Dyes in History and Archaeology

DHA32

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Espace Encan

LA ROCHELLE   FRANCE

3–4 October 2013

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Abstracts

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Dyes in History and Archaeology
DHA32

LA ROCHELLE FRANCE 3-4 October 2013
PROGRAMME OF ORAL PRESENTATIONS

Thursday October 3rd

8:30 **Registration and placement of posters, coffee**

9:30 Welcome

10:00	**Session 1. Chair :** **"True Purple, imitation purple"**

10:00 **To be (purple) or not to be**
Maurizio Aceto, Angelo Agostino, Gaia Fenoglio, Ambra Idone, Monica Gulmini, Rolf Haubrichs, Pietro Baraldi

10:20 **Organic lake pigment analysis of Koru tumulus at Daskyleion in the Persian period**
Ali Akın Akyol, Emine Torgan, Kaan Iren, Recep Karadag

10:40 **Using a "false shellfish purple" to dye wool**
Cristina Maria Barrocas Dias, M. Silva, A. Manhita, Teresa Alexandra da Silva Ferreira

11:00 **Questions**
11:15 **Coffee and Posters**

11:45	**Session 2. Chair :** **"Importance of dyeing recipes"**

11:45 **From botanical source to analytical result: the influence of recipe and plant source on appearance and composition of anthraquinone and flavonoid dyes and pigments**
Jo Kirby, Maarten van Bommel, Alexia Coudray, Thibaut Devièse, Ioannis Karapanagiotis, Catherine Higgitt, Dimitrios Mantzouris, David Peggie, Rachel Morrison, Art Ness Proaño Gaibor, Mark Richter, Joanna Russell, Heike Stege, Ina Vanden Berghe

12:05 **Black dyed wool from five Belgian Archives (1650 – 1850) versus historical recipes and urban regulations**
Natalia Ortega Saez, Ina Vanden Berghe, Olivier Schalm, Joost Caen, Bert De Munck

12:25 **Resurrecting Turkey red: Adapting an historic process for modern re-creation and analysis**
Julie Wertz, Anita Quye, David France, Lesley Richmond

12:45 **Questions**
13:00 **Lunch and Posters**

14:30	**Session 3. Chair :** **"Reds"**

14:30 **MALDI-TOF-TOF mass spectrometry for the identification of natural red dyes**
Sophie Dallongeville, C. Tokarski, C. Rolando, Nicolas Garnier

14:50 **Changing the aglycone composition of madder-derived pigments**
Vincent Daniels

15:10 **Red Dyes used for Rouge Cotton (Enji-wata)**
Yoshiko Sasaki, Ryohei Fukae, Ken Sasaki

15:30 **Questions**

15:45 **Coffee and Posters**

16:15	**Session 4. Chair :** **"Pigments"**

16:15 **Shearings and clippings: mediaeval production of red lake pigments**
Indra Kneepken, Art Néss Proaño Gaibor, Arie Wallert

16:35 **Identification of pigments and dyes used on polychrome clay sculptures and wooden artifact from the Astana Tomb of the Tang dynasty (AD618-AD907), Xinjiang, China**
Yimin Yang, Huiping Zhen, Yi Si, Qiuju He, Bo Wang, Changsui Wang

16:55 **Cochineal and its lake pigments: historic reconstructions from Winsor & Newton's archives**
Maria J. Melo, Vanessa Otero, Tatiana Vitorino, Leslie Carlyle

17:15
Pigments, organic colorants and binding media in the Cyprus Orthodox icons tradition
A. Lluveras-Tenorio, I. Degano, F. Parlanti, I. Bonaduce, K. Rasmussen, G. Lorenzetti, S. Legnaioli, V. Palleschi, D. Demosthenous, M.P. Colombini

17:35
Questions

17:50
End

2nd visit to the Museum: 19:15

Friday October 4th

9:00	**Session 5. Chair :** **"Dyes in History seen from Asia"**

9:00 **Embroidered networks: Indo-Portuguese textiles, their dyes and diverse origins**
Inês Cristóvãoa, Ana Claro

9:20 **Evolving industries: Identifying yellow dyes in 17th-century 'Indo-Persian' carpets**
R. Santos, J. Hallett, A. Claro, B. McCarthy

9:40 **Dyes and Dyeing in the Ming and Qing Dynasties (1368-1911) in China: Preliminary Evidence Based On Primary Chinese Sources**
Jing Han, Anita Quye

10:00 **Reconstruction of the palette of Qing dynasty textile dyes**
Feng Zhao, Jian Liu

10:20 **Questions**

10:35 **Coffee**

11:05	**Session 6. Chair :** **"The beginnings of the era of coexistence of synthetic and natural dyes"**

11:05 **Feeling blue, dye red - Early synthetic organic dyes: substantive cotton dyes** Matthijs de Keijzer

11:25 **Scientific research on natural dyes in Turkey, in the period of 1930-1950**
Emre Dolen

11:45 **Treasures from a Leeds Dye Chemist: A Century-Old "Tyrian Purple"?**
Isabella Whitworth, Zvi C. Koren

12:05 **Questions**

12:20 **Lunch**

14:00	**Session 7. Chair :** **« Archaeological and historical textiles: new approaches”**

14:00 **Comparative study of the accelerated ageing of Andean natural organic colorants by colorimetry and chromatography**
Caterina Cappuccini, Thibaut Deviège, Catherine Higgitt

14:20 **Natural dyes in new archeological and ethnographic researches in Azerbaijan**
Fariz Khalilli, Shola Bayramov

14:40 **The approach to the characteristics of eighteenth-century silk colour palette**
Ewa Mianowska-Orlińska, Maria Cybulska

15:00 **Questions**

15:15 **Coffee**

15:45	**Session 8. Chair :** **"Natural dyes: traditional techniques inspire innovation"**

15:45 **Application of Bacteria from Korean Traditional Indigo Vat to Indigo Reduction**
Younsook Shin, Kyunghee Son, Eun Sil Choi, Dong-Il Yoo

16:05 **Natural dyeing techniques for the restoration of ancient tapestries: Innocolors Project**
Isabelle Clonier, Paola Croveri

16:20 **Questions**

16:45 **Closing remarks**

17:00 **End**

Gala dinner: 20:00

To be (purple) or not to be

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The use of purple dyes or paints to impart colour to parchment of precious codices is mentioned since Late Antiquity [1]. Usually, codices dyed with Royal purple were Holy Writings texts with golden or silver inks on purple-dyed parchment. In the ancient literature, though, recipes explicitly describing the practice of colouring parchment are rare. As a consequence, our knowledge concerning the colourants effectively used is far from complete [2]. One reason is due to the fact that there is sometimes ambiguity, in bibliographic sources, among the term "purple", which recalls the use of Tyrian purple dye, and the actual compounds used to dye in purple. Moreover, purple codices have been rarely analysed and not often the results have allowed to identify a definite colourant. At present, indeed, we have no single evidence of the use of Tyrian purple in codices, so that the presence of less valuable alternatives must be hypothesised, such as orchil from *Roccella*, *Dendrographa*, and *Lecanora* genera of lichens or folium from *Chrozophora tinctoria*; anthraquinonic dyes such as kermes or madder could be present as well, possibly applied in sequence with indigo.

Anyway, we have no clear information even in cases where alternative dyes were present on parchment, since the non-invasive identification of orchil and folium is difficult. Very little spectroscopic information is available from the scientific literature (in very few instances these dyes were identified on artworks). From these considerations, it appears clear that more studies are needed to verify data from bibliographic sources.

In this work some preliminary results from non-invasive analysis on purple codices are shown. The manuscripts involved are dated from the VIth to the VIIIth century: they are known as *Vienna Genesis* (Vienna, Österreichische Nationalbibliothek), *Krönungevangeliar* (Vienna, Schatzkammer), *Evangeliario di Sarezzano* (Tortona, Archivio Diocesano) and *Codex Brixianus* (Brescia, Biblioteca Queriniana). These manuscripts were analysed with X-ray Fluorescence Spectrometry (XRF), in order to verify the occurrence of bromine, with Fiber Optic Reflectance Spectrophotometry (FORS) and Spectrofluorimetry in order to identify dyes. The results suggest that the presence of Tyrian purple cannot be ascertained; if present, it is only a minor component. The most important contribution to the purple colour of parchment is in fact inferred by orchil or folium.

References

[1] S. Baroni, Pergamene purpuree e scritture metalliche nella tradizione tecnico artistica. Un quadro introduttivo, in *Oro, argento e porpora*, ed. S. Baroni, Tangram Edizioni Scientifiche, Trento, 2012.

[2] C. J. Cooksey, Tyrian purple: 6,6'-Dibromoindigo and Related Compounds, *Molecules*, 2001, **6**, pp736-769.

ORGANIC LAKE PIGMENT ANALYSIS OF KORU TUMULUS AT DASKYLEION IN THE PERSIAN PERIOD

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ABSTRACT

The Persian king, Cyrus the Great, powered through Anatolia, conquering all in his path in 546 BC, his empire into regional satrapies; one of these was Daskyleion, where recent excavations are performed by Mugla University. A tumulus called Koru and dated to Persian Period have been excavated since 2011 in the necropolis area at Daskyleion. The unique finds dedicated to three royal people from burial chamber and a person, probably unsuccessful thief, from the ante chamber were found in Koru Tumulus. The sediment, stone, ceramic, metal/slag, glass, textile, mortar/plaster, wooden and pigment samples beside archaeobotanical samples from Koru Tumulus and Daskyleion have been examined with the scientific research project in Ankara University since 2011.

