentified red dyes. Although outside influence appeared to have had some impact on dye choice, local residents continued to use traditional dyes throughout the region's prehistory, even in times of increased regional interaction. A significant difference in the use of various dyes between coastal and more inland sites was observed, especially during the Late Intermediate and Late Horizon periods (ca. 1000–1532 CE), indicating increasing differences in social status and access to dyestuffs. Our results furthermore corroborate recent insights concerning the dating of artefacts found in archaeological contexts in the region.

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Identification of dyestuffs used in Peruvian ancient textiles

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In the ongoing investigation for the identification of dyes in Peruvian Andean historical textiles [1-4], the aim of this study is to determine the natural dye components in present day Peruvian plants and compare them with historical textile dyes by reversed-phase HPLC with diode-array detection (DAD). Alpaca wool fibers dyed with tinctorial plants used currently by Peruvian Andean and Amazonian communities; as well as various archeological textiles from Paracas, Nasca and Huari cultures (500 B.C – 1100 A.D) were analyzed for the presence and relative abundance of dye components.

By comparing the relative composition of the various archeological dyes found with those pigments from various plant species, this study has found that the compound purpurin from plant red "Chapi" - *Calceolaria leptantha* Pennell (an endemic species to Peru [5]) was also predominantly present in Paracas, Nazca and Huari cultural periods; while animal red (cochineal from the scale insect *Dactylopius coccus*) was only present in Huari cultural period.

A database of the Peruvian dye plant composition is gradually being built up from which comparisons can then be made to ancient dyes. This study presents the preliminary results with some possible identifications of archeological textiles. The results obtained by HPLC-DAD analysis are in the procces to be confirmed by UHPLC-QTOF through a collaboration with University of Toulouse III-Paul Sabatier.

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Dyes in Italy during the first millennium BC

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The paper presents the first results of dye investigation from several, primarily Etruscan and Palaeovenetic archaeological sites of Italy, ranging in date from the 8th through 1st century BC. Very few ancient dye investigations have been carried in Italy until the present study, primarily due to lack of ancient textile studies in general and the fact that the vast majority of prehistoric Italian textiles are preserved in charred or mineralised state. Wild madder, woad and shellfish purple have been identified among others and indicate the presence of sophisticated dyeing technologies in the Apennine Peninsula by the Early Iron Age. The results are placed in the wider context of European dye culture of the first millennium BC.

Typically variable? A chemical study of commercial aniline dyes in a 19th C sample book

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The industrialised nineteenth century saw a significant number of dyeing instructions and manuals with dyed textile samples being published for commercial dyers and colourists. Such books were important for sharing general knowledge that kept dyers up-to-date with the range of colours from increasing numbers of new synthetic dyes that gradually supplemented, and finally superseded, natural dyes. Multiple copies of books were printed throughout the latter half of the century, with physical swatches of fabric, snippets of yarn or bundles of unprocessed fibres attached to pages alongside details of how they were dyed. Some sample books showed comparable colours from synthetic and natural dyes, offering the dyer and colourist choices.

The dyes of textile samples in surviving sample books seem relatively well-preserved, protected between the pages of the books from damaging environments, particularly light. The combination of textile samples, technical details and publication date entice textile historians, designers and dye researchers alike to study these valuable primary sources of material evidence. One such book was written by David Smith, a dyer and manufacturing chemist in the north of England. Called 'The English Dyer', Smith published his book in 1882 with 500 dyed samples per book [1]. It includes all the aniline dyes in commercial use in the early 1880s. In his introduction Mr Smith personally vouches for dyeing all the samples himself, establishing credibility with his intended readership of practising dyers, manufacturers and merchants (and now us).

Being fortunate to own a copy of Smith's book, I have begun studying it by analytical research. Smith included at least two instructions and associated samples for each aniline dye: with and without additives; varying concentrations; different fibres. I originally intended to select one example of each aniline dye for analysis by ultra-high performance liquid chromatography with photodiode array detection (UPLC-PDA) to add to the CTCTAH's reference database. But then I questioned how chemically accurate the different samples were. Could I trust my choice to be a reliable analytical reference for each dye - that is, would it be chemically representative? Could I trust Smith's confidence in the dyes he said he had used?

These thoughts provoked the need to understand the historical context for 'norms' of variability in making, supplying and using early synthetic dyes. For this pilot study, I analysed yarn samples next to 9 dyeing instructions in Smith's book that named aniline purple (including R, red shade and purple aniline) and 19 that named aniline violet (including B, BB, R, blue shade and violet aniline) to see how much the chemical profiles for each specifically-named dye varied. Using UPLC-PDA and DMSO/oxalic acid extraction [2], significant variability and subtle variation between samples with exactly the same name was found.

Chemical variability in aged historical commercialised materials is highly complex. Having already researched the impact of industrialised manufacture on the quality of early synthetic plastics from the mid to late nineteenth century, I am certain the synthetic dyeing industry faced similar issues of by-products from synthesis, chemical variability in the starting materials, and different levels of acceptable control by the manufacturer [3]. Smith's book is one of many historical manuals and instructions with the potential to bring us closer to engaging with material evidence from well-provenanced, true commercial historical contexts. By extending this chemical study to comparable publications that I have permission to analyse, I intend to shed light on typical variability in industrialised dyes and the essential role that sample books play.

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Dye and metal thread analyses of some tomb covers in Istanbul Fatih Mosque Complex

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Some Ottoman sultan and sultan family's tombs are in Istanbul Fatih Mosque complex. One of these tombs belongs to Naksidil Valide Sultan and her family. Naksidil Valide Sultan is wife of Ottoman 27th Sultan Abdulhamid I and mother of Ottoman 30th Sultan Mahmud II. She was born in 1768 and died in 1817. According to Turkish historians, Naksidil Valide Sultan is believed that Bonaparte French emperor's Joseph Bonaparte's wife's cousin.

Identification of an art object material of cultural heritage had received significant attention, because of its importance for the development of appropriate restoration and conservation strategies [1]. The tomb covers are an important part of Ottoman textiles art objects. For this reason, the tomb covers were analysed for restoration and conservation strategies. In this work, total 31 tomb covers samples were analysed in the Tomb of Naksidil Valide Sultan. Samples analysed are silk yarns and metal threads. HPLC-DAD (high performance liquid chromatography with diode array detection) method was used for dyestuff analyses. Extraction from samples were carried out with HCl/MeOH/water (2:1:1) solution [1-2]. Luteolin, ellagic acid acid, genistein, ect. were detected in silk yarns. Elemental percentage and thickness of metal threads on tomb covers were analysed a using SEM-EDX (scanner electron microscopy with energy dispersive X-ray spectroscopy). According to elemental analysis results, high amount gold and silver metals were detected in the metal threads. In addition to this, carbon (C), oxygen (O), sulphur (S), chlorine (Cl) and calcium (Ca) were detected as contamination elements (Figure 1).

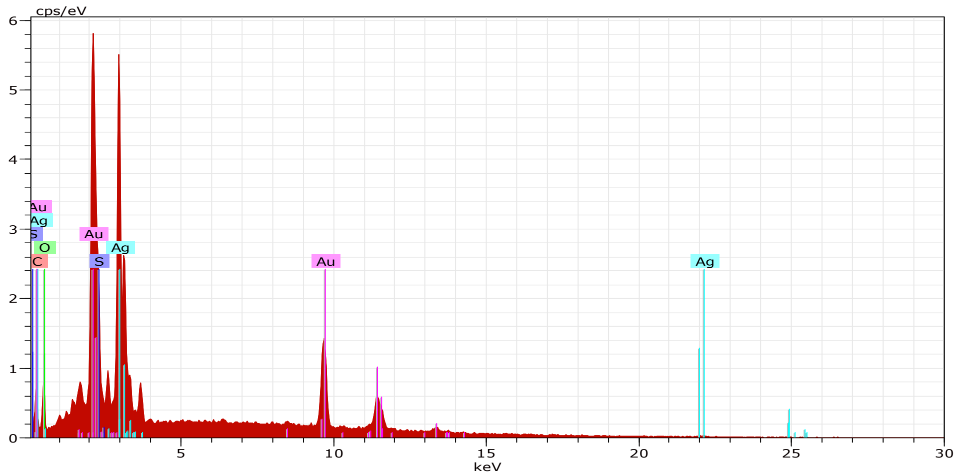

Figure 1. EDX spectrum of the tomb cover (inventory number: 52).

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Timeline of colours in Dutch fashion
Rijksmuseum costume collection, 17th to 20th century

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The Rijksmuseum of Amsterdam has a large collection of costumes, accessories and other textiles. A selection of the 100 most remarkable costumes (17th to 20th century) was made and a catalogue with pictures, art historical and technical information will be published early 2016.
As part of the necessary research on these costumes the colorants are analysed and identified in an effort to disclose the story of dye sources and techniques used in the Netherlands and eventually place them in a fashion timeline.

Besides the black, purple and blue colours a special focus will be given to the soft colours: lilac, salmon, pink, golden, magenta, orange and light green.
The colourful fabrics and embroideries were first examined under a digital microscope in order to determine their colour and physical appearance. Tiny samples were taken for colourant identification by means of UHPLC/PDA (Ultra High Performance Liquid Chromatography/Photodiode array detection) while in some cases mordant analysis were also performed using SEM/EDX (Scanning electron microscope/Energy dispersive X-ray spectroscopy).

A great variety of colourant sources were identified amongst which: galls, woad, orcein, safflower, logwood, brazilwood, cochineal, saxon green as well as several synthetic colourants.
Based on the historic, economic and linguistic[1,2] relevance, these colourants offer a surprising and adventurous journey through the colourful fashion history of the Netherlands.

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Yellow dyes of historical importance IV. Sawwort (*Serratula tinctoria* L.) and weld (*Reseda luteola* L.) in the Florentine Dye company "Francesco di Giuliano Salviati e Comp., tintori d'arte Maggiore", 1483-1498

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This presentation is the continuation of several former presentations at DHA meetings: it is the fourth part of the first author's series "Yellow dyes of historical importance" (DHA 13, 14 and 16/17) and it offers a focus on the yellow dyes that allowed the Salviati company of *Arte della Lana* (specializing in broadcloth production) to export so many green broadcloths to Constantinople and the Ottoman Empire, as presented last year at DHA 33 in Glasgow.

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

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

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

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

Among the treasures of information the three books provide, we chose to study the sourcing and use of two yellow dyes of historical importance, sawwort and weld, by this company. It had never been possible to do this for a mediaeval dye company in such detail before.

This research has brought really striking information:

- on the relative importance of dye plants collected in their wild, natural environment (exemplified here by sawwort) and of a massively cultivated dye plant such as weld;
- on the areas from which the plants were sourced;
- on the quantities used.

It also opens fascinating perspectives on the rhythms of crops, on a possible depletion of wild resources, and/or evolutions in fashion influencing the choice of one source of yellow dye in preference to the other.