The most impressive finds were the purple coloured pigments that covered all inside of the burial chamber of the Tumulus. The chemical origin of red colours on textile were primarily identified as iron oxide besides Mg, Al, Si and Zn were also identified by XRF analysis. C, O, Al, Si, S, Ca, Fe and Br elements were identified in pigments and textiles analysis by SEM-EDX. HPLC-DAD (High performance liquid chromatography coupled with diode array detection) was applied for the identification of dyestuffs of textiles and pigment in king's tomb. The ancient pigment sample were determined main components indigotin, 6 bromo indigotin (6,6'-dibromoindigo) and 6 bromo indirubin (6,6'-dibromoindirubin). That was the main chemical constituent of the tyrian purple dye originate from a type of rock snail by the name murex (family muricidae), known royal purple as natural dye.

Key Words: Daskyleion, pigments, tyian purple, indigotin, murex, HPLC, SEM-EDX

Using a "false shellfish purple" to dye wool

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In ancient times the purple color was associated with power and royalty, becoming legendary the price of the shellfish purple dye used to color the purple textiles [1]. Less expensive substitutes were always in high demand and the use of lichens, in particular *Roccella* species, as a "false shellfish purple" was already reported in ancient Rome [1]. Until the 19th century the commerce of lichen dyes was an important source of income in several regions of the World [2].

Some compounds identified in the lichens are structurally unique and mostly restricted to fungi, being among those the depsides and depsidones, the precursors of the "false shellfish purple" dyes [3]. Using lichens for dyeing purposes requires their previous immersion in ammonia-rich aqueous solution (e.g. urine), during which, the depside or depsidone are hydrolyzed, and the resulting products react by a sequence of condensation reactions with the incorporation of the nitrogen from the ammonia to give various purple orcein derivatives [2]. Purple, bright red or orange colored textiles can be obtained with lichen dyes, with the textile final color tailored by adjusting the dyeing bath concentration and pH, and by the use of mordants.

In this work, *Lasallia pustulata* L. samples were used to produce the orcein derivatives and the resulting solution was used to dye wool samples.

The sequentially extraction of the lichen samples with acetone and methanol enabled the identification of the *Lasallia pustulata* L. chemical composition. The lichen extracts were evaluated by LC-DAD-MS (liquid chromatography coupled with diode array and mass spectrometry), and several depsides were identified in the extracts based on the UV and mass spectra obtained on-line.

The "false shellfish purple" was obtained by immersion of the lichen samples in a concentrated aqueous ammonia solution. The reaction leading to the formation of the purple chromophores was monitored by the periodic LC-DAD-MS analysis of the dyeing bath for three weeks.

The resulting solution was used to dye wool samples without and with the presence of alum, and colorimetry was used to record the wool color.

Extraction of the dyed wool samples and LC-DAD-MS analysis of the resulting extract enabled the identification of the chromophores responsible for the color of the wool samples.

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Dyes in History and Archaeology DHA32 (La Rochelle, FRANCE - 3-4 October 2013)
Abstract for oral presentation

From botanical source to analytical result: the influence of recipe and plant source on appearance and composition of anthraquinone and flavonoid dyes and pigments

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High performance liquid chromatography (HPLC) analysis is widely used to determine the nature of the organic colorants used to produce dyes or organic pigments in archaeological or historical artefacts. On the basis of the presence and proportion of colorant components detected, the specific botanical source employed may be determined. This paper presents results of on-going work within the European project *CHARISMA (Cultural Heritage Advanced Research Infrastructures: Synergy for a Multidisciplinary Approach to Conservation/Restoration)* exploring the influence of the source of the plants used and the method of pigment preparation or dyeing ('recipe') on the final colorant composition, and how any variations in this composition relate to the appearance of the resulting dyes or pigments [1].

Specimens from two groups of plant species widely used in Europe since ancient times were collected from known geographical locations and growing environments [2]. Four anthraquinone (*Rubia tinctorum* L., *Rubia peregrina* L., *Galium verum* L. and *Galium mollugo* L.) and three flavonoid (*Reseda luteola* L., *Genista tinctoria* L. and *Serratula tinctoria* L.) sources were chosen. All specimens were taxonomically confirmed. The species within each group were chosen as they have similar dyestuff profiles, potentially confusing analysis.

HPLC analysis of methanol/water extracts of the plant sources confirmed that each species could be distinguished. Variations in the colorant components between individual plant specimens within each species could be observed, confirming the influence of environmental factors (including where and how the plants were grown, when they were harvested and plant stocks used) on dyestuff profiles.

Dyed textiles and organic pigments were prepared from these plants following standardised recipes based on historical recipes [3]. The recipes allowed the main factors affecting appearance to be explored, including extraction or dyeing time and temperature and the choice of mordant (dyed textiles) and the extraction or reaction temperature and solvent, and the order of addition of reagents (pigments). Colorimetric and visual assessment and HPLC analysis was then undertaken to determine whether there was any correlation between sample

appearance, recipe and the analytical results. Soft extraction methods were used for the HPLC analysis to preserve glycosides.

For the dyed textiles, correlations between recipe, sample colour and the colorant components present were noted. With the flavonoids, for any given recipe and plant species, it is also apparent that the variations in the composition noted between plant specimens have little effect on the composition in the dyed textile, although it remains possible to distinguish the different plant species. With the anthraquinone dyes and the pigments, the situation is more complex [4,5].

This study has established some of the factors that can affect the final composition of dyes and organic pigments and suggests that the recipe can have a greater effect on the colorant components present and the colour obtained than the source of the particular plant used. This has important implications for how HPLC analytical results are interpreted, the types of questions that analytical study of organic colorants can address and in understanding how raw materials and recipes were sourced and understood by dyers and pigment manufacturers.

Financial support by the 7th Framework Programme of the European Union (CHARISMA Grant Agreement n.228330) is gratefully acknowledged (http://www.charismaproject.eu/).

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Black dyed wool from five Belgian Archives (1650 – 1850) versus historical recipes and urban regulations

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The visual study of black dyed wool suggests that some fibres deteriorate faster than others. The production techniques used to dye is known to be a major cause. The present study focuses on the correlation between the dyeing techniques applied to historical woollen textiles, evidenced by the determination of the relevant organic and inorganic markers, and the contemporary production techniques studied by consulting the historical literature on techniques and urban regulations. [1,2]

Sixty woollen samples from five well defined and precisely through archives dated (c.1650–1850) collections in Belgium were analysed with respectively HPLC-PDA and SEM-EDX. An important constant in the dye analysis of the historic samples is that multiple combinations of dye sources were applied, even more than what can be expected out of historical recipes. The analyses demonstrated the presence of galls and logwood which are the most currently identified dye sources, followed by an indigoid source (indigo or woad), madder, weld or dyer's broom and occasionally also fustic, redwood and sandalwood. Element analysis shows that iron salts are much more frequently found than copper salts and mixtures of both.

The comparison of: (1) ingredients found in urban regulations, (2) ingredients found in historic recipes and (3) dye sources and mordants found in historic samples and determined as such by chemical analysis, resulted in three main types of dye combinations listed below. Those three groups can be divided in subgroups. Several variations on the same theme are possible. Furthermore, two important discoveries appear. Firstly black dyeing according to Type II, e.g. the combination of tannin with iron salts, is not prescribed at all in urban regulations but found frequently in the chemical analysis of historical samples. Secondly, the evidence found on some wool samples shows that the range of dye sources combined in historical textiles is wider than what one would expect out of historical recipes and urban regulations.

- Type I: Blue underground over dyed with red dye
- Type II: Tannin + Iron salts
- Type III: Blue underground + Tannin + Iron salts.

Scientific committee and acknowledgements:
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Dr. Wim Mertens, Fashion Museum, Antwerp, (MOMU), Nationalestraat 28, 2000 Antwerp, BE

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Dyes in History and Archaeology 32
Abstract submission for oral presentation

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'Resurrecting Turkey red: Adapting an historic process for modern re-creation and analysis'

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The historic dyeing process known as 'Turkey red' or 'Andrinople red' was practiced in Europe for nearly two hundred years and was significant to the textile economy of Glasgow in the nineteenth century. While many contemporary publications about dyeing Turkey red exist, it is widely observed that the process involves a good deal of technical know-how that may not have been documented, either to protect trade secrets or because it was deemed unnecessary to record. There is variation in the recipes available, but a general trend in ingredient use remained constant from the mid-eighteenth to the late-nineteenth centuries save for the disuse of madder roots after the synthesis of alizarin such as evidenced in archival documents existing from the United Turkey Red Company based in the Vale of Leven near Glasgow [UGD13 13/4/2]. The use of other ingredients remained consistent and the process was still time-consuming despite this technological advancement.

To date, there is no comprehensive technical description of Turkey red dyeing that considers the role of every type of ingredient based on primary sources about the historic processes. One aim of this interdisciplinary project is to analyze a series of historic accounts[1,2,3] to identify trends and differences in Turkey red dyeing methods and to 'distil' a single dyeing method from these sources. The method will be executed in two stages: first, using laboratory-grade reagents that fulfil the same theoretical chemical role and second, using ingredients that are as authentic as possible as documented in historic accounts to confirm suspected chemical role.

Difficulties addressed thus far in the project include the consideration of environmental conditions in the dye works and sourcing historic ingredients. Contemporary sources do not describe the temperature and humidity of the dye works, variations in which could significantly affect the dyeing process; this assumption is based on historic accounts of method transfers across climates[4]. This aspect of the project is being addressed by the ReINVENT network, which brings together interdisciplinary viewpoints for people who are

[1] Edmund Knecht, Christopher Rawson, and Richard Loewenthal, *A Manual of Dyeing*, vol. 2, (London: Charles Giffin & Company, Limited, 1893).
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reconstructing practices from historic textile industries.[5]. Ingredients like rancid olive oil or *huile tournante* which were widely available during the days of Turkey red dyeing are no longer easy to source and modern health and safety regulations regarding the handling of animal droppings and blood add a new level of precautions to the dyeing process.

Further on this project aims to develop a method to analyze textile artefacts and determine whether it is possible have a reliable 'Turkey red test' as well as identify madder-dyed Turkey red textiles versus synthetic alizarin ones, through possibly distinct chemical signatures of madder extract and of synthesized alizarin. The source material for this will largely come from the United Turkey Red Company collection in the Scottish Business Archive at the University of Glasgow with the main analytical method being Ultra High-Performance Liquid Chromatography (UHPLC), which allows for minimal sampling and optimized results. This project may provide valuable information about the provenance of textile artefacts and how best to preserve this part of our cultural heritage.

[5] http://www.stickssn.org/site/pages/projects/reinvent.php

MALDI-TOF-TOF mass spectrometry for the identification of natural red dyes

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A new analytical approach is proposed for the identification of natural red dyes used in historical textiles. The most widely used method is based on high-performance liquid chromatography coupled with either diode array detector (DAD) or mass spectrometer (MS). This method is sample-consuming, commonly 20 µL of sample are required for injection. Moreover, the analysis time varies between 30 min and 1h for one sample.

Here, we proposed an approach based on MALDI-TOF-TOF mass spectrometry. This technique offers several advantages in comparison with the classical LC-MS method. First, a small volume of sample is needed for the analysis (0.5 µL) which is particularly interesting for investigations concerning archaeological samples. Then, it is time-saving: the mass spectrum is recorded in a few minutes. In addition, after MS analysis, the sample may be analyzed in MS/MS mode to obtain fragmentation patterns of ions of interest for further structural characterization. Prior to the mass spectrometry analysis, the samples were purified using micro-solid phase extraction (µ-SPE) tips. The analyses were carried out in negative mode (1) by LDI and (2) by MALDI using tetrathiafulvalene (TTF) and 9-aminoacridine (9-AA). The use of a MALDI matrix successfully improved signal intensity and signal/noise ratio allowing a better detection of the glycosylated compounds.

This methodology was applied on various samples. In particular we will present results concerning (1) madder roots extracts obtained from different madder species (*Rubia tinctorum, Rubia peregrina and Rubia cordifolia*) ; (2) wool fibers, cotton and linen dyed with various madder species and according to different procedures. This last part aims to show the role played by the dying procedure in the identification of the molecular markers characteristic of the madder dye.

Changing the aglycone composition of madder-derived pigments.

Vincent Daniels

Analysis shows that the aglycone composition of pigments made from madder-type plants can vary. Pigments from ancient objects are often high in purpurin or pseudopurpurin compared with the alizarin content. This can be explained in two ways, either that pigments were made from plant material naturally reflecting this composition or that the composition has been altered during the manufacturing process. This paper will review the literature on different ways the aglycone content might be influenced. The solubility of the dye/pigment-precursors is critical in determining the composition of the pigment. This data has hitherto been unavailable but in this work it has been experimentally derived for alizarin. purpurin and pseudopurpurin in water and aqueous alum solution, at various temperatures. The analytical results for several pigments made for this research will be shown.

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Red Dyes used for Rouge Cotton (*Enji-wata*)

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Enji-wata (Rouge Cotton) was a traditional color material to be made by soaking red dyestuffs into cotton sheet in China and had been used as cosmetics or color materials. In Japan, it was widely used for Japanese style painting and *Yuzen*-dyeing in *Edo* period.[1)] Use of safflower (*Carthamus tinctorius*), Japanese (or Chinese) madder (*Rubia akane*), sappanwood (*Caesalpinia sappan L.*), lac and/or cochineal have been described in ancient Chinese (and Japanese) documents.[2)] However, their actual ingredients including red dyestuff have been still unclear by the disappiarance of *Enji-wata* in the end of 19thC. HPLC analyses for several *Enji-wata* showed use lac and/or cochineal in samples specified as natural dyes, which were confirmed by ESI MS spectra. SEM-EDS for the other samples revealed that Na and Cl were detected as major inorganic elements. These results were explained by the existence of inorganic chemicals in red synthetic dyes.

Further observations for their chemical components in lac were made by changing extraction solvents from water to DMF (*N,N*-dimethylformamide). HPLC analyses of DMF extracts from *Enji-wata* using lac, indicated two distinguishable types in the chemical ingredients shown in Figure; in the case of *Enji-wata* 12, major ingredient was red pigments such laccaic acid A, and in the case of *Enji-wata* 55, it was more hydrophobic yellow pigments. These differences were observed in the analyses of stick lac with various origins, too. The former types were observed in lac from India and south part of China and latter were observed in south-east Asia including Thailand.

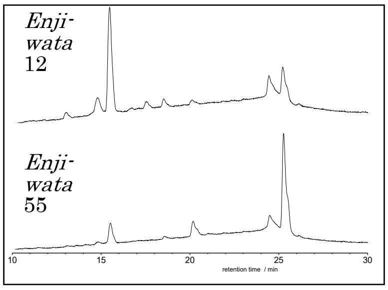

Figure Typical two types of HPLC chromatograms of DMF extracts from *Enji-wata* (rouge cotton) monitored at 450nm

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abstract:

DYES IN HISTORY AND ARCHAEOLOGY 2013

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'SHEARINGS AND CLIPPINGS: MEDIAEVAL PRODUCTION OF RED LAKE PIGMENTS'

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Mediaeval panel paintings from the Northern Netherlands have recently been subject of technical examination. In the course of this study – next to various inorganic pigments – several organic lake pigments have been identified.
Some of these required further attention.
As a rule lake pigments were prepared by provoking a reaction between potash alum, and some alkaline substance (lime, chalk, potash, egg shells, soda ash, or marble dust). In this reaction, aluminium hydroxide [$Al(OH)_3$] is formed as a fine, almost gel-like, precipitate. In the process, the organic coloring component is co-precipitated to form a very stable complex with the aluminium. The aluminium hydrate formed in the process has a low density, and its refractive index is close enough to that of the binding medium to lend transparency to the lakes.
The colourants for making lake pigments were the same as the ones used in the textile dyeing industry. In the Netherlands, the most important red textile dye was madder, extracted from the roots of the herbaceous perennial *Rubia tinctorum* L. They tend to yield a rather warm deep red colour. Other, cooler, more crimson shades of red were obtained from the dried bodies of the female kermes insects (*Kermes vermilio* Planchon, and *Kermes ilicis*). These scale insects were primarily found in Southern France on the small evergreen kermes oak (*Quercus coccifera*). Due to the laborious process of harvesting the roots and particularly the insects, red organic colourants were very expensive commodities. Often, red-dyed scraps of textile, shearings of red wool, i.e. waste material, was collected and processed to recover the coloring material. The colorants were made into red lake pigments that could vary from crimson, over scarlet, and burgundy, to maroon.
Examination of some mediaeval panel paintings from the Northern Netherlands gave convincing evidence for the use of such 'shearing-lakes'.
On the basis of relevant descriptions in the *Antwerp recipe book* (Antwerp, Museum Plantijn Moretus, MS M64), and the "*Van den Varwenen*" (Göttingen, Niedersächsische Staats- und Universitätsbibliothek, Cod. Hist. nat 51), historically appropriate reconstructions of the lake pigments were made.
These reconstructions served to understand the differences in colour, working properties, and composition between the 'shearing-lakes' and the conventional lakes prepared directly from the colouring compounds (madder roots, kermes insects). This helped to better understand the working properties and chemistry of these lakes, both in the reconstructions as on the paintings.
Reconstructions and paint samples were examined with various methods of microscopy, spectrometry, and chromatography.
Comparison between the different approaches for lake production, may elucidate the functionality of mediaeval terminologies, formulae and methods.

Identification of pigments and dyes used on polychrome clay sculptures and wooden artifact from the Astana Tomb of the Tang dynasty (AD618-AD907), Xinjiang, China

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Abstract: The Astana graveyard is located in the Gobi Desert in the Turpan basin, Xinjiang, China, and considered as the public cemetery of ancient Gaochang Country dated to a period between the Western-Jin (AD265-AD316) and the Tang Dynasty (AD618-AD907). Large amounts of clay sculptures with multicolored painted patterns, including warriors, horses, tigers, etc, have been unearthed from the graveyard. Also, a piece of wooden artifact with 9 colors was unearthed and is rich in cultural connotations. In this study, Raman microscopy was employed to identify pigments and dyes remained on clay sculptures from a tomb and the wooden artifact dated to the Tang Dynasty. Many mineral pigments including gypsum, red lead, carbon black, haematite, atacamite, cinnabar, massicot and orpiment were found. This appears to be the earlier report of the use of massicot as a pigment in Xinjiang. Cross-sectional observation revealed that the thickness of the pigment layer among clay samples varied and the white ground layer of pigments was anhydrite, which suggested the influence of mural painting tradition from the West. Two plant dyes gamboge and indigo were identified. Specially, the gamboge was confirmed by HPLC-ESI-Q/TOF. It is the earliest example that gamboge was used as yellow dye in China up to our knowledge. The results show that the Gaochang people had mastered skills proficiently, including the preparation, deployment and usage of pigment. The investigation of pigments, dyes and ground layers will provide reference for the restoration and conservation of these precious artworks, and more evidence of pigments and dyes trade business and cultural exchanges.