The failed experiment.
An attempt at reviving the Polish cochineal dyeing in eighteenth-century Poland

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In parallel with the formation of domestic industry in eighteenth-century Poland, including silk industry, attempts were made to create scientific institutions undertaking, inter alia, the studies on native plants. A large factory complex in Grodno in Lithuania (now in White Russia) with research institute and School of Agriculture, established by Antoni Tyzenhauz, under-treasurer of Lithuania, at the behest of King Stanisław August Poniatowski, is an interesting example of combining these two activities. Development of textile production in Poland increased an interest in dye plants, although they weren't cultivated on large scale during that period. The contemporary botanists focused their attention to a native flora of Lithuania and an insect which for centuries was a source of red dye. We attempt to analyse the eighteenth- century archival materials concerning the organization of textile manufacturies in Poland, scientific journals and publications dedicated to the cultivation of dye plants, including host plants of Polish cochineal, and reintroducing of Polish cochineal in the dyeing industry.

How much scientific information could be preserved in an embroidery thread?

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The paper is part of an extended study (1996-2015) dedicated to the almost unknown Romanian "gold embroideries". Apart from the results themselves, the research performed until now confirm the importance of interdisciplinary work in common textile restorers - scientific investigators teams. Investigation on natural dyes, presented at earlier DHA meetings, suggested a possible correspondence between color, dye source, fibre functionality and the genuine manufacturing technique. Is this hazard or a new criteria for gold embroideries dating & provenience? At DHA33, results obtained on 43 embroideries were presented. Identified based on donor inscriptions and technical/artistic analogies, the embroideries come from 6 monasteries (including Putna) built in the same region, under the same dynasty reign (1386 - 1527). Using an inter-connected criteria methodology, a "mark" of Prince Stephan the Great embroidery workshops was discovered: the green contour of human faces and hands, red mouth and blue/ocre detailed hair, seem to be specific for all the gold embroideries he donated.

The same methodology will be now applied on a more specific, narrow, group of embroideries: epitrachelions from Putna Monastery collection, contemporary with the above mentioned ones. The present study is focused on two “twin” epitrachelions, apparently identical at a first glance. The original manufacturing technique looks similar: dark violet silk damask for the embroidery support, green silk thread for the face contour, red mouth and blue/ocre detailed hair. The only notable difference is the inscription mentioning the donor's name: Stephan the Great of Moldavia (1457-1504), on one of them. According to the Romanian literature, the inscripted epitrachelion is a copy realized in a Moldavian workshop, by using a Byzantion model, brought by Maria Asanina Paleolog, the second wife of Stephan the Great. Both pieces are considered masterpieces of medieval liturgical embroideries. During restoration research their technical difference became clearer. Could dye analysis, metal threads composition and morphology bring new information? Are the chromathic criteria preserved in the epitrachelions group? Is the methodology working for different groups of lithurgical objects? Are these features working as a work-shop signature? It became a question if dye analysis may enrich the results and contribute to the objects dating, from this point of view.

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The politics of colour – recovering the dye producing lichens of the Scottish highlands in June 1916

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The Royal Botanic Garden of Edinburgh holds a rare textile pattern book of over a hundred wool flannel samples dyed with lichens collected by Edward Stewart, Fellow of the Botanical Society of Edinburgh, between 30th May and 16th June 1916. Stewart's Report on his travels is detailed – the reason given for his task, anxiety about the continuing de-population of the Highlands – and the results of his explorations were submitted, with the pattern book, to the newly formed Board of Agriculture for Scotland in 1917. Despite the unremitting rain, and the difficulties of transport in the middle of the war, Stewart was able to interview local people to ask where lichens grew and how dyes were traditionally made from them. He made a collection of the most promising examples noting where each was found. This paper will follow Edward Stewarts two week journey, describe lichens he found and the colours they revealed and the consequences of the loss of a craft dyeing past.

Using Stewart's collection, Dr Thomas Stewart Patterson set out to test the lichens for colour, brightness and fastness, under Laboratory conditions at the University of Glasgow. We have, therefore not only botanical descriptions of lichens and their Highland habitat in the early 20thc but textile samples showing the colours each was capable of, from the brightest pink to dark reds, bronzes, drabs to the softest grey – a systematic investigation of the colours of native dye plants. As well as the 'crotal' lichens used in the manufacture of tweed, Paterson identified other colour producing lichens and plants. Although these were known and used in generations past, dye recipes in folk-lore or passed by word of mouth were often anecdotal. Paterson's work is especially interesting at a time of economic difficulty in Scotland and when the dye industry was turning increasingly to the development of synthetic colours.

I am indebted to the Staff at the Royal Botanic Garden Edinburgh Herbarium and Library for showing me the Report and sample book and for permission to publish.

Lecanora Tartarea found on the rocks of Ben Lui near Tyndrum dyed with concentrated ammonia in Dr Patterson's sample book.

Dye analysis of historical textiles from Okinawa and Indonesia Was there any exchange of dyeing techniques between these regions?

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It is well known that both Okinawa and Indonesia have produced high quality textiles. Based on "the Rekidai Hoan", diplomatic records of the Ryukyu kingdom, that ruled the current Okinawa prefecture, Japan and some neighboring islands from the 15^{th} to the 19^{th} C, dye materials such as sappanwood were exported from South East Asia to the Ryukyu kingdom. In addition to dyestuffs, many textiles were mentioned in the record as examples of diplomatic gratitude. Because not only dyestuffs and textiles could be exchanged between these two areas, but also dyeing techniques, I analyzed the dyes in certain textiles, especially heirlooms and costumes worn by people of high rank in their societies, to investigate whether similar dyeing techniques were used in both regions. In this study, I chose Indonesia to represent South East Asia because it was one of the centers for exporting sappanwood to the Ryukyu kingdom.

Material The time period for the studied objects is from the 15^{th} to the 19^{th} C. Ryukyu kingdom: 28 objects (107 samples), Indonesia: 10 objects (28 samples).

Methods Samples of thread or yarn, each 3-5 mm long, were extracted in pyridine: water: 1.0 M oxalic acid in water (95: 95: 10). The extracts were evaporated under vacuum, then redissolved in MeOH: water. The solution was injected and analysed using the following system: Shimadzu LCMS-2020, including autoinjector, gradient pumps and diode array detector; column, Phenomenex Luna C18 (2 x 150mm, pore size 3 µm), flow rate: 0.18 mL/min; mobile phase, a gradient of water and acetonitrile containing 0.1 % formic acid.

Results and discussion

<table>
<tr><th></th><th>Red</th><th>Yellow</th><th>Black or dark</th><th>Blue</th></tr>
<tr><td>Ryukyu kingdom</td><td>Sappanwood (the samples had faded to yellow)
Only two red samples showed cochineal and chay root, respectively.</td><td>Plants containing berberine as major compound.
Plants containing flavonol (M=610, 638). This dye source is unknown.</td><td>Indigo plants
The dark hue was likely obtained by multiple dyeing</td><td rowspan="2">Compounds from indigo plants were detected from both areas. Some samples showing pseudo-indirubin might have been dyed with woad.</td></tr>
<tr><td>Indonesia</td><td>16^{th} – 18^{th} C
Morinda citrifolia,
Mainly
Chay root, cochineal and lac were often found together.</td><td>Chay root, turmeric, plant containing flavonoids (different compounds were detected in Ryukyu textiles)</td><td>Ellagic acid, Morinda citrifolia. Iron mordant is expected.</td></tr>
</table>

From the results of these dye analyses, different dyes were detected for the red, yellow and black (or dark) specimens from each region. Colorless compounds detected in many sappanwood dyed samples from the Ryukyu kingdom confirm reports in the "Rekidai Hoan" that mention large quantities of sappanwood having been imported into the Ryukyu kingdom. One interesting point about sappanwood is that none of the Indonesian textile samples was dyed with it even though Indonesia was the center for the production of sappanwood. It may have been well known there how easily the red color of textiles dyed with sappanwood faded. Aside from sappanwood, there seems not to have been much exchange of dyestuffs and techniques between the Ryukyu kingdom and Indonesia.

Acknowledgement This study was supported by a grant from the Sekisui Chemical Co., Ltd. I would like to thank the following, who provided samples and information: Dr. Blythe McCarthy, Smithsonian Institution; Dr. Takako Terada, Kwassui Women's College, Japan; Dr. Tokushiro Takaso, University of Ryukyu, Japan; Ms. Miki Komatsu, National Heritage Board, Heritage Conservation Center, Singapore; Mr. Eiichi Ito, Library of Congress.

A Study of Dyeing in the Ming and Qing Dynasties (1368-1912) from Multiple Perspectives

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Colour held special significance in ancient China, acting as an indispensable element of official decrees to distinguish ranks. The Ming (1368-1644) and Qing Dynasties (1644-1912) saw the rapid development of textile handicrafts with the flourish of commodity economy and the prosperity of world trade. However, current knowledge of textile dyeing techniques in China during this time period is limited. This paper pioneers the multi-disciplinary exploration of dyeing techniques in the Ming and Qing Dynasties based on literature research of historical dye recipes [1] [2], the chemical analysis of historical and archaeological samples and the art historical investigation of dyeing in the social context.

Altogether 198 samples from 51 pieces of provenanced historical and archaeological costume and textiles at 11 collections mainly in China and the UK were carefully taken. Major factors taken into consideration included colour and the time period, type and status of textiles. Ultra-performance liquid chromatography coupled to photodiode array detection (UPLC-PDA) was applied and dye sources were identified by comparing analytical results with data in the library of common dyes in ancient China [3].

Results show that literature records and analytical results are consistent to a large extent in terms of the choice of dyes. Exceptions include the common use of turmeric, the preference of pagoda bud and the rare appearance of smoketree and gallnut in the analytical results. Single-dyeing and multi-dyeing methods recorded are also largely in accordance with those revealed by the analytical results, but the use of safflower alone for dyeing, which was recorded frequently, is not found in the samples. Differences in multi-dyeing include the combination of safflower and Amur cork tree and the few cases combining three dyes (only the combination of sappan, pagoda and smoketree were found) in the analytical results. These inconsistencies are probably because of some practical reasons such as the colouring effect and availability of dyes, or because of spatial differences or special dyeing methods in certain workshops.

The analytical results reveal that all five ground samples from yellow dragon robes are dyed by pagoda bud. Judged by detailed decrees for colour in the Qing Dynasty and official dye recipes for the colours in decrees, all these robes belonged to emperors. Along with official dye recipes for other yellow shades in decrees, it can be seen that detailed decrees on colour and dyeing techniques to obtain more shades and to control the consistency of these shades promoted each other. Further investigation shows that the realisation of dyeing activities also depended on a national wide network for the circulation of technique, raw materials and products. The flourish of commodity from the mid-Ming Dynasty fostered the development of private textile workshops and the specialisation of dyeing workshops. When viewing dyeing in the global frame, it is found that China communicated with the rest of the world by exporting dyes including safflower, Indian madder, gallnut and importing dyes like cochineal and then synthetic dyes.