Key words: Micro Raman spectroscopy, HPLC-ESI-Q/TOF, Astana graveyard, pigments, Gamboge, indigo

Cochineal and its lake pigments: historic reconstructions from Winsor & Newton's archives

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Commercial artist's oil paints commercially available today do not reflect those from the 19th century, both in relation to the oil binder as well as in the formulations for the colorants. In order to understand the degradation mechanisms that are in play in such a complex environment as a 19th century oil painting it is necessary to have historically accurate reference materials [1]. In a recent publication on 19th century chrome yellow pigments we have shown that the Winsor & Newton archive page-image database provides efficient access to a unique source of information on 19th century artists' materials and their commercial preparation.

The W&N 19th Century Archive is a unique primary resource covering hand-written formulation instructions and workshop notes for pigments, paint, grounds and varnishes, currently available as a page-image database [2]. Approximately forty percent of all the Researcher's Edition database records correspond to red lake pigments, based principally on madder and cochineal lake pigments.

In this presentation we will discuss W&N's formulations for the different cochineal lake colours that they manufactured during the 19th century. By varying processing conditions such as the starting materials or the addition of extenders, W&N was able to produce and sell a variety of different red hues.

Selected reproductions for cochineal lakes, from the W&N archives, are characterized by FORS (fiber optic reflectance spectroscopy), microspectrofluorimetry, infrared and Raman spectroscopy [3], enabling us to compare the reconstructed pigments and oil paints with original paint samples from Portuguese nineteenth century artist's materials and paintings.

Figure 1: Oil paint tubes possibly from Amadeo de Souza-Cardoso (1887-1918), one of the most important Portuguese artists

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Pigments, organic colorants and binding media in the Cyprus Orthodox icons tradition

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The present work focuses on the characterisation of the paint materials used by Cypriot iconographers in Orthodox icons through the centuries. A total of 8 samples were collected from 7 different icons, dated from the 12th to the 18th century, originally placed in 3 different churches in Morphou and Nicosia (Cyprus), and currently conserved at the Archbishop's Laboratory in Nicosia.

A multi-analytical approach comprising spectroscopic, chromatographic and mass spectrometric techniques was used in order to identify the pigments and fillers, the organic colorants and the binding media. In particular, the main goal of the research was to identify the paint materials used to produce red hues.

Pigments and fillers identification was performed using micro-Raman spectroscopy and Fourier Transform Infrared spectroscopy (FT-IR). In order to determine the binding medium, Pyrolysis Gas Chromatography–Mass Spectrometry (Py/GC/MS) and Chromatography–Mass Spectrometry (GC/MS) were used. The study of the organic colorants was performed by Liquid chromatography mass spectrometry (LC-MS/MS) analysis. The extraction capabilities and drawbacks of a mild extraction based on the use of a EDTA/DMF solution as well as the optimization of the chromatographic and MS/MS parameters for the analysis of red lakes in painting samples will be presented.

The main results on the painting technique, the red pigments and colorants applied, and their distribution in the sample build-up will be discussed. In detail, results showed that both inorganic pigments and organic colorants were used to create the red hues in the icons. Cinnabar was identified in almost all the paint layers studied though in some cases red lead was also determined. European cochineal and kermes were identified in the red paint layers, in combination with the inorganic pigments. Moreover, animal glue and calcium sulfate were used for the preparation layers, while egg was used as binding medium in the red paint layers.

Embroidered networks: Indo-Portuguese textiles, their dyes and diverse origins*

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* This presentation results from a research project entitled "*Textiles, Trade and Taste: Portugal and the World*" (TTT), [http://www.cham.fcsh.unl.pt/ttt/index.html]

Textiles were among the most highly appreciated commodities imported from India to Portugal during the 16th and 17th centuries. From the time of the first contacts between Portugal and Asia, embroidered textiles originating especially from Bengal and Gujarat arrived in significant quantities in the Portuguese ports, destined for Portugal and Europe [1]. Interest in these objects increased dramatically in the 17th century and they came to gain increasing prominence in Portuguese daily life. This enthusiasm not only encouraged the arrival of a wide range of types, in terms of origin, style and technique, but also inspired new Portuguese products in the "style of India", which have received little attention until now. Distinguishing these two types of production – India and Portugal – is a very difficult task owing to the fluid circulation of raw materials (silk and cotton), diverse dyestuffs, artistic models (pattern books, etc.), technical knowledge, and even artisans, between these vastly disparate regions of the globe.

Furthermore, although Indo-Portuguese embroideries have been the focus of numerous important studies over the past few decades [2], these have mainly considered the design and technique (stitches) of the decorative embroidery, and only very rarely other important features, such as the materials, support structure or seams, which, potentially, are highly significant for helping to identify different locations of production.

Hence, the research project, *"From there come these precious riches": Indian embroidered textiles in Portugal (16th and 17th centuries)*, takes an interdisciplinary approach that confronts descriptions in historical sources with new material and technical evidence never considered before.

To date, 30 large and important textiles in the Museu Nacional de Arte Antiga (Lisbon) have been thoroughly examined to record the fine details of their manufacture, including characteristics of the decorative and functional stitches used, form of the embroidery, treatment of the seams, number of cloths and their width, layered structure of the quilted panels, etc. Samples of warp and weft threads and embroidery have also been taken from half the group to characterize the fibres (microscopy) and dyes (HPLC-DAD). Microscopically, it can be distinguished two kinds of silk: cultivated (*Bombyx mori*) and tussah (*Antheraea mylitta*) [3] used to do the embroideries, and cotton as well. The dyes analyzed can be divided in two different groups according to their origin, for instance, from Asia it was identified *Rubia cordifolia* L. (red and orange), *Kerria lacca* (red) and a source rich in berberine (yellow); from Europe it was found Cochineal (red), red wood (pink) and *Reseda luteola* L. (yellow).

Together, the technical and material information is beginning to reveal distinct groups, which we are beginning to associate with different origins, a possible centre in Portugal as well as at least three locations of production in India. This data also offers important information for studying the method and organization of the embroiderers' work, and for clarifying the international networks responsible for the circulation of textiles and raw materials in this period.

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Evolving industries: Identifying yellow dyes in 17th-century 'Indo-Persian' carpets

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Owing to their aesthetic features and precious materials, fine Iranian rugs were only within reach of the elite in the 16th century: the court, mosques, churches and some European nobility. In the early 17th century, 'Indo-Persian' carpets began to appear in significant numbers in Portugal in parallel with a major shift in the production of carpets in Iran [1].

The transformation in textile production in the late 16th to early 17th century arose due to the personal interest of Shah Abbas, a weaver himself, who sought to strengthen the Iranian economy by developing a major carpet industry, which would be competitive in the international market. To meet the demands of international taste for carpets of large dimensions, workshops focused on minimizing production time and costs through developing new designs, which involved less expensive materials, thus making Iranian carpets more accessible to a wider range of consumers [2]. At the same time carpet production was also being undertaken in India, and travel accounts report that Persian weavers migrated to work for the Mughal court [3]. This context raises problematic questions about how, where and when carpets of the 'Indo-Persian' type were produced.

A new study aims to resolve these questions through an interdisciplinary approach (involving history, art history, technical and chemical analysis). 'Indo-Persian' carpets selected from the large Portuguese public collection and other important collections from the USA are being examined as possible products of this transformation.

Analysis of stylistic characteristics and chronological transformations of designs is providing a better understanding of the evolution of the industry and the progressive introduction of European influence. Through the characterization of the natural dyes used it is also possible to establish the regional use of various dyes, and hence the possible area of production of the carpets [4]. This project focuses on red, yellow, orange and brown colours, which have proven to be extremely useful for determining origin, as recent carpet studies have revealed [4, 5].

This paper will present preliminary results on yellows belonging to carpets attributed to India and Iran analyzed using Liquid Chromatography and Mass Spectrometry (LC-MS). The results have shown different combinations of yellow dye sources pointing to different dyeing traditions.

The results of this work, together with other studies, are part of the research programme: *Textiles, Trade and Taste. Portugal and the World* (TTT), being conducted by scholars at the Centre for Overseas History (CHAM), and which aims to enhance our knowledge understanding of the impact of the new overseas trade networks established by the Portuguese in the 16th century on the development of one of the great forms of artistic expression of Iran.

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Dyes and Dyeing in the Ming and Qing Dynasties (1368-1911) in China: Preliminary Evidence Based On Primary Chinese Sources

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There are growing interests in historic Chinese dyes and dyeing, but there have been few studies on dyeing in a particular period. Thanks to the prosperity of commerce, dyeing techniques developed very quickly in the Ming and Qing Dynasties. In this presentation, the preliminary results from our investigation into dye plants and dyeing recipes of this period by the interdisciplinary approaches of literature research and experimental research will be presented.

The first stage is the summarization and analysis of documented evidences from the historical periods of interest (Liu 1563, p.25; Pan 1992, p. 340-343; Fang 1981, p.157; Fan ?, cited in Li 1991, p.84; ? 1754, cited in Wang *et al.* 2011, p.126-127). Initial research into the dye plants by historical literature research revealed that only five red and yellow dye plants were recorded frequently in the Ming and Qing Dynasties. They were respectively sappanwood (*Caesalpinia sappan*), safflower (*Carthamus tinctorius*), amur cork tree (*Phellodendron chinense*), smoketree (*Cotinus coggygria*) and pagoda tree bud/flower (*Sophora japonica*). Dye plants such as madder (*Rubia* species), turmeric *(Curcuma longa)* and gardenia (*Gardenia jasminoindes)* were replaced. Regarding the botanical provenance of plants for dyeing, the species of Chinese dye plants has not been clear from previous research. Research on ancient plant species in the field of Chinese herbal medicine was introduced to specify the species of the dye plants. As a result, some mistakes in respect to the species of dye plants were corrected. 1) Aromatic turmeric (*Curcum aromatica*) was not used for dyeing in the ancient time. 2) The gardenia used for dyeing is *Gardenia jasminoindes Ellis f. longicarpa Z．W．Xie et Okada* rather than *Gardenia jasminoindes Ellis.* 3) 'Fan hong hua' (saffron) may not have been used for dyeing, as 'hong hua' (safflower) was. Moreover, by studying the dyeing recipes mentioned above, it was found that red dyeing and brown dyeing were more frequently recorded. The records of single-dyeing and over-dyeing, direct dyeing and mordant dyeing varied among different documents. By dyeing experiments according to the ancient dyeing recipes, the following regulations were found. 1) Commonly recorded dyes usually have good dyeing effects, while dyes occasionally recorded do not work very well. 2) Tannin helps the connection between cotton and most dye components. However, some plant dyes such as madder, sappanwood and smoketree do not work well with tannin because the dyes change colour in acidic environment. 3) There are visible differences in dyeing effects by using similar dye plants of different species, by dry-heating dye plants and by changing the acidity of dyed textiles.

NB: This research will be further developed when the two pieces of original recipes and more other recipes are available this summer.

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Reconstruction of the palette of Qing dynasty textile dyes

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Abstract

To reconstruct the palette and dyeing methods of Qing dynasty textile dyes, we have been searching for Qing dynsaty dyeing recipes for several years. Fortunately, some eighteenth century dyeing recipes, which were used in the imperial weaving and dyeing workshop in Beijing, were obtained at the China No.1 Historical Archives in 2005.

This talk will focus on some dyestuffs and twenty colors which were commonly used in Qing dynasty textiles. Safflower (*Carthamus tinctorius L.*), sappanwood (*Caesalpinia sappan L.*), pagoda tree (*Sophora japonica L.*), young fustic (*Cotinus coggygria*), amur cork tree (*Phellodendron amurense*), indigo-type plant dyes, etc. were identified by high performance liquid chromatography with photo-diode array and mass spectrometric detection in a range of colors of the Qing dynasty silk textiles treasured at the China National Silk Museum. All of the dyestuffs identified in the historical silk objects were also mentioned in eighteenth century recipes. Safflower was the major dye for several reddish colors, such as bright red, pink and orange; Sappanwood was used for dyeing silk red in Ming dynasty, but it was only applied as a top dye, along with other dyestuffs, in the eighteenth century. The buds of the pagoda tree, one of the native yellow dyestuffs in China, was most widely used on silk to obtain a bright yellow, whereas, young fustic, was commonly used to produce a golden yellow. Indigo-type plants were used to produce blue silk textiles during the Qing dynasty before the end of nineteenth century. Finally, color measurements (CIE lab) were also performed on both historical silk textiles and reconstructed samples in order to evaluate color differences.

Feeling blue, dye red
Early synthetic organic dyes: substantive cotton dyes

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Abstract

The lecture highlights the history, the production and the properties of the early synthetic substantive dyes. One important property of the early synthetic organics is their great affinity for animal (protein) fibres such as wool and silk. Unfortunately, they had virtually no attachment to vegetable (cellulose) fibres like cotton and linen. This changed in 1883 when the chemist Paul Böttiger, working in the dyestuff laboratory of the Farbenfabriken vorm. Friedrich Bayer & Co. AG in Elberfeld, Germany, discovered a substantive red dye by coupling 1-naphthionic acid with doubly diazotized benzidine. He kept the details to himself, left Bayer and filed in February 1884 a patent (German patent 28753) for this new process. Böttiger attempted to sell rights to the firms Bayer, BASF and Hoechst, but they showed little interest. The Agfa company bought the patent and manufactured in 1885 the dye under their trade name Congo red, a popular name in Germany at that time of the 1884 Berlin West Africa Conference.

In 1883 the German chemist Carl Duisberg (1861-1935) joined Bayer and one year later (in 1884) he experimented with new coupling components. One of these chemicals was 2-naphthionic acid (Brönner's acid). After coupling with doubly diazotised o-tolidine a light red precipitate was produced. In March 1885 a patent (German patent 35615) for tolidine dyes was registered by the Bayer firm. The dye became known as Benzopurpurine B and came on the market in the autumn of 1885. It was not successful, because of its dull, brick red tone.

Further experimenting by Duisberg led to an even better red dye compared to Congo red. It was made by coupling 1-naphthionic acid with doubly diazotized tolidine and sold as Benzopurpurine 4B.

Agfa filed opposition against the Benzopurpurine patent because the two dyes (Benzopurpurine 4B and Congo red) were too similar in their chemistry. The court ruled that Benzopurpurine was not patentable. In the end the executives of Agfa and Bayer decided that the

Benzopurpurine patent became an addition to Agfa's Congo red patent and agreed on a cross-licensing arrangement forming a cartel, soon known as the Benzopurpurine convention, to protect their mutual interests. A greater threat for both companies came from the Berlin firm Ewer & Pick in 1889, which claimed that the original Congo red patent was invalid. In the end the highest German court ruled in favour of the convention.

The advantages of these substantive cotton dyes are: their direct and easy application without using mordants and their low price. Their disadvantages are: a poor light-fastness, an inadequate fastness to washing and acid-fastness. In the 1893 book by Adolf Lehne he writes: 'after six days of light exposure (in September) the colour of Congo red and Benzopurpurine B changed strongly (brown, respectively light brown), for Benzopurpurine 4B the colour faded strongly (brownish)'.

Progress was made and around 1890 substantive dyes in different colours were marketed using the name Congo, such as Congo rubine, Congo Corinth, brilliant Congo, Congo orange, Congo brown, Congo blue and Congo Violet.

Scientific research on natural dyes in Turkey, in the period of 1930-1950

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In the early-Republican years, Turkey was an agricultural country. Efforts towards industrialization were interrupted on the aftermath of the 1929 world economic crisis, and consequently, giving a fresh impetus to agriculture, and making use of the country's own resources came into the agenda in an intense fashion. Taking the examples in Germany into account, The High Institute of Agriculture was established in Ankara in 1933. The Institute reorganized the pre-existing agriculture, forestry, and veterinary schools under a new roof, and its mission was educating the necessary personnel, as well as finding solutions to the problems of Turkey through scientific research in these fields.

At the Institute, in an attempt to explore and evaluate the resources in Turkey, scientific research into natural dye has begun. Natural dye had a great significance in Turkey in the past, as much as being an important export item, and the research at the Institute aimed at replacing the use of synthetic dyes with natural ones, and rendering the use of natural dyes more widespread. The first Ph.D. in chemistry was completed at this Institute in 1936, and the dissertation was on the extraction of natural dyes from dye plants, and using them in dyeing. In one other dissertation, the relative advantages and disadvantages of natural and synthetic dyes were discussed, and it was concluded that using natural dyes is more advantageous for Turkey. Another dissertation was on dyeing with multiple dye plants: dyeing formulas were developed, and a number of fastness degrees for natural dyes were specified. Throughout the period, those researchers have also written numerous popular and semi-scientific articles, and put an intense effort into re-introducing natural dyes in Turkey, and putting them into use again.

After 1950, the turn towards import-oriented economic policies left natural dyes out of the agenda. In the period under consideration, Turkey was unique in the world, in terms of undertaking systematic scientific research on natural dyes and natural dyeing. The aim of the paper is to analyze this research in detail.

Treasures from a Leeds Dye Chemist: A Century-Old "Tyrian Purple"?

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An old archive of documents and artifacts relating to a Leeds dye manufacturer emerged from a Devon attic in 2008; it had never previously been researched.

Named Wood & Bedford, the company's beginnings were in the early 1800s. Later it became the Yorkshire Dyeware and Chemical Company, and then the internationally known Yorkshire Chemicals. Although the company changed names, in its 180-year history it never underwent a takeover and its main factory on Kirkstall Road, Leeds, was occupied from 1850 until the demise of the company in 2004. The Kirkstall Road site was only recently demolished and cleared.

Most items in the archive dated from the mid-nineteenth century to the first quarter of the twentieth, a fascinating period of dye history when natural dyes overlapped and were gradually replaced by synthetics. The archive had been passed down to Charles Chalcraft by his mother, whose maiden name was Bedford. Three generations of the Bedford family built a high reputation as chemists and dye manufacturers in Leeds.