This research reveals both dyeing techniques in the Ming and Qing Dynasties and their relationship with the society and the world. The research results not only promote the knowledge of Chinese dyeing history but also contribute to the overall understanding of world dyeing history in this period.

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Comparison of Malaysian and Indian ikat technique. Color and design analysis

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Laboratory of Natural Dyeing “Natural Art” has been exploring natural dyestuff used in traditional techniques of cloth decorating. The paper presents artistic and historic background of such technique as ikat -this technique is famous in Asia, South America, Africa. Important part of presentation is comparison of ikat technique in India – Pochampally region and Malaysia. In this centers of weaving ikat cotton and silk fabrics the peoples still are using natural dyeing sources.The **pua kumbu**, the hand-woven warp **ikat** textile of the Iban, represents the quintessence of Iban culture. It is, depending on the design, historical archive, a mythological or religious story or a personal tale. It is a statement about the soul of the weaver and her relationship with the spirits. The process of mordanting yarns in preparation for dyeing and weaving was seen as a way of managing the spiritual realm. In this presentation will be demonstrated step by step the process of mordating and dyeing cotton yarns in **Rumach Garie** Iban long house on Borneo island. Mordanting is the part of the weaving process where the natural oils present on raw or untreated cotton yarns are stripped away so that the fibres can absorb a particular type of vegetable dye. In **Rumach Garie** weavers and dyers use 3 very important dyes: **Engkudu –** the colour obtain from the tree **Indian mulberry** *Morinda Citrifolia,* **Engkerbai** *Psychotria Virdiflora,* **Tarum –** the blue colour from indigo *Marsdenia tinctoria* and others compounds. The search for the durable colour is the knowledge combining chemistry, textile industry, art, magic and rituals, which have their roots also in the folk culture. In old epochs a dyer was called an artist not without reason.


1


2.

Fig. 1.2. Preparing dyes and cotton yarns for mordating process

Many design patterns may have ethnic, ritual or symbolic meaning or have been developed for export trade. Traditionally, ikat are symbols of status, wealth, power and prestige. Because of the time and skill involved in weaving ikat, some cultures believe the cloth is imbued with magical powers. A wide range of colors can be obtained from dyeing plants. The mortar has a significant impact on the color as it modulates it. The secret of color fastness belonging to complicated mordating process.

The interaction between civilization and nature is like a running cycle where there is interdependence for survival between the mankind and environment. This historical methods of cloth decoration in India and Malaysia are still developed by famous designers at the world.

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The problematic of bleeding of indigo dyed threads of a group of central Asian silk samites dated from the 7-8th century

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The starting point of this research was a master-thesis in textile restoration, which dealt with two silk samites (weft-faced compound twill) from Central Asia, belonging to the Abegg-Stiftung's Collection (inv. nos. 5681 and 5682). Those objects are archaeological finds radiocarbon-dated to the 7th-8th century. The samites show coloured patterns made of 8 different weft threads, among others light and dark blue. During the master-thesis, an aqueous cleaning method was elaborated for inv. no. 5682. While testing the water fastness of each different thread, the blue dyes were bleeding in water, challenging the planned wet cleaning. Micro-chemical analyzes as well as High-performance liquid chromatography (HPLC) were carried out and confirmed that indigo is the implicated dye.

Vat dyes are especially light and water fast due to their chemical features and indigo needs to be reduced such as being soluble in water. Indigo threads showing poor water fastness are unusual.

However, indigo, and especially dark colorations achieved through multiple dyeing bathes, is also known to poorly resist abrasion. In such case, layers of molecules could loose coherence when submerged in water, releasing indigo particles. Yet, this does not explain that the light blue threads are also bleeding.
We tested a hypothesis that could explain the dyestuff bleeding. In some cases, when the fibres are strongly degraded, some very small particles of blue silk could form colloidal dispersion and look as if the dye was solubilized. We used Raman spectroscopy to verify whether the blue particles of those extracts were only indigo or if they also contained silk. The resulting spectrum corresponded to pure indigo and we rejected the hypothesis of the presence of small silk particles.

We collected further information on the appearance of the fibres by performing a microscopic observation of fibres mounted in Meltmount*1.662. We noticed that a lot of small blue particles were distributed on the surface of the fibres, which itself is not blue-coloured. On the contrary, silk fibres dyed with indigo in the Abegg-Stiftung were blue and presented no surface particles. In order to better understand the problem, we observed other blue threads from about 10 samites from the same time of creation and provenance (some already washed), which water fastness was also tested. Already washed threads showed less surface particles. Moreover, we could see a clear link between the presence of particles and the tendency to bleed. This difference could be explained by different colouring methods, raising a new question: has the indigo been used as a pigment instead of as a dye?

To answer this question we project to perform the following analyzes: identification of a potential binding medium present on the fibres and a potential mordant, as well as practical tests of silk colouring with indigo pigment.

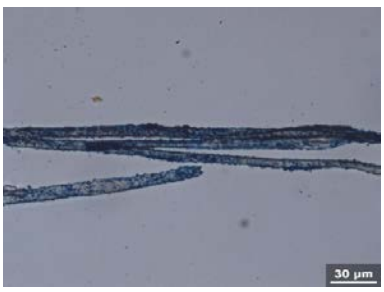

Figure 1: Fibres from inv. no. 5682 showing particles on the surface.

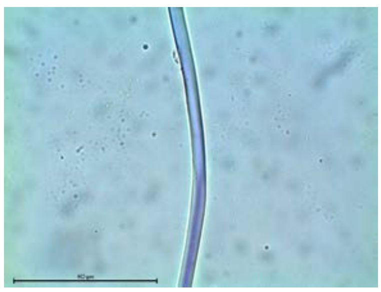

Figure 2: Fibres from a silk fabric dyed in the Abegg-Stiftung without particles on the surface.

Characterization of Madder compounds present in lake and textile, throw ammonia extraction and micro-sampling with Ag-gel matrix associated with SERS analysis

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Until the introduction of synthetic dyes in the XIX century, artworks were realized using lakes and textiles prepared from natural raw materials. The precipitation of lake pigments and the dyeing process generally occurs due to the formation of a complex with different cations. The complexes thus obtained are particularly stable and insoluble in water or common organic solvents. So, to perform the analysis, it is necessary to break the complex and then extract the compounds.
The method most commonly used until now had been a mixture of organic solvent with strong acid as HCl or H_2SO_4 [1]. This method ensured high yield of extraction producing, however, hydrolysis of original compounds in the sample and allowing only the identification of the main aglycones.
Our new extraction method [2], based on the use of ammonia in association with sodium EDTA, was developed to preserve the glycoside compounds present and then get closer to the real molecule pattern involved in lake precipitation and dyeing process.
In fact, understanding the chemical nature of the compounds is very important, to adequately respond, for example, to questions regarding the proper storage conditions, the dating or the provenance of an artwork.
In order to indentify the Madder compounds presents in the ammonia extract of lake and textile, in the first step of the research, samples of Madder lake and wool dyed with *Rubia tinctorum* L. were prepared, following the recipes contained in ancient and medieval recipes [3,4].
Then, chromatographic separation of ammonia extracts were performed and the fractions obtained were analyzed using NMR, ESI-MS, to identify the isolated compounds, and HPTLC-SERS (Surface Enhanced Raman Spectroscopy) was performed.
The choice to perform this particular type of investigation is related to the fact that in real cases it is very important to apply techniques that allow a rapid, minimally invasive and highly sensitive identification of natural organic dyes and micro-invasive SERS techniques present these characteristics.In particular, attention has focused on the use of solid matrices and, among those subject of the most recent publications, was particularly interesting the Ag-Agar matrix [5], for the extraction of dyes from textiles and their subsequent identification by SERS.
Basing on the experience gained and the problems found in the use of the Ag-agar matrix we developed a new analytical protocol [6], applying for the first time an Ag-gel matrix to painted surface.
We introduced a new type of gel which, due to its transparency, the lower gelling temperature and the greater rigidity is better compared to the Agar and, in addition, a specific KIT (patent pending) was designed, which contains devices expecially designed and everything necessary for the execution of the protocol and aimed to make it simple, rapid and reproducible.
The results of micro-sampling tests allow us to affirm that the average size of the micro-samples taken from painted surface with the technique developed are much lower than a millimeter (~20 μm). Moreover, from the video-colorimetric investigations conducted, it is clear that there is no visible change in the optical properties after the micro-sampling.
To interpret the SERS spectra of micro-samples of lake and textile extract on our Ag-gel matrix, we use as reference the spectra obtained from fraction analysed by HPTLC-SERS.

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The quest for folium

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The *folium* dye, extracted from *Chrozophora tinctoria* (L.) A. Juss., has been cited many times in ancient treatises for its use in painting art [1-3]. We can therefore safely state that its use was common, with main concern to miniature painting. Despite this, its identification in artworks is inexplicably rare [4], most probably for a lack of diagnostic information. A recent work attempted to contribute to its analytical characterisation [5] and its presence has been evidenced in some instances on Western European manuscripts [6] but what is still missing is the comprehension of the chemical nature of the dye.
In this study we have employed different analytical techniques in order to gain structural information on *folium*. Besides this, some simple experiments have been carried out to verify whether the information emerging from ancient treatises were reliable or not; in particular, it was verified that the behaviour of the dye in relation to pH, i.e. *folium rubeum*, *folium purpureum* and *folium saphireum* at respectively acid, neutral and alkaline pH, is far from that described in bibliographic sources. The main difference in colour is actually given by the maturation state of the cuticles, which are blue in unripe fruits, purple in ripe fruits; this can explain the origin of *folium saphireum* and *folium purpureum*. However, complexes of metal ions with folium have different colours, with Fe^{3+}-folium complex being red: could a possible contamination with iron, rather than pH, be the origin of *folium rubeum*?
The whole characterisation procedure started with an extraction step in cold water. Folium is apparently very soluble in water, showing therefore a marked *hydrophilic* nature. At the same, though, the coloured fraction of the extract can be completely adsorbed on a reversed phase resin, which means that folium shows also a marked *hydrophobic* nature. We can reach agreement with everyone by stating that folium has rather a marked *amphiphilic* nature, i.e. it contains molecules with polar, water-soluble groups attached to nonpolar, water-insoluble aliphatic or, most probably aromatic structures bearing the coloured part.
After elucidating this aspect, a purification step on a C18 resin was carried out. This allowed the elimination of uncoloured hydrophilic compounds and the separation of some coloured fractions. By methanol/water gradient elution it was possible to separate a yellow and an orange fraction, rich in flavonoids, but also some fractions with different purple tones. These were subjected to hydrolysis with a pectolytic enzyme, in order to remove the hydrophilic part of the molecule, which is made of oligosaccharides according to NMR analysis. Further on, the solution previously subjected to enzymatic treatment was extracted in methoxybenzene from which it emerged a purple residue that can be safely considered as the hydrophobic part of the molecule. Works are in progress with HPLC-MS, SERS-Raman, MALDI-ToF-MS, and NMR in order to finally define the structure of the dye.

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ABSTRACTS OF POSTER PRESENTATIONS

Red dyes used for Kalamkari textiles

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Kalamkari textiles are superb examples of the skills of the master dyers in India. These textiles, produced primarily by a combination of mordant and resist dyeing, were exported to the West with Portuguese traders and the East India companies of England and the Netherlands from the mid16th century on. By using primary colours, a variety of yellows, indigo and a brilliant red mordanted with either iron or alum, an astonishing range of colours and shading was obtained.

Fig. kalamkari fragment from the V&A collection (IS 489:25-1883)

Contemporary accounts from European observers (Roques 1678, Beaulieu 1734, Coeurdoux 1742 and Roxburgh 1790's) [1] describe the complex techniques used for the manufacture of kalamkari mentioning chay root (*Oldenlandia umbellata* L.) as the source for the different red shades, while some accounts also refer to other dyes. Various plant sources were historically used in India to produce red on cotton textiles, such as safflower (*Carthamus tinctorius* L.), sappan wood (*Caesalpinia sappan* L.), Indian mulberry (*al)* (*Morinda citrifolia* or *tinctoria* L), munjeet/manjeet or Indian madder (*Rubia cordifolia* L.), dyer's madder (*Rubia tinctorum* L.), red creeper (*Ventilago madraspatana* Gaertn.*)* [2] and since the end of the 19th century, also synthetic alizarin was applied.

The actual study focuses on the red dyes used in Indian cotton textiles. Ten fragments, including some printed textiles, from the Victoria & Albert museum were chosen for investigation on the basis of date and geographical location since dyes might differ over time and particularly between Western and Eastern India. The fragments date between 1400 AD and the last quarter of the 19th century and originate from the Coromandel coast and from Western India. Chay root was found in eight of the ten fragments, while dyer's madder and Indian mulberry were identified in the two other. In parallel, new dye experiments were executed with chay root recently imported from India to attempt to obtain the famous strong red colour and to identify the related dye composition.

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Degradation of glycosylated aglycons of natural dyes

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The fading of natural dyes on historical textiles is a complicated process. Study is complicated by the low concentration of dyes on fibres, the amount of various components of dyes derived from natural sources, the degradation products of dyes, and by the degradation products of textile fibres. The aim of the work was to determine the changes in the concentrations of chromophores following the artificial aging of fabric dyed with madder roots. Detection by mass spectrometry was focussed on ruberythric acid (alizarin O-primoveroside), alizarin O-glycoside, alizarin, alizarin methyl ether, lucidin primoveroside, lucidin O-glycoside, lucidin and lucidin ethyl ether.
An important step for analyses is the type of dye extraction from the fibres. Hydrochloric acid, the most commonly used hydrolyzing agent, breaks the O-glycosidic bond with aglycone and is compatible with mass spectrometry. Formic acid is a ‘weak’ hydrolyzing agent that preserves the O-glycosidic bond, is compatible with mass spectrometry and can be easily evaporated following extraction.
Two types of artificial aging were chosen: thermal and photooxidation. Photooxidation aging had a greater impact on the degradation of dyes on fibres than thermal aging. In the first phase of dye fading when thermal aging was employed, the concentration of aglycone alizarin increased, which was interpreted as the result of the breaking of the O-glycoside bonds of ruberythric acid and alizarin O-glycoside. With photooxidation aging, the increase in the aglycone alizarin concentration was not recorded. The most stable chromophores and most concentrated pigments in the madder were O-glycosides and O-primoveroside alizarin. For this reason the aglycones of dyes are the most commonly sought components in analyses of original colour.

This research is supported by the grant project from the Czech Science Foundation entitled “Medieval Textile and Dyeing Technologies – Archeometry of Textile Finds” 14-06451S (2014-2016) .

Identification of natural dyestuffs of four historical naval ensigns in the Istanbul Naval Museum with high pressure liquid chromatography (HPLC)

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Restoration and conservation of historical textiles is an important issue for the museums. The main goal of restoration and conservation is to conserve the objects with their original forms and to transfer them to next generation. First and foremost step for achieving this aim is to be known the main components of this objects. If the main components of historical objects are known, restoration and conservation process can be done according to them.

Istanbul Naval Museum is one of the important museums in Turkey, yet the textiles there in have not yet been evaluated through chemical analysis. In this study, the natural dyestuff components of four historical naval ensigns in the Istanbul Naval Museum were identified qualitatively with high pressure liquid chromatography (HPLC) method. In the component of this samples; carminic acid, carminic acid + elagic acid + luteolin, carminic acid + berberine and carminic acid + elagic acid were identified.

The naval ensigns that is subject to analysis: The first of which has red and yellow colour is used in the Battle of Lepanto, in 1571. The second of which has red colour is used in period of Selim III (late18th century). The third of which has red colour is used by Ottoman Navy during the 19th century. And the fourth of which has red and yellow colour, has a component (berberine) which has not been observed in any result of the dyestuff analysis in Turkey.

It is thought that the data gathered as a results of this analysis would be an important source for the restoration and conservation of this artefacts, and it would provide information regarding the artifacts's historical past.

Examination of dyed silk fabrics with dyer's sumac (*Cotinus coggygria* Scop.) according to different mordants

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Dyer's sumac or young fustic (*Cotinus coggygria* Scop.) is a bush that can grow to 18 feet in height and has oval, long-stemmed leaves. The large clusters of fruit in late summer are especially noticeable, giving rise to its common name in German, *Perückenstrauch*, wig tree. The clusters can be a foot long and consist of numerous featherlike fruit stems, only a few of which, however, actually bear small berries [1]. Dyer's sumac grows Mediterranean area, Asia Minor, the Caucasus, Iran, Afghanistan and Canary Islands. Into the 19th century in Europe, its heartwood was much used as a source of dyestuffs for yellow. During World War I, the Turkish army had uniforms and tents dyed with dyer's sumac.

In this present paper, firstly, silk fabrics were mordanted with alum ($KAl(SO_4)_2.12H_2O$) and gall oak plant. Iron mordanting process were applied for 60 minutes at 65 ^oC and room temperature. Other mordanting and all dyeing processes were performed for 60 minutes at 65 ^oC temperature. Used natural dye and mordant percentages are shown in Table 1. A reversed phase high performance liquid chromatography (RP-HPLC) with Diode Array Detection (DAD) method was utilized for the identification of dyestuffs present of silk fabrics dyed. Extraction from samples were carried out with HCl/MeOH/water (2:1:1) solution [2-3]. Gallic acid, ellagic acid, their derivatives, fisetin and sulfuretin were detected in the dyed silk fabrics. Colour values of fabrics dyed were measured a using CIEL*a*b* (colour space) spectrophotometer.

<table>
<tr><th>Mordant</th><th>Mordant Percentage</th><th colspan="2">Mordanting pH</th><th>Natural Dye</th><th>Natural Dye Percentage</th><th colspan="2">Dyeing pH</th></tr>
<tr><td>gall oak</td><td>5</td><td colspan="2">6.0</td><td>dyer's sumak</td><td>50</td><td colspan="2">6.5</td></tr>
<tr><td>gall oak</td><td>10</td><td colspan="2">6.0</td><td>dyer's sumak</td><td>50</td><td colspan="2">6.5</td></tr>
<tr><td>gall oak</td><td>15</td><td colspan="2">6.0</td><td>dyer's sumak</td><td>50</td><td colspan="2">6.5</td></tr>
<tr><td>gall oak</td><td>20</td><td colspan="2">5.5</td><td>dyer's sumak</td><td>50</td><td colspan="2">6.0</td></tr>
<tr><td>gall oak</td><td>25</td><td colspan="2">5.5</td><td>dyer's sumak</td><td>50</td><td colspan="2">6.0</td></tr>
<tr><td>alum</td><td>6</td><td colspan="2">3.5</td><td>dyer's sumak+gall oak</td><td>50</td><td colspan="2">5.5</td></tr>
<tr><td>alum</td><td>6</td><td colspan="2">3.5</td><td>dyer's sumak+gall oak</td><td>50+5</td><td colspan="2">5.5</td></tr>
<tr><td>alum</td><td>6</td><td colspan="2">3.5</td><td>dyer's sumak+gall oak</td><td>50+10</td><td colspan="2">5.0</td></tr>
<tr><td>alum</td><td>6</td><td colspan="2">3.5</td><td>dyer's sumak+gall oak</td><td>50+15</td><td colspan="2">5.0</td></tr>
<tr><td>alum</td><td>6</td><td colspan="2">3.5</td><td>dyer's sumak+gall oak</td><td>50+20</td><td colspan="2">5.0</td></tr>
<tr><td>alum</td><td>6</td><td colspan="2">3.5</td><td>dyer's sumak+gall oak</td><td>50+25</td><td colspan="2">5.0</td></tr>
<tr><td>alum+iron</td><td>6+1</td><td colspan="2">4.0</td><td>dyer's sumak+gall oak</td><td>50</td><td colspan="2">6.5</td></tr>
<tr><td>alum+iron</td><td>6+1</td><td colspan="2">4.0</td><td>dyer's sumak+gall oak</td><td>50+5</td><td colspan="2">6.0</td></tr>
<tr><td>alum+iron</td><td>6+1</td><td colspan="2">4.0</td><td>dyer's sumak+gall oak</td><td>50+10</td><td colspan="2">6.0</td></tr>
<tr><td>alum+iron</td><td>6+1</td><td colspan="2">4.0</td><td>dyer's sumak+gall oak</td><td>50+15</td><td colspan="2">5.5</td></tr>
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<tr><td>alum+iron</td><td>6+1</td><td colspan="2">4.0</td><td>dyer's sumak+gall oak</td><td>50+25</td><td colspan="2">5.0</td></tr>
<tr><td></td><td></td><td>65 °C</td><td>room temp.</td><td></td><td></td><td>65 °C</td><td>room temp.</td></tr>
<tr><td>iron</td><td>3</td><td>5.5</td><td>5.5</td><td>dyer's sumak+gall oak</td><td>50</td><td>6.0</td><td>6.5</td></tr>
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<tr><td>iron</td><td>3</td><td>5.5</td><td>5.5</td><td>dyer's sumak+gall oak</td><td>50+20</td><td>5.5</td><td>5.5</td></tr>
<tr><td>iron</td><td>3</td><td>5.5</td><td>5.5</td><td>dyer's sumak+gall oak</td><td>50+25</td><td>5.5</td><td>5.5</td></tr>
</table>

Table 1. Percentage of mordant and natural dyes.