The archive contained material relevant to the family's manufacturing and research successes, as well as its close connections to the family of Sir William Henry Perkin. A selection of the documents and artifacts was connected to the orchil trade, on which the early fortunes of Wood & Bedford were based. Orchil is a dye made from lichen and was used to dye silk and wool various shades of purple.

One of the more astounding discoveries associated with this archive was that it included a small envelope signed by Charles Samuel Bedford declaring the content of the packet to be "Tyrian Purple". But what was really inside the envelope? Was it truly Tyrian Purple – the "Dye of Dyes", prized above all – from about a century ago? The talk will discuss the Bedford family of dye chemists and their connections to this archive of colourful treasures.

Comparative study of the accelerated ageing of Andean natural organic colorants by colorimetry and chromatography

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Abstract:

Natural organic colorants extracted from plants and insects are frequently highly fugitive. Exposure to light not only alters the appearance of such colorants, but changes their chemical composition. In studying archaeological textiles, it is therefore important to understand colorant deterioration in order to interpret analytical results obtained, explore possible changes in appearance and to inform conservation, preservation and display strategies.

As part of an on-going British Museum research project on colorants associated with Andean textiles [1], an accelerated light-ageing experiment has been undertaken. From the collection of over 260 samples of raw materials from plants and insects and of wool or cotton dyed with these sources that has been collected, a subset of 30 reference samples have been selected. These include the most commonly identified colorants based on the literature review and analytical work at the British Museum. The samples include colorants from different chemical classes (including carotenoids, anthocyanins and flavonoids), different dyeing techniques (direct and mordant dyes) and on different supports (wool, camelid fibre or cotton) and in each case the dyeing procedures have been accurately documented. Undyed samples of wool and cotton have also been included in this study to evaluate the degradation of the fibres themselves in order to address conservation concerns and inform work on species identification of camelid fibres.

In order to explore colorant sensitivity, identify degradation markers and investigate deterioration mechanisms, the experiment has been designed to allow both colour change and modifications in the chemical composition of the dyes to be monitored. For the latter, HPLC-PDA analysis is being used, for which a soft extraction method using dimethylformamide and oxalic acid has been selected allowing changes in acid-labile components that may be significant to be followed.

This paper will present the experimental design and the results of the colorimetric and chromatographic study. While the use of a soft extraction method precludes quantitative chemical analysis, the colour changes observed during the ageing will be related to the changes in chemical composition. These changes provide insights into the deterioration of the different colorant classes and the influence of the nature of the fibre and depth of dyeing. The chromatographic results from the accelerated ageing experiment will also be compared with data obtained for early to late Horizon Andean textiles from the Central and South Coasts present in the collections of the British Museum and Musée du quai Branly to contribute to a better understanding of the colourant sources used in pre-Columbian textiles [2, 3].

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NATURAL DYE IN NEW ARCHAEOLOGICAL AND ETHNOGRAPHIC RESEARCHES IN AZERBAIJAN

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The history of natural dyeing in Azerbaijan is very old. Azerbaijan's possession of rich flora and its being early cultural source posed influence on the development of this craftsmanship field.

The results of archaeological excavations conducted in medieval Agsu town and continuance of dyeing work in old methods in Basgal Silk Center today substantiate to express thought on the historical development way of natural dyeing.

A dyeing shop which has large dye pitchers inside was revealed during archaeological explorations launched in medieval Agsu town since 2010 March. Dye layer on the pitchers' inner wall and dye powders poured on the ground were analyzed under guidance of Prof.Dr.Recep Karadağ in Marmara University of Turkey. It was clear that madder was remained into the pitchers (madder - Rubia Tinctorium L.). Generally, Azerbaijan's export of madder in 18th century was reflected in official documents. More than half of taxes collected from the population of medieval Agsu town were achieved from dye.

Basgal Village of Ismayilly region engaged historically in dyeing. Dyeing workshop was restored in Basgal as a result of the development of natural dyeing started with public initiative and introduction again to the people, and Silk Centre was created there. The dyers who used the branches of bush called 'saragan' at dyeing prepare local textile named 'kalagayi'.

Natural dye currently keeps its previous importance, nevertheless people approach indifferently to the usage of natural dye. MIRAS Social Organization in Support of Studying of Cultural Heritage intends to implement different projects to enliven natural dye in Azerbaijan.

The approach to the characteristics of eighteenth-century silk colour palette

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Modern dyeing was born at the beginning of the eighteenth century in France, when the empirical approach to dyeing was replaced by scientific one. The breakthrough was the establishment of the Chamber of Trade - Bureau du Commerce, managing the affairs of trade and production of textiles, and later establishment of Inspecteur général du royaume des teintures. In 1731 Charles de Castenay Dufay (1698 -1739), Member of the French Academy was appointed to this post. He has developed new dye instructions, based on chemical formulas. New ways of dyeing became widely used in the textile industry, especially in silk manufacturing. Patterns of silks became more painterly. Graphical approach and schematism gave way to freedom, and seeking the natural beauty. Weavers and designers focused on creating harmonious colour schemes and combinations of shades. Fighting to preserve the primacy of the international market, Lyon's silk manufactures were distinguished by particularly sophisticated designs. Lyon's design was at a high level thanks to outstanding designers. A new approach to the design of silk, saturation of colours and introduction of shading to achieve a three-dimensional effect was first applied by Jean Revel (1684-1751).This aesthetic transformation resulted from a desire to make woven patterns closer the painted works of art. It was undoubtedly effect of new dyeing, creating new opportunities for textile designers. The individual centres have developed their own colour schemes and range of colours. French silks in the 30ies of the 18th century, thanks to above mentioned Ravel, was characterized by an extremely wide palette, and English silks from an early 18th century - by vibrant colours of threads, especially those coloured with yellow dyes. How much the technological changes influenced the then industry, is shown by preserved fragments of silks, that are treasury of of knowledge about the fashionable colours and combinations of colours. Preserved samplers, signed with the names of the artists, and silks made according to their designs, allow reproduction of the colour palette they used when designing patterns, as well as the names of colours that now are often forgotten

This colour characteristics of the patterns appears sometimes in publications, but so far, it has not been a major subject of studies. Colour combinations characterizing particular periods of design and applied by various weaving centres, may become an important tool in the studies on textiles, just as the currently used technical and formal characteristics of the fabric taking into account the size of patterns repeats, their form and composition, and parameters such as the construction and width of fabric, properties of selvedge, etc. This paper is an attempt to create such a research tool.

<Oral presentation>

Application of Bacteria from Korean Traditional Indigo Vat to Indigo Reduction

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Indigo-blue is one of the oldest natural dyes for blue color and is traditionally produced from indican by innate enzyme in indigo plant [1]. Indigo is insoluble and, therefore, for commercial dyeing, it is converted to the colorless and soluble leuco-form by chemical reduction using sodium dithionite. This conventional procedure generates environment-polluting, highly alkaline effluents, in addition to by-products containing sulphur [2]. Thus, we expect that the processes using microorganism participated in indigo reduction may solve these problems in an environmentally friendly manner, also providing another possibility of improvement for low reproducibility. In the previous study, we identified the bacterial population or community resident in indigo vat traditionally used in Korea. 16S rRNA sequences-based meta-genomic approach paved a way for the understanding and interpreting the bacterial community related to natural indigo fermentation. These results could be a basis for developing the bioprocess of indigo reduction by mimicking fermentation method [3].

The purpose of this research is to develop the eco-friendly bioprocess of indigo reduction using isolated bacteria with indigo reducing activity confirmed in the previous study. Researches on the optimization of bacteria culture and the application to indigo reduction dyeing were carried out.

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NATURAL DYEING TECHNIQUES FOR THE RESTORATION OF ANCIENT TAPESTRIES

INNOCOLORS project (Crosstexnet ERA-NET Project)

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This Franco-Italian INNOCOLORS project has the originality to combine totally disjoint and complementary skills deriving by different sectors in the same project: Industrial production processes, restoration of European heritage and development of natural dyeing processes.
The exploitation of new natural products and technologies in the field of restoration will be presented during this oral communication.

Starting from '90s, following studies carried out at Opificio delle Pietre Dure in Florence, pre-metallized dyes are used in tapestry restoration. These industrial dyes for proteinaceous fibers are widely used in restoration workshop due to their practicality, inexpensiveness, fastness preparation and light stability.
Using binary or tertiary mixture of pre-metallized dyes all chromaticity can be obtained in order to reproduce necessary fibers colors for the integration intervention. Different reference triangles of colors can be build up: mixing yellow, red and grey colors is possible to obtain nuances useful for tapestries restoration. For this purpose, the *Centro per la Conservazione ed il Restauro La Venaria Reale* has developed and used a match card of 66 colors on wool.

The innovative idea of this study was to make a shade card using natural dyes according the reference colors, a good lightfastness of dyed yarns and a dyeing process easily workable by CCR. To achieve the best color matching, twenty natural dyes, marketed by the French company *Couleurs de Plantes,* have been tested by CRITT horticole.

Following the optimized recipes different dyeing tests were carried out at CCR laboratories to obtain the suitable colors to integrate a Flemish tapestry actually in restoration. Samples of dyeing fibers prepared have been characterized by spectrocolorimetric analysis and their morphology has been observed by optical and electron microscopy. Light fastness has been evaluated through accelerated ageing test (UV-VIS light).