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Eco-friendly indigo dyeing using extract from orange peel waste

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In recent years, the awareness of need for sustainable development is growing stronger due to the depletion of natural resources. Increasing greenhouse emissions and awareness of the need for sustainable development in terms of safely reusing waste and biomass, the trend towards transformation of waste/biomass to valuable materials and energy i.e. valorization, is growing stronger. [1] A significant amount of food waste is generated every year during processing and consumption of agriculture products, such as fruits peels among others. An increasing number of research and development efforts have been focused on the conversion of waste, biomass and various residues into energy, fuels and other useful materials [2,3].

The application of orange peel extract in indigo reduction was studied for developing eco-friendly indigo dyeing process. We report a novel indigo dyeing process of using the extract of *Citrus unshiu* (madarine orange) peels as an eco-friendly reducing agent with antioxidant and antimicrobial activities. Antioxidant and antimicrobial activities of extracts were measured and total sugar content also was measured. Its reduction power of synthetic indigo was evaluated by reduction potential measurements and dyeing tests. *Citrus unshiu* peels were extracted in water and this extracts was tested to investigate whether it has antioxidant and antimicrobial activities. The extract showed relatively high DPPH radical scavenging activity and contained high sugar content of 64%. It was confirmed that the extract contained several reducing sugars such as fructose, glucose, and galactopyranose. Reduction of indigo was occured rapidly in a solution containing the orange peel extract and it reached to the maximum color yield in one or two day. The reduction potential of the extract was stabilized at about -550 ~ -600mV depending on concentration of the extract. At higher concentration of the extract, reduction lasted for longer time and stronger color yield. The results showed that the orange peel extract could provide a biodegradable, nontoxic, cleaner alternative to sodium dithionite in indigo dyeing.

ACKNOWLEDGEMENTS
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Effect of cryoprotectant on bacterial reduction in indigo dyeing

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The advent of synthetic indigo in 1897 led the industry to abandon the traditional fermentation dyeing methods. Currently sodium dithionite, due to its economic properties, is the most important reducing agent used in the dyeing industry including indigo. However there are some disadvantages, such as, it is relatively unstable, toxic to environment, and difficult to control the system. Other technical problems are remained related to the difficulty in controlling processes and the non reproducibility of the obtained shades. For these reasons, many attempts have been made to replace sodium dithionite with more environmentally friendly alternatives, such as catalytic electrochemical reduction [1], biodegradable reduction including glucose and other reducing sugars [2], and the microbial reduction including biotechnological process [3].

In previous study, we investigated the microbial reduction of indigo by using four strains of bacteria isolated from the naturally fermented indigo vat. They were named by *Dietzia sp.* KDB1(KC433534), *Nesterenkonia sp.* KDB2(KC433535), *Nesterenkonia sp.* KDB3(KC433536), and *Nesterenkonia sp.* KDB4(KC433537) and registered in the Genebank. We confirmed their reducing ability toward synthetic indigo as well as natural indigo. For improving convenience of their use, storage, and transport, we tried to make them powder form using freeze-drying method. Cryoprotectants were used to reduce cell damage of bacteria during freezing.

In this study, the freeze-dried bacteria were used in indigo reduction dyeing to study the effect of cryoprotectant type on reducing ability of bacteria. Reduction potential, dye uptake and pH of indigo reduction bath were measured.

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

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Hair-dyeing by using *Rubus coreanus Miquel* sludge

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Hair dyes are classified into three types such as temporary, semi-permanent, and permanent ones depending on the duration of dyed hair color. Historically, the use of hair coloring was dated back to the ancient Egypt. The extracts from henna, chamomile, indigo, wood, bark, leaves or flowers have been used for hair coloring in the past [1]. However, many synthetic colorants have been discovered and have replaced natural vegetable dyes. Commercially, 70% of the sales related to hair dye industries are derived from synthetic permanent dyes [2]. Chemical processes of permanent coloring are described by oxidative reaction producing polymerized pigments. Natural dyes are normally non-oxidative semi-permanent type among hair color formulation. Compared with permanent dyes, they produce delicate changes in shades of color that is faded slowly and progressively. Synthetic hair dyes have been replaced by some natural dyes such as anthocyanins, anthraquinones, and lawsone for red, quercetin, curcumin, and ellagitannin for yellow, indigo carmine and antocyanin blue for blue, curcumin, p-benzoquinone, juglone for brown shade [3-5].

As a source of anthocyanins, we focused on the fruits of *Rubus coreanus Miq*. (common name; bokbunja in Korea) which are mainly used for traditional wine production [6]. The wine process of maceration generates a large amount of sludge (marc) which contains seeds and pulp. The seed waste is the potential source of seed oil that can be applied for foods, lubricants, fuel for paraffin lamps, or additives for paint formulations [7]. Hot water extract of the pulp contains free and combined organic acids, neutral sugars, pectin, and anthocyanins [8].

In this study, we obtained the extract of colorants from the sludge of the traditional bokbunja wine process by applying hydro-extraction, enrichment by evaporation, and freeze drying techniques. The dyeing on to human hair was performed at some pH values by using the commercial condition; 0.4g of human hair, 100% (on the weight of hair) of the powder of colorants, liquor ratio 1:5, 40 and 30min. The extract was evaluated by UV-Vis spectroscopy, antioxidant property and antimicrobial activity measurements. Color of the extract in aqueous solution was red at pH 2, violet at intermediate pH condition, and brown at pH 9. Color properties and colorfastness to light and washing were also analyzed for the hair samples dyed with the extract. With the variation of pH, the color of dyed hair was observed mostly BG-RP at pH 2-5 and then changed to YR-GY at pH>6. For the dyed hair samples, light colorfastness was relatively good; the rating 3 was maintained up to 40 hrs. The rating of wash colorfastness was remained 3 for 25 cycles. Results of color analysis and fastness tests confirmed that the colorants from the *Rubus coreanus Miquel* were successfully applied to hair-dyeing.

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Cosolvent effect on micellar solubilization of indigo

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The blue dye indigo is one of the oldest natural dyestuffs and has been known to since ancient times. It is used to be extracted from plants and used for coloration of textiles. Identification of indigo that belongs to vat dyes is very difficult owing to the low stability and solubility. Therefore solubilization of poorly soluble or insoluble dyes has been a very important issue in screening studies of historical art objects [1-3].
The most commonly used techniques in solubility studies are pH adjustment, cosolvency, micellization and complexation. Micellar solubilization is a powerful alternative for dissolving hydrophobic dyes in aqueous environments [3]. As organic solvents ethanol, glycerol, poly(ethylene glycol), and propylene glycol, N,N-dimethylformamid (DMF) known as "cosolvents", have also been widely used in screening studies, because of their large solubilization capacity for poorly soluble organic molecules and their relatively low toxicity [4].

The present study is focused on the characterization of solubilization of indigo dye by anionic surfactant sodium dodecyl sulfate (SDS) in the absence and presence of DMF. Solubility studies of indigo were performed according to the addition of excess amount of dye into surfactant solutions. The solution containing increasing amount of water cosolvent system was prepared and solubilization capacity of the SDS was studied using spectrophotometric method. In order to see the cosolvency effect on micelar solubilization the results were compared. The phase solubility diagrams drawn from UV spectral measurements are of the A_L type and indicate an enhancement of indigo solubility in the presence of SDS as well as in the presence of DMF.

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The analysis findings that will form the basis of textile conservation process in the Ankara Ethnography Museum

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This study was carried out in an ongoing research within the scope of textile conservation process on some woven fabrics obtained from the Ethnography Museum in Ankara. The Ankara Ethnography Museum was opened in 1927 with the attempt of Mustafa Kemal Atatürk. Turkish folk clothes and belongings from the Seljuk period until the present day compiled from various regions of Anatolia are exhibited in the Ankara Ethnography Museum.

The Ethnography Museum doesn’t have a conservation department and artifacts on display are not subjected to the conservation process. Some of the technical-aesthetic details and periods (roughly) are available for exhibited and stored artifacts based on the user's declaration. However dye, age and texture analysis of the fabrics which will be essential for the conservation and restoration of the artifacts have not been done. For this reason in order to contribute to the Ethnography Museum and protect cultural values, with special permission from the museum, yarn samples of stored silk fabrics are examined by the help of an optical microscope for detecting the fiber type and the yarn samples of stored silk fabrics examined by the help of high-performance liquid chromatography method that has been configured with dad detector for detecting the dye type of yarn for each color.

In this poster presentation, technical features such as dyes, age, type of yarns and texture analysis have been given which are obtained from the samples of woven fabrics reflecting the traditions of Anatolia.

Inorganic substrates of lake pigments: data from post-byzantine Greek icons

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Organic lake pigments have been extensively used in the context of post-byzantine painting and the dyestuffs used for their production have recently constituted the subject of various studies [1, 2]. Although the inorganic substrates on which dyestuffs are adsorbed affect pigment's hue and other properties, they are quite rarely subjected to investigation [3]. In a set of approximately 40 post byzantine icons the micromorphological characteristics as well as the elemental composition of the inorganic part of lake pigments were explored using SEM-EDS. An attempt was made to correlate the analytical results with pertinent recipes found in post-byzantine, Greek painting manuals [4].

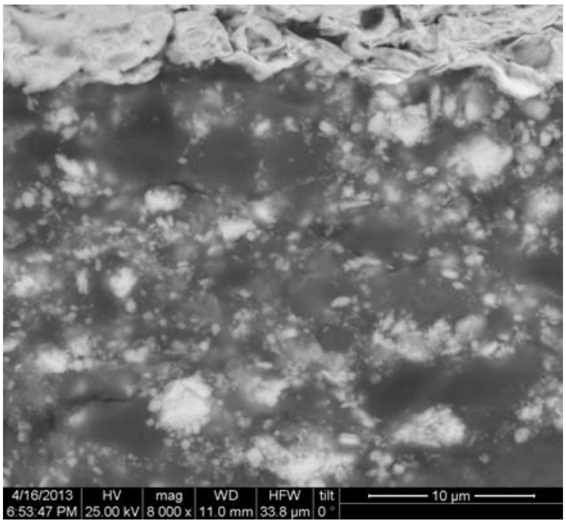

Figure 1. Paint layer cross section of a late 18th century Greek icon. Lake-dominated domains (grey) and 'lead white'-dominated domains (white). SEM, BSE, 8,000x.

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Turmeric: to eat or to dye? A natural historical dye

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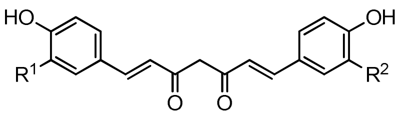
History reveals that the art of vegetable dyeing has been in practice since ancient years. Identification of pigments and dyes contained in artworks and historical textiles is of fundamental importance for the study of their manufacturing technology and to their conservation and long-term preservation. Turmeric or curcuma, also known as Indian saffron, is a popular spice, and ingredient in traditional Ayurvedic medicine and in modern medicine as antioxidant, anti-inflammatory and anti-carcinogenic agent, as well as colouring agent. It is obtained from the ground roots of *Curcuma longa* L., a plant growing abundantly in East Indies and China (Figure 1). Its chief bioactive components are the brilliant yellow compounds curcumin, demethoxycurcumin, and bisdemethoxycurcumin, along with other minor curcuminoids (Figure 2) and from the chemical point of view they are 1,3-diketone derivatives. Turmeric is used as a preservative, colourant and flavouring agent in food products including baked foods, pickles and meat products (E100). On the other hand, it has been used as a direct dye on cotton, wool and silk, and in artwork and historical textiles mainly in combination with other dyes, for example with cochineal used for dyeing of silk [1,2].

(a) (b) (c) (d) (e) (f)

Figure 1. (a)-(b) *Curcuma longa* L., (c) Rhizome, (d) dried Rhizome, (e)Turmeric, (f) From Royal Ontario Museum.

Curcuminoids have been reported to be extracted successfully under mild processes (TFA, HCOOH-EDTA, oxalic and citric or acetic acid) but fail to be extracted via the widely used HCl extraction method [2,3]. Interestingly, they can be identified successfully by surface techniques as time-of-flight secondary ion mass spectrometry [4] and surface enhanced raman spectroscopy [5].



Curcumin, R^1=R^2=OCH_3
Demethoxycurcumin, R^1=OCH_3, R^2=H
Bisdemethoxycurcumin, R^1=R^2=H

Figure 2. Curcuminoid compounds in turmeric.

Based on the importance of curcunin in history and archaeology and on our continuous interest on curcumin [3] as well as on the chemistry of carbonyl and 1,3-dicarbonyl substrates [6] we consider that a presentation of the available data about turmeric including the history, the chemistry, the dyeing recipes, the extraction methods as well as the identification methods will be useful to the researchers on this field.

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The Byzantine *Epitaphioi* of Mount Athos: historical and technological context

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According to the World Heritage Committee, Mount Athos is considered to be of an outstanding universal value, as it is the most important monastic centre of the Christian Orthodox Church. This research focuses on the findings from three (3) Byzantine liturgical textiles known as *epitaphioi*, which from a historical point of view are the most important of Mount Athos. The textiles are displayed in Vatopediou, Ksiropotamou and Stauronikita athonian monastic collections. One of the *epitaphioi* is a donation from the byzantine emperor Ioannis VI Kantakouzenos (Fig.1).

Epitaphios is a multi-component artwork which before any preventive or interventive treatment physicochemical analysis should be applied, revealing the component materials and the state of degradation.

Physico-chemical techniques such as HPLC-DAD is employed in this research to identify the colouring materials. Other techniques (Optical Microscopy & SEM-EDX) were employed for further studies. Dyes which were identified in the *epitaphioi* are as follows: kermes, indigo (or woad), weld, madder, and interestingly cochineal which could have been originated from the Polish insect (*Porphyrophora Polonica* L.).

Figure 1. Detail form the byzantine *epitaphios* of Kantakouzenos displayed in Vatopediou monastery, Mount Athos.

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HPLC-DAD-MS and LDI-MS strategies for anthraquinoid lakes identification in paint samples

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Lakes are artificial pigments obtained from one or more organic natural dyes, extracted from roots, plants, or shellfish, and fixed by absorption or complexation on an insoluble and inorganic material. Red anthraquinoid lakes, such as madder lake, kermes lake, cochineal lake and Indian lac, have been the most important and widely used for painting purposes and some great examples of lakes used as glazes are exhibited in European paintings since XIV century [1].

From an analytical point of view, identifying the lakes in paint samples is challenging because of the high amount of binding media in which they are dispersed and the simultaneous presence of several organic materials and non-original compounds as consequence of ageing and environmental contamination. In addition, the low percentage of dyes used in traditional lakes (1-3 % w/w) and the difficult extraction of dyes from the matrix further complicate the analysis [2]. Thus, the interference in the analyses of the lakes possibly caused by the presence of the binders has to be investigated and an analytical procedure able to detect anthaquinoid dyes at very low concentration avoiding matrix effect has to be developed.
This study deals with the optimization of methods for the detection of the anthaquinoid dyes achieved through the analysis of reference materials and paint model systems evaluating the role played by the binders by means of chromatographic and mass spectrometric techniques, such as High Performance Liquid Chromatography with Diode Array and Mass Spectrometric detector (HPLC-DAD-MS) and Laser Desorption Ionization - Mass Spectrometry (LDI-MS).

The procedures developed aim at identifying organic dyes by these different techniques maximizing the information achievable while minimizing the amount of sample needed. Different solvents of extraction and injection and experimental set ups have been tested in order to build up the most efficient strategies.
The most significant results for reference materials, paint model systems and relevant samples from Greek mural paintings will be presented.

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Red pigments of Boraginaceae family: A historical overview

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It is well established that nature stands as a source of dyes and pigments for thousands of years. The plant family Boraginaceae has been extensively used in antiquity as a natural dyestuff, as documented in multiple cultures such as Ancient Greek, Roman, Egyptian, Japanese and Chinese.

"Ἄγχουσα" (Anchusa, *Alkanna tinctoria* Tausch, alkanet) has been reported as a natural colorant in the Papyri Leidensis X and Stockholm. Additionally, murasaki (*Lithospermum erythrorhizon* extract) has been used in ancient Japanese textiles as plant dye. The aim of this study is to present a historical overview of the use of Boraginaceaous species as natural dyes and colorants.

Today, extracts and constituents derived from Boraginaceaous roots are mainly used as pigments for food and drink coloring (confectionary, ice-cream, wines, sausage casings, oleomargarine and shortening, traditional Korean liquor), cosmetics (lipsticks, face colorants, soaps and hair dyes), dyeing fibers such as silk, wool, cotton and others.

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Non-destructive analysis of pigments in Byzantine paintings.

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In Byzantine and Christian Museum we have the opportunity to apply non-destructive techniques such as Raman spectroscopy and XRF for identification of pigments. Many samples of pigments have been studied from two famous collections, the Yannis Papadellis collection and the Fotis Sarris collection. Both of them, are a kind of approach of reconstruction of the described colorant materials by Dionysius of Fourna.

In the frame of the celebration of “Fotis Kontoglous year” (2015), the Byzantine and Christian Museum is organizing a special exhibition. In this exhibition we shall expose all this material, which consists of historic pigments, such as: cinnabar, lapis lazuli, orpiment, bolo di Armenia, ochre from Constantinopolis e.c.t. The painter Yannis Papadellis was a pupil of Fotis Kontoglous and he had a conflict with him, about the nature of a blue pigment. On the other hand the painter Fotis Sarris was a scholar of the post-Byzantine painting's technique and his systematic color collection, covers all the hues of the pigments used by the hagiographers. The interpretation and clarification of the terminology of Byzantine colorants by the help of this study, is one of our purposes. The other is the interactive communication with the visitors, about the making of an Icon, through the identification of its materiality, using non-destructive technique (Raman, XRF). The analytical results from Raman spectroscopy and X-ray Fluorescence shall be useful for any scholar who needs to study the Byzantine Painting. The total of analytical data shall create a Data Bank for the Byzantine and Christian Museum and through its Webpage shall be available for the users of the Museum's site.

Partial Solvation Parameters: An holistic approach in solubility prediction –Application in anthraquinone dye.

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In conservation science, interventions could either secure the continuation of the life of an artifact or accelerate its destruction. Understanding the properties of the surface under examination as well as those of materials to be used (such as organic solvents) is of primary importance for the selection of the appropriate intervention method. Diagnostic methods can offer information regarding the surface under examination. In several cases the surface examination points out that conventional treatment is insufficient owing to complex or multilayered surface morphology. Solubility prediction is an important tool that can be used in order to set up the adequate protocol of intervention. Hansen's solubility parameter approach is the most widely used, however it appears to be insufficient in fully describing the interactions between the solute and the solvent.

Recently a new definition of solubility parameter has been proposed which overcomes some of the inherent restrictions of the original definition and expands its range of application. **P**artial **S**olvation **P**arameters (PSPs) are molecular descriptors that combine elements from quantum mechanics with the Abraham's QSPR/LSER solvatochromic and Hansen's solubility parameter approaches. Using the PSP approach the molecule of the solute as well as the molecule of the solvent are fully analyzed. All the possible interactions that could take place between the molecules (hydrogen bonding, Van der Waals interactions ect) are calculated resulting to four partial solvation parameters that reflect the dispersion the polar the acidic and the basic character of any molecule. The main purpose of the present work is to present the PSP theory, compare it to the popular tool of Hansen solubility parameter and apply the proposed theory for the prediction of dyes solubility. An example of solubility prediction for anthraquinone dye is presented.

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Chemical Analysis for Coloring Materials Used for "Guanyin with Rainbow Halo" stored in Scripps College, USA

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"Guanyin with Rainbow Halo (Photo)" owned by Scripps College (USA) is a Buddhist picture painted on a silk canvas. At the opportunity of repairing the picture, chemical analyses for the coloring materials used for it were performed.

Paintings normally use inorganic pigments. To determine whether the Buddhist painting used organic pigments together with inorganic ones, a nondestructive analysis based on the visible reflection spectrometry was performed in association with the X-ray fluorescence spectrometry (XRF) [1, 2]. Also a SEM-EDX analyzing technique was performed for investigating the initial lining paper that has been colored.

Photo Guanyin with Rainbow Halo

Features of the painting found by this analysis include:
A pigment of white lead was used for painting in white.
Different red pigments were used depending on the parts:
Lac, cinnabar and sappan wood were used for painting the background (Figure), jacket and skin respectively.
To paint in blue/green, pigments of malachite and azurite were used, though an organic pigment of indigo was added to azurite to create a darker blue, and to malachite to create delicate transition in the color of the halo.
An organic pigment of gamboge was used for painting in yellow.
A technique for painting on the back of the silk canvas with a pigment of white lead was effectively used for creating different balances in color.
The entire surface of the canvas is coated with very thin layers of malachite and smaller amount of azurite.

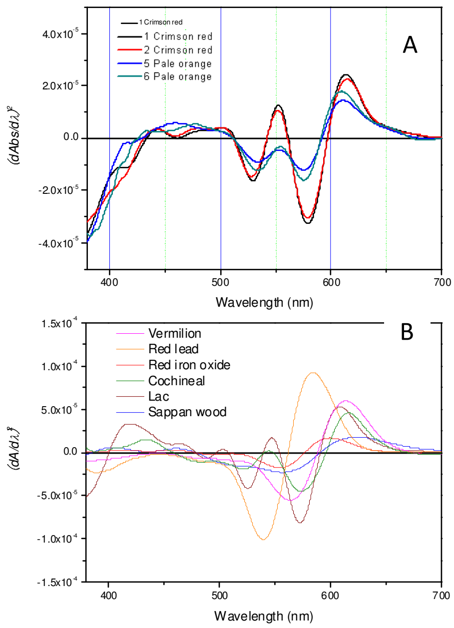

Figure 2nd-derivative reflectance visible spectra of red colorant used for the background and pedestal
A: 1,2 background, 5,6 pedestal
B: Standard red colorants

Analyzing coloring materials used for a painting normally uses an XRF analyzing technique which is available for inorganic coloring materials only. Using another nondestructive analyzing technique based on the visible reflection spectrometry together with the conventional XRF analysis enable to detect also organic coloring materials. Using effectively both inorganic and organic pigments, it was found that the picture was painted using many colors richly.