Posters displayed during the conference

Serap Ayaz Seyhan, Çağlar Demirbağ and Emre Dölen, **The Analysis of the Relative Abundance of the Dyestuffs Obtained from Kermes (*Kermes vermilio*) in the Northwest of Turkey***

Christine Brunet, Oscar Chiantore, Isabelle Clonier, Paola Croveri, Anne de la Sayette, Laura Degani, Julia Gazères, Valérie Girardin and Roberto Pertile, **INNOCOLORS – A European collaboration to promote natural dyes for industry and restoration of cultural heritage**

Çağlar Demirbag, Serap Ayaz Seyhan and Emre Dölen, **Identification of Indigoid Dyes Found in *Rapana venosa* by High Performance Liquid Chromatography with Diode-array Detection***

T. Ferreira, H. Moreiras, A. Manhita, C. Frade, E. Lopes, P. Tomaz, P.S. Rodrigues, J. Mirão, A. Candeias, C. Dias and A.T. Caldeira, **Material characterization of a Liturgical Cope belonging to D. Teotónio of Braganza (16th Century)**

Anne-Laure Gagez, Boris Letribot, Jean-René Chérouvrier, Dominique Cardon, Anne de la Sayette, Laurent Picot and Valérie Thiéry, **Characterization of precursors of dye from gastropods of *Ocinebrellus inornatus* and *Ocenebra erinacea* detected on the Island of Ré in the Atlantic coast of France**

Vugar Guliyev and Irada Gadirova, **Dyeing in carpet art in Azerbaijan***

Monica Gulmini, Ambra Idone, Manuela Moi, Matilde Borla, Cinzia Oliva and Maurizio Aceto, **Selected Coptic textiles from the collection of the Egyptian Museum of Turin: a non-invasive survey on dyeing materials***

Lamya Hayat, **Extraction of a red dye from the roots of Arnebia decumbens from Kuwait desert of multi-medicinal values***

Sevim Karabulut, Türkan Yurdun, Gülbin Erdoğan and Emre Dölen, **An Evaluation of Barbarossa Hayrettin Pasha's Naval Ensign of the 16th Century in Istanbul Naval Museum with Dyestuff Analysis***

Ioannis Karapanagiotis, Dimitrios Lampakis, Anna Fostiridou, Svetlana Vivtenko, Panagiotis Manoudis and Lilian Achilara, **Cochineal, wild madder and other colourants detected in Hellenistic/Roman figurines**

Susan Kay-Williams, **Exploring the development of dye sample books 1856–1905**

Chika Mouri and Blythe McCarthy, **Dyes on Japanese silk mountings in the last 300 years***

Irina Petroviciu, Ileana Cretu and Mihai 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)***

Katarzyna Schmidt-Przewozna, Malgorzata Zimniewska, Jakub Kowalinski and Barbara Romanowska, **Dyeing Plants as a source of Beautiful Colour for knitted linen fabrics***

Katarzyna Schmidt-Przewozna and Jakub Kowalinski, **Natural dyestuffs as connection between the world of history, culture and technical applications. Promotion of historical methods by INF&MP***

Younsook Shin, Min Choi and Dong-Il Yoo, **Indigo Dyeing Using Organic Reducing Agent from Food By-product**

Younsook Shin, Kyunghee Son and Dong-Il Yoo, **Reduction of Indigo using Yeast Strains**

Emine Torgan, Berrin Altuntepe and Recep Karadag, **Silk dyeing and lake pigments obtaining from *Helichrysum arenarium* and their analysis***

M. Toussirot, W. Nowik, E. Hnawia, N. Lebouvier, A-E Hay, A. de la Sayette, M-G Dijoux-Franca, P. Cabalion, D. Cardon and M. Nour, **Characterization of *Morinda citrifolia* L. dye and its identification in cultural heritage artifacts from New Caledonia**

Ina Vanden Berghe and Mª Julia Martínez García, **Purple dyeing with strawberry tree and alkanna according to the Classical recipes: insights in the dye content of this particular vegetable purple dyeing recipe***

Abstracts are included for posters marked *

The Analysis of the Relative Abundance of the Dyestuffs Obtained from Kermes (*Kermes vermilio*) in the Northwest of Turkey

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Dyer's kermes is found only on the kermes oak (*Quercus coccifera* L). Regions of the Mediterranean area where such ecosystems can be found are in France, Yugoslavia, Spain, Greece and Turkey(1). In ancient times, these insects were thought to be of a vegetable nature, and were used in medicine. Kermesic acid (kr) is used in various fields such as textiles, medicine, food and cosmetics and it does not damage to human health and the environment (2,3).

The main constituent of this insect, kermesic acid (CI 75460), is the aglycone of carminic acid (cochineal), and this acid is responsible for producing the red color of the dyes. Kermes also contains a small proportion of another yellow-orange anthraquinone colorants, flavokermesic acid (fk) (1).

Verhecken and Wouters has shown that it is in fact laccaic acid D (4). These scientists have also revealed the presence of eight other colorants, as yet unidentified and the relative abundances in the acid hydrolyzed extract were: 15 % fk and 85 % kr (Yugoslavia), 18 % fk and 82 % kr (Spain), 20 % fk and 80 % kr (North-Africa), 27 % fk and 73 % kr (France) (5,6,7).

We couldn't find any information about the dyestuffs composition of Kermes in Turkey. In this study, we analyzed the relative abundance of the dyestuffs from Kermes.

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Identification of Indigoid Dyes Found in *Rapana venosa* by High Performance Liquid Chromatography with Diode-array Detection

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Indigo and indigoid dyes are molluscan dyes and have been known since pre-Roman times (1). Apart from coloring objects, they were integridents of many traditional prescription. At the present time their new analogous are synthesizing for the treatment of some important diseases as cancer and diabetes (2).

Indigo and indigoid dyes obtained from certain species of molluscs. One of this species is *Rapana venosa* (Synonyms: *Rapana thomasiana* or *pontica*). This Asian gastropod is an invasive species in Black sea (3).

The aim of the study was identification of the indigoid dyes found in *Rapana venosa* A reversed-phase HPLC with diode-array dedection has been used for identification of indigoid dyes.

Rapana venosa molluscs were provided from Central Fisheries Research Institute (Trabzon, Turkey) and they were collected from eastern Black sea.

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Dyeing in carpet art in Azerbaijan

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Azerbaijan is one of the old dyeing centers. As an evidence we can show old history of Azerbaijani carpets. Azerbaijani dyeing is mainly used in arts of weaving, more accurately carpet, carpet without pile (called ‘palaz’), felt, kalagayi and other fields.

During weaving carpets, dyeing of cotton yarns is considered one of main works. Weavers started to prepare dyeing products of craftsmanship more than leaves and flowers, seeds, rind, wood and other parts of the plants as well as fruit and vegetable since old times till end 19th century and early 20th century and they used them in dyeing of wool, silk and cotton yarn. The strings dyed by weavers till 20th century were primitive position, their being delicate reflected in the carpets at museums profoundly. Sheik Safi is a good example.

Cotton yarns are dyed in natural way mainly with dyes of flora composition. This work style seemed simple, requires from dyer great skill. In order to get 7 main colours including red, green, yellow, blue, dark-blue, black, white and their shades, leaves of walnut bark, sumakh, indigo, mulberry, quince, and walnut tree and stems of madder bush and various means are used. For example, in order to get yellow and semi-tone of this colour, onion peel, apple peel and mulberry leaves gathered in autumn; for madder-red and pink colours and indigo for dark-blue, blue and green colours. Regretfully, natural dyeing is forgotten and chemical dyes appeared and applied. MIRAS Social Organization aims at re-developing natural dyeing in Azerbaijan.

Dyes in History and Archaeology DHA32

Selected Coptic textiles from the collection of the Egyptian Museum of Turin: a non-invasive survey on dyeing materials

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The Coptic collection of the Egyptian Museum of Turin includes about 250 textiles. Many of them are decorative parts that have been cut out from tunics or fragments deriving from larger textiles, although the collection also encompasses whole tunics and headdresses. The conditions of the textiles are largely inhomogeneous: some of them are excellently preserved whereas others are in bad conditions possibly due to restorations that were undertaken at the beginning of the past century.

A minor part of the collection derives from Schiaparelli's excavation in Ashmunein (Hermopolis), while the provenance of most of the textiles, which were donated to the Turin Museum by the Cairo Egyptian Museum at the beginning of the 1900, is unknown.

In order to shed light on provenance, date of production, conservation and materials, and to highlight possible similarities or differences among the fragments, a selected set of Coptic textiles presently stored for studying and cataloguing is the object a multidisciplinary project that will consider the textiles from an iconographic and technological point of view. In particular, the project is focused on the study of textiles fibers and weaving technologies under the optical microscope, as well as on the application of non- invasive and invasive analytical techniques in order to investigate the dyeing materials.

A non-invasive screening was performed by UV-Vis-NIR reflectance spectroscopy [1] and fluorimetry [2,3] employing portable instruments equipped with fiber optics that allowed an *in situ* survey. Due to the bad conditions of some textiles, more robust information can be obtained by performing a large number of analysis on the same object and by considering together the information obtained from the two analytical techniques.

Both fiber optics reflectance spectroscopy (FORS) and fiber optics fluorimetry respond in few seconds and allow the rapid highlighting of some peculiar information on the dyes. In particular, the presence of indigo is easily detected by FORS, and also the vegetable or animal nature of some anthraquinonic red dyes can be assessed. Moreover, the techniques also allowed us to sort out, among the red or reddish hues, those that could not be attributed to the presence of the most popular red dyestuffs (i.e. *rubia* species and coccids).