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Storing grains during Ninevite 5 Period in the Khabour basin: ways and methods used

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Within about 3000 BC began the process of urbanization, shifting to build big cities, northeast Syria, in the beginning of the Early Bronze Age. The archaeologists were able to identify the above-mentioned urbanization process in different civilized criteria according to the region where it was established. For example, in the Upper Mesopotamia specifically from Nineveh, north of Iraq, to the Khabour Basin in the northeast Syria called the Ninevite 5 period. This period was characterized by several features the most important was the organization and functional specialization followed in the sites of the Khabour Basin, this organization was differs somewhat from previous periods, and characterized by the presence of storage facilities in the Middle Khabour Basin, it seems that these sites had shared the work among themselves to serve certain purposes, either internal or external like export and trade. Thus, these storage facilities remain one of the most special civilization characteristics till the end of the Ninevite 5 period, and then they have been disappeared. On the other hand, the settlement stopped in some areas while stayed as it is in others for some time before moving to the next period "Akkadian Empire".

Figure 1 The typical pottery of Ninevite 5 period "Incised and Excised Ware".

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Dye extraction from *Dialium guinense*, characterization and application on cellulose fabric

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Natural dye was extracted from the bark of the plant *Dialium guinense* using ethanol extractant on the plant biomass. The dye was purified by crystallization and its coloring potentials studied. Lustrous crystalline dye with a melting point of 130^{o}C with a chemical yield of 5% and wavelength of maximum absorption of 434nm was obtained. The dye was further characterized using GC-MS and the extracted colorant applied on cotton fabric using 3 different mordants with chromium salt giving the best dyeing effect on the dyed fabric.

Colorimetric study of Chinese traditional dyeing and ageing silk textiles

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Chinese traditional vegetable dyeing has a long history and is recorded in many ancient books. In this article, simulated experiments were strictly made to reappear nearly sixty dyeing techniques which were recorded in ancient Chinese texts like *Exploration of Works in Nature* and *Duo Neng Bi Shi*. Meanwhile, sixty dyeing silk samples were obtained. In order to study the principle of dyeing fading, simulation experiments covering thermal ageing and hygrothermal ageing were conducted. This article focuses on the colorimetric study of the dyeing and ageing dyeing silk samples. Color index a^* and b^* is used to explore the change of the chromaticity [1]. The colorimetric result (Figure 1) shows that traditional dyeing has its own chromaticity range and characteristic. On the whole, the color of traditional dyeing is mild and smooth which also reflects Chinese philosophical thought. Hygrothermal ageing has more impact on fading than thermal ageing. Furthermore, loss of dye is also an important reason for the discoloration of silk textiles in buried period. In general, color index b^* will increase in aging process except yellow dyestuff. There is a significant relationship between the category of pigments and fading principle. This article may direct the reconstruction of traditional handicraft. It may also benefit the mechanism study of dye ageing and identification of dyestuff, which occupies an important place in ancient textile conservation.

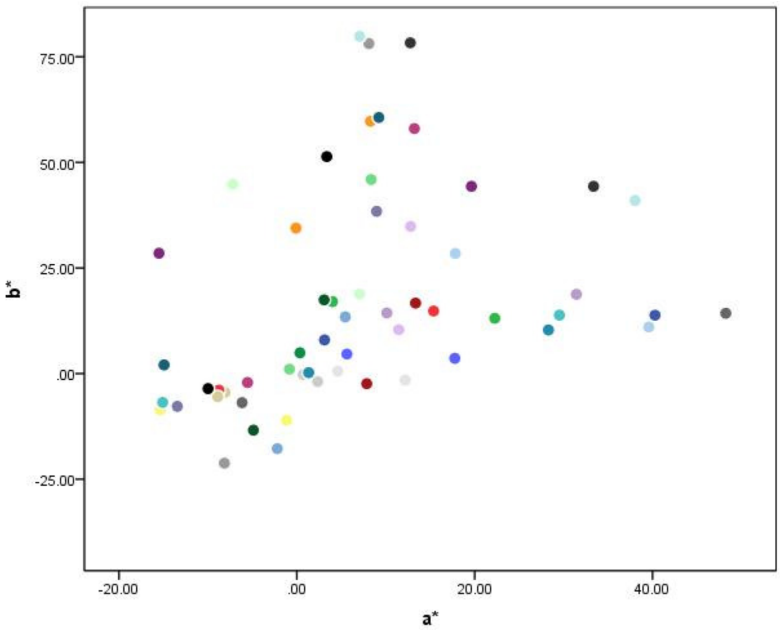

Figure 1. Scatter diagram of dyeing chromaticity

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Proposal of a new mild extraction technique for organic dyes in historical artworks

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For what concern the ancient dyes used in tapestries or in lake-pigments, many works are focused on few molecules thought as responsible for the colour. For example, for dyed yarn in red, we are used to think about *Rubia tinctorum* L. or cochineal as common dyes and to alizarin and purpurin or carminic acid as the main corresponding chromophores. This approach can be very useful to understand where the colour comes from and which plants or insects had been used, thanks to these few “marker” molecules.
Nonetheless, this approach is not sufficient if we need to preserve the artwork and hypothesize the degradation path. Considering complex matrices such as madder, which our work was focused on, we need to consider also other compounds, which could influence the hue during the dyeing processes and be involved in lake precipitation. [1]
In order to have a pattern of molecules which refer to, we start from the isolation of madder roots compounds, through chromatographic separations, using an extract obtained in the same condition of dye bath [2]. The identification of compounds was performed through ^{1}H-NMR, ESI-MS and ESI-MS/MS experiments.
In the second step, a new mild extraction method (Fig.1) [3] through ammonia solution has been carried out on many dyed yarns and lakes, obtained following the ancient recipes [2]. The extract has been analyzed to identify which molecules or class of compounds would have been fixed on the yarn during the colouring processes or involved in the precipitation of the lake-pigment.
The analyses conducted on the ammonia extract (^{1}H-NMR, ESI-MS and NMR-DOSY experiments) show immediately that this technique has allowed the extraction of glycosylated compounds. For example, in DOSY spectrum (Fig.2) we notice that aromatic moieties have the same autodiffusion coefficient of other glycosides parts.

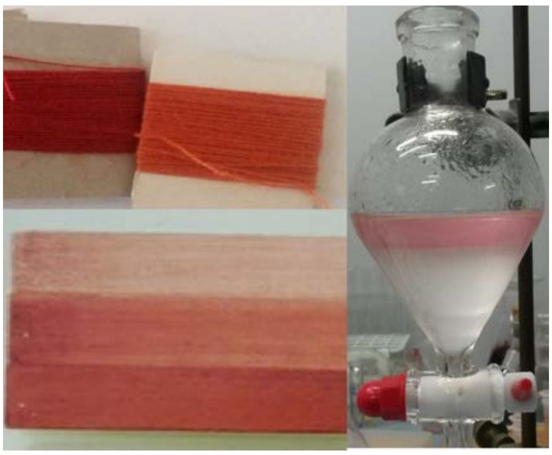

Fig.1. Extraction of dyes from textile and lake in organic solvent, after a treatment in ammonia

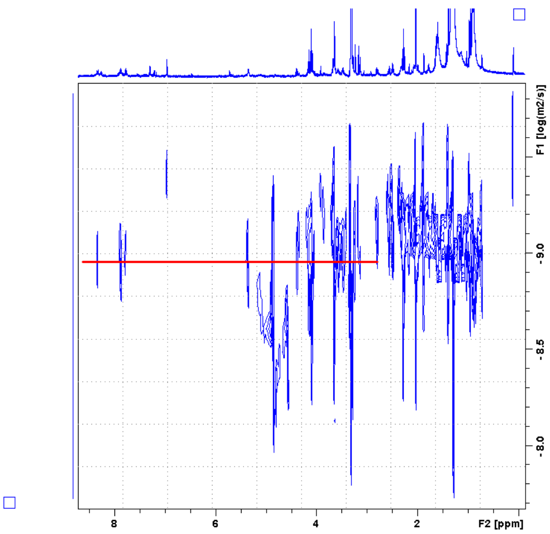

Fig. 2. -^{1}H-NMR (CD_3OD-d4, 400 MHz) DOSY of madder yarn extract (NH_3 extraction method).

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Raman spectroscopy pigment identification in a painting from J. F. Mücke

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"Vukovar landscapes" is a series of oil on canvas paintings made in mid-19th century by an unknown author [1]. Only one of the landscapes is signed, by Joseph Franz Mücke, a royal painter of Habsburg dinasty, presumably ordered by count Emmerich Josef Eltz as a decoration for his Manor in Vukovar, Croatia. Of all candidate authors, Mücke is the only one who was known to live in Vukovar in the period the landscapes were made. One of the clues toward the discovery or confirmation of the true author could be given by comparing the painting pigments used in signed and unsigned landscapes. Raman spectroscopy with 785 nm laser is used to identify the pigments used for the signed painting "The Gardens". Raman analysis reveals the author's palette [2]. For blue colours indigo pigment was found with addition of calcite for lighter hues. Green colours contain malachite with possible mixture of other earth pigments, like terre-verte. Orange-brown colours are obtained using either a mixture of red lead, red earth and yellow earth pigments or terra umbra. All earth pigments contain traces of quartz. Elemental analysis, like XRF, is proposed for complete characterization of Mücke's palette [3].

Figure 1. Raman experiment of "Vukovar landscapes" painting in Eltz Manor, Vukovar, Croatia.

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Reviving the ancient indigo cultivation and industry in southern Jordan as a source of income for the local community: from historical and archaeological evidence to a modern trial

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Reviving cultural heritage and know-how can be a powerful source for sustainable development. This is the formula that the UNESCO project "Empowering Rural Women in the Jordan Valley" has been applying in Jordan, where a group of rural women have been involved in piloting a cultivation of *Indigofera tinctoria* and experimenting natural sources to dye their handmade textiles [1].

Ghor el Safi is a village south of Dead Sea and is one of Jordan's poverty pockets [**Σφάλμα! Το αρχείο προέλευσης της αναφοράς δεν βρέθηκε.**]. The ancient *Zoara* (now Ghor el Safi) was an important agricultural and trading centre during the Roman-Byzantine and early Islamic periods. During the later, indigo and sugarcane production were important goods, as testified by archaeological evidence and historical sources. Large-scale indigo processing facilities have been identified in the area of Ghor el Safi and in the Dead Sea region. In addition, objects used in the indigo processing were found during archaeological excavations in Ghor el Safi, including a large perforated jar, a copper crucible and textiles dyed in indigo. These finds, together with historical sources, testify an early production and use of indigo in the Jordan Valley. Such production must have continued at least until the beginning of the XIX century, when indigo and other natural dyes were replaced by synthetic dyes [**Σφάλμα! Το αρχείο προέλευσης της αναφοράς δεν βρέθηκε.**].

The aim of the UNESCO project is to revive the ancient know-how of indigo production in the Jordan Valley, in view of safeguarding a traditional heritage and providing income generating opportunities for the local community. Reintroducing indigo could also be an opportunity to increase biodiversity in the area and benefit the local agriculture, in view of the properties of the crop.

To this end, a preliminary research on *I. tinctoria* was undertaken and a pilot cultivation was established in Ghor el Safi to investigate the best agricultural practices to grow and harvest the crop. One dunum of land (corresponding to 1,000 square meters) has been cultivated with *I. tinctoria* seeds with the application of several treatments. The first harvests gave promising results, despite the harsh properties of the soil in Ghor el Safi [4]. In view of introducing the best dye extraction and dyeing procedures, UNESCO supported an exchange encounter with experts from Oman, the sole country in the region where *I. tinctoria* is still cultivated and processed according to traditional techniques transmitted from generation to generation. Thanks to the support of the Omani Authority for Crafts Industries, three experts shared their know-how with the women of Ghor el Safi. The results of this exchange were very positive and dye extraction and dyeing process were successfully achieved relying on traditional methods: for the first time since its disappearance, locally-grown and processed indigo was used as a dye in Jordan.

Currently, the indigo pilot cultivation is under monitoring and final results will be collected by the end of the project (December 2015). Local indigo is already in use by the women of Ghor el Safi for the production of their textiles, and preliminary data show that indigo-dyed products have a very good market feedback. A feasibility study is planned to determine the agricultural and economic potential of the crop, which could be expanded to the larger community of the Jordan Valley.

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Antimicrobial activity of dyed silk fabrics with madder and gall oak

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For a long time, natural dyes have been used for purposes such as the colouring of wool, mohair, cotton and silk fibres as well as fur and leather [1]. Natural dyes can be obtained from plants, animals and minerals. Natural dyes are reported as potent antimicrobial agents owing to the presence of a large amount of compounds such as antraquinones, flavonoids, tannins, naphtoquinones etc. which possess strong antimicrobial properties. Though a plethora of natural antimicrobial agents exist especially against common human pathogens however; very few studies have been reported in the literature regarding the antimicrobial properties on textile materials with respect to the human pathogenic strains [2]. Anthraquinones, naturally occurring in the madder roots (*Rubia tinctorum* L.), have been used for dyeing fabrics or fibres especially to the colour red and they have also been used as a lake pigment rarely since ancient times [1].

In this study, five silk fabrics were mordanted with alum ($KAl(SO_4)_2.12H_2O$) after washing process. A fabric was dyed with madder roots plant (*Rubia tinctorum* L.). Other four fabrics were dyed with together madder roots plant (*Rubia tinctorum* L.) and gall oak (*Quercus infectoria* Olivier). In these four dyeing, madder percentage remained constant while gall oak increased rate. High Performance Liquid Chromatography (HPLC) using Diode- Array Detection (DAD) was used for identification of natural dyestuffs present in these materials. Colour values of fabrics dyed were measured a using CIEL*a*b* spectrophotometer.

Antimicrobial functionality of the five silk fabrics are established. Tests were conducted against the *Staphylococcus aureus* (ATCC 6538; Gram positive bacterium) and *Escherichiacoli* (ATCC 25922; Gram negative bacterium). Antimicrobial testing was carried out by using the quantitative test method. *Staphylococcus aureus* and *Escherichiacoli* were grown in nutrient broth medium for 24 hr at 37 ±1 ^{0}C. The fabric specimens (4.80±0.1 cm) were placed in container and sterilized for 15 min at 121 ^{0}C. An aliquot of 1000µl bacterial suspensionswere added to the center of a 4.80±0.1 cm fabric and incubated for 24 hr at 37 ±1 ^{0}C. The fabric were resuspended in dilution medium. Ten fold serial dilutions were made to samples and each dilution was plated nutrient agar plates were incubated for 24 hr at 37±1^{0}C. Bacterial colonies were enumerated. The number of survival microorganism was determined by counting the colonies as colony-formingunit (CFU/ml) and reduction rate of bacteria was calculated. According to the all analyses results, the best dyeing recipes for antimicrobial activity are determined.

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Traditional use of saffron, safflower and celidonia for yellow-gold dye in the Ancient Mediterranean World: references from written sources

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The orange-yellow colour in classical antiquity played an especial role in the social and religious rituals [1]. Virgin women usually dressed this yellow colour. Also, girls danced as bears in the sanctuary of Brauron, in honour of the goddess Artemis with a yellow robe. This cloth was dyed with a yellow-orange dye (*croceus*) extracted from saffron. Hymenea mantle, the tunic of love, the essential attribute of the young wife and the oldest wedding veil, were also of this colour [2]. This colour in antiquity had religious significance and it was considered as a symbol of joy [3]. According with references of written sources from Mycenaean period, Lineal B tablet, until recipes of Papyrus Greeks from Roma Egypt, the yellow colour in antiquity was primarily obtained from two plants: *Crocus sativus* L. or saffron and *Carthamus tinctorius* L. or safflower.

Saffron contains some essential oils that were prized in antiquity. This dye was known and used by the ancient inhabitants of the island of Crete in the Minoan and Mycenaean period. Theophrastus and Dioscorides describe several varieties of saffron known for their virtues and applications in perfumery, dyestuff and medicine. From Egypt, saffron was exported to Asia (c. 40- 70 a. C.), through Egyptian ports on the Red Sea. The tradition of dyeing wool or silk with both two plants for obtaining a yellow-gold colour isn't unique to Egypt and it's preserved in Syria and Iran. We have interesting recipes for dyeing with saffron, safflower and an enigmatic plant named celidonia (*Thapsia* ssp.) in the Papyrus *Graecus Holmiensis* and Papyrus X Leiden that we will analyse in this paper [4].

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Dyes from Boraginaceae species: from ancient codes to modern medicine

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There are few natural products with histories as rich as those of the enantiomeric naphthoquinones alkannin and shikonin (A/S, Figure 1). Their story can be traced back many centuries, where extracts from the roots of *Alkanna tinctoria* (*A.t.*) in Europe and *Lithospermum erythrorhizon* (*L.e.*) in the Orient have been used independently as natural red dyes and crude drugs with the magic property of accelerating wound healing.

The first recorded use of *A.t.* roots is found in the works of Hippocrates and Dioscorides for the treatment of ulcers. Since then, the medicinal properties of the plant either have drifted into folklore, or been forgotten.

In 1976 Papageorgiou revived the study of these plants and discovered the science behind ancient codes. The results of his experiments confirmed the wound healing, antimicrobial and anti-inflammatory properties of *A.t.* root extracts and was the first to identify alkannin derivatives as the active components. He developed several pharmaceutical preparations, the clinical trials of which proved their outstanding efficacy in patients with indolent ulcers, burns, wounds. These were approved by the National Organization for Medicines (Greece) (Histoplastin Red®, Epouloderm®, HELIXDERM®) [1,2].

Since then, our research focuses on chemistry, biology and technological applications of A/S. The discovery of oligomeric A/S brought new extensions in chemistry of naphthoquinones. The significant antioxidant activity and anti-leishmanial action of A/S were confirmed. New clinical trials of HELIXDERM® on diabetic and indolent ulcers present impressive results. Drug delivery systems for A/S (microcapsules, liposomes, hyperbranched polymers, chimeric systems, nanofibers) have been formulated.

The ancient medicinal properties claimed for *A.t.* and *L.e.* have been confirmed by scientific experimentation the last 35 years [1,2], while in parallel these natural products are still in use for their red- or purple- dyeing properties [3]. Alkannins and Shikonins are today considered a class of medicines that greatly augment the modern therapeutic arsenal, confirming that natural products can be promising for the development of new pharmaceuticals.

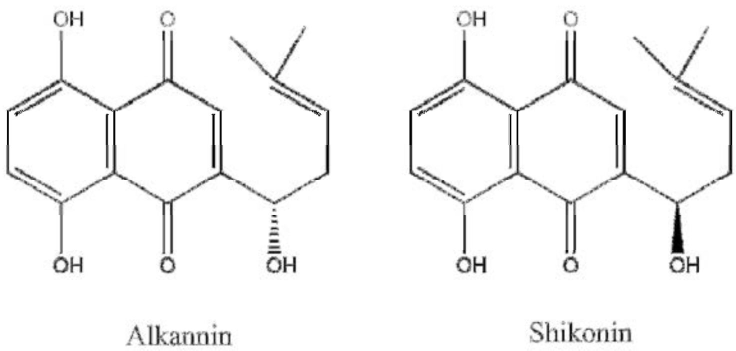

Figure 1. The chiral pair alkannin and shikonin

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Dyeing camel wool with acetic acid extract of *Hibiscus rosa sinensis* flower for Sadu House of Kuwait

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The target of this work is to extract a local natural fixed dye for coloring camel wool as a substitute for synthetic dyes used by the Bedouins ladies in the Sadu House of Kuwait (a society that protect the interests of the Bedouins and their ethnic handicrafts). As it wanted to keep the tradition of tent and rug weaving natural in all the steps. The powdered petals of the red flower of Hibiscus rosa sinensis (HRS) was treated with different organic solvents and yielded various extract colors ranging from yellow to peach, pink and red. The 5% acetic acid extract of (HRS) red flower had good yield and deep red color, relatively it was the solvent of choice as it has no harmful effects on the environment and the workers' health. Using different mordants like alum and some metal chlorides manifested in a wide range of fixed colors varying from beige, rust, brown, green, pink, dark red / purple to lilac which intensified on dyeing at 85°C.**Colors obtained with cotton and camel wool, treated with S cl_2 as one of different mordants and impregnated with 5%A.A (HRS) flower extract under heat (85C°) or room temperature.**

	Dyeing at 85ºC		**Dyeing at Room temperature**	
Mordant	**Cotton**	**Wool**	**Cotton**	**Wool**
Non mordanted				
Stannous chloride				

The color obtained neither washed out with strong detergents nor faded away upon exposure to sun light for 42 hours (Gasmelseed etal). Anthocyanin; the red extract of (HRS) function as antioxidant and an anti solar agent as it absorb the harmful sun rays that lead to cancer formation (Sharma et al., 2004), namely skin cancer.

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