Unfortunately the non-invasive approach lacks in information for yellow dyestuffs, although groups of samples were identified according to few common spectroscopic features.

The overall investigation allowed us to obtain preliminary information on the dyestuffs employed and to recognize the presence of different materials employed to obtain similar hues. Moreover, the non-invasive survey allowed us to select a limited number of representative samples to be subjected to further analysis.

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Extraction of a red dye from the roots of *Arnebia decumbens* from the Kuwait desert of multi-medicinal values

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The extracted dye from *Arnebia decumbens* roots had a rich red color. Checking its biophysical properties by applying it, as ethanol solution, on the skin, it absorbed both UVA (400 nm – 320 nm) & UVB (320 nm – 290 nm). This observation indicates that the dye helps in protecting the exposed skin from harmful short waves.

The dye also had variable inhibitory effects on the growth of 5 different microorganisms: *Bacillus subtilis* (BS); *Sarcina lutea* (SL; = *Micrococcus luteus*); *Saccharomyces pastorianus*; *Candida albicans* (CA) & *Escherichia coli* (EC) (1)& (2).

Checking on the chemical properties of the red dye , it was noticed that it did not fade in exposure to light and had an excellent wash fastness (3).

By knocking the iron molecule embedded in the dye molecule with other elements like magnesium, manganese, copper, cobalt, etc, at a time, a range of colors were obtained. Accordingly the dye was used as a natural dye, in place of the synthetic dyes, to color wool and cotton used for rugs and tents of the Bedouin cultural society of Kuwait (Al Sado).

Since the dye has the property of absorbing short waves, this was tested to see if it absorbs also free radicals. By mixing the dye with an ointment, it was applied on ulcers of diabetic foot and leg. It gave very positive effects.

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An Evaluation of Barbarossa Hayrettin Pasha's Naval Ensign of the 16th Century in Istanbul Naval Museum with Dyestuff Analysis

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Istanbul Maritime Museum is one of the important museums in Turkey, yet the textiles therein have not yet been evaluated through chemical analysis. The subject of this study is the analysis and examination of the naval ensign in the Istanbul Maritime Museum, used by Barbarossa Hayrettin Pasha, during the time (1534–1546) he was Kapudan-ı Derya ("Chief of the Sea", Great Admiral of the navy of the Ottoman Empire). Barbarossa Hayrettin Pasha (ca. 1478 Lesbos – d. 4 July 1546, Istanbul) is one of the famous mariners of the Ottoman history, and is the first Kapudan-ı Derya of the Ottoman State.

The naval ensign that is subject to analysis is 287 x 200 cm in size, it is self-patterned in green colored silk. The scriptures and figures applicated to the ensign are of white silk fabric. These appliqués are Sura al-Fath (the Victory Chapter) from the Qu'ran, the names of the four caliphs of Islam, Zulfiqar (the bifurcated sword of Caliph Ali), claw (the shape of hand), and a six-cornered star. The dyestuff analysis of the ensign is made with HLPC, and a metal mordant analysis is conducted with SEM. Moreover, with CIELab system, a colorimetric analysis of the ensign is undertaken, and the surface morphology is evaluated with respect to oxidation, degree of damage, superficial abrasions, and the effect of environmental conditons thereon.

Restoration and conservation of historical textiles is an important issue for the museums. First and foremost step in the restoration of historical artifacts is chemical and physical analysis. 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 artefact, and it would provide information regarding the artifact's historical past.

Dyes on Japanese silk mountings in the last 300 years

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Elaborate, handwoven silk textiles are used to frame and protect Japanese hanging scrolls and screens. At the Freer Gallery of Art and Arthur M. Sackler Gallery, Smithsonian Institution, silk samples have been saved during remounting of paintings over the last several years.

To determine the natural dye and synthetic dye compounds used on the silk, more than 100 silk samples were analyzed by High Performance Liquid Chromatography–Diode Array Detector-Mass Spectrometry (HPLC-DAD-MS). Although many studies have been done to identify natural dyes, farther research is needed for synthetic dyes. In addition to published references (1), we analyzed fabric samples in "A Manual of Dyeing," published in 1893 to address this lack of comparative data.

Initial examination of data from analysis of the mounting silks has found berberine, rutin and myricetin rhamnoside pointing to possible dye sources of the bark of Amur cork tree, flower bud of pagoda tree and bark of bayberry respectively for yellow dyes. Identification of hematein determined that logwood was used as a black dye. Many of the blue and green textiles showed both indigotin and indirubin indicating a plant source was used. Most of the brown textiles contained ellagic acid. For other blue and green dyed textiles, the synthetic green dye, guinea green B and/or similar compounds were often found.

The textiles may have come to the mounting studio with an original dye; they may have been overdyed by the mounters, and they may also have been dyed during later conservation treatments. Due to the possibility of multiple dying steps, the results of this dye study are currently being examined in light of traditional knowledge supplied by the conservators in the paintings conservation studio at the Freer|Sackler. For example, traditionally mounters have used natural dyes such as Yasha (Alnus cone) in the painting conservation studios (2). In addition to understanding the dyes used on these textiles, this research furthers current efforts to document and reproduce mounting silks by the Freer|Sackler painting conservation studio.

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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)

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Located at the confluence of the main Euro-Asian trade routes, Romania preserves rich textile collections that reflect the triple influence of the Byzantine, Western and Eastern worlds, grafted on an individual specificity, representative for the 14th-19th centuries. Since 1997, many of these textiles have been studied in terms of dye analysis, first by LC-DAD, as a joint research between Romanian institutions and the Royal Institute for Culture Heritage in Belgium (KIK/IRPA) [1,2] and more recently by LC-DAD-MS, based on an analytical protocol which has been developed in Romania [2,3], based on the experience accumulated by the Romanian specialists from the European projects, such as ARTECH.

The Cultural Heritage Agency of the Netherlands OCW-RCE was one of the first European laboratories who investigated natural dyes in museum textiles, analysis performed by Ms. Judith H. Hofenk de Graaff and Ms. Wilma G. Th. Roelofs dating from the early 1970s. All these results, carefully organised in projects, are now stored in a computerized archive. Access to this database of analytical results was recently possible, for selected researchers, within the ARCHLAB facility of CHARISMA project.

The poster presents the results obtained within EURODYE, an ARCHLAB users' project which aimes to integrate textiles from Romanian collections in a European context. The natural sources of dyes in Romanian textiles were compared with data available in OCW-RCE archive. Sources detected in 15th-16th c. brocaded velvets from Romanian collections, such as *Reseda luteola* L (weld), *Cotinus coggygria* L. (young fustic), *Porphyrophora polonica* L. (Polish Cochineal) were also detected by the OCW-RCE specialists in European textiles from the same period. According to the OCW-RCE archive, sources such as *Kerria lacca* Kerr (lac dye), *Datisca cannabina* (bastard hemp), *Delphinium semibarbatum* L (isparak), mostly used in Oriental textiles and also identified in religious embroideries from Romanian collections, were never detected in textiles from Western Europe. *Kermes vermilio* P. (kermes), detected in precious textiles from Western Europe, was also identified in the valuable religious embroideries from Romanian collections.

The poster would like to underline how access to well organised archives of analytical data, such as that provided by CHARISMA/ARCHLAB, represents the ideal opportunity to better valorize individual results, with consequences in better integration of the local cultural heritage in a larger European context.

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DYEING PLANTS AS A SOURCE OF BEAUTIFUL COLOUR FOR KNITTED LINEN FARBICS

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ABSTRACT

The presentation deals with the research on knitted linen fabrics dyeing with natural dyes, with the emphasis on the influence of modrants on the obtained colours. The palette of colors consists not only the earth hues, but intensive and saturated colours as well. The possibilities of improving intensity and fixation of colours in knitted linen fabrics by premordating process will be presented. Such pretreatment enables obtaining the additional colour effects from dyestuff of plant origin. The results of tests have shown that some of naturally dyed linen knitted fabrics are characterized with good resistance to sweat, washing and light.

The selected dyestuffs – the source of primary colours and their shades – were used in direct dyeing, moreover the dyeing with pre-mordanting and post-mordanting techniques were conducted. Fifty different natural dyes (of plant and animal origin) were tested at Natural Dyeing Lab of INF&MP, using novel and historical techniques. The catalogue of the resulted colour samples applied on the linen knitted fabric was prepared. All samples were made according to the elaborated at INF&MP technology of natural dyeing and were tested for their resistance to sweat, washing and light. The common belief claims that colours of naturally dyed fabric are faded and not stable. However our results proved that several plant and techniques give positive results in the scope of colour resistance parameters.

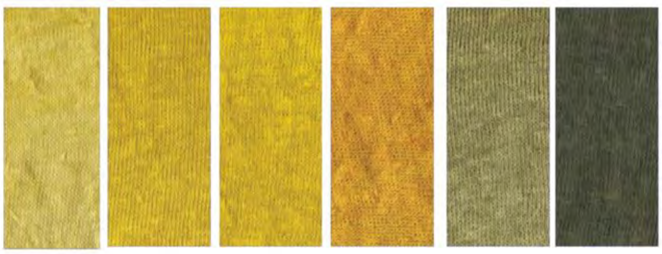

Figure 1. The samples dyed with French marigold *Tagets species* L

The wearing of garments made of knitted linen fabrics dyed with natural colorants influence in positive way the physiological comfort of human body and improve the psychical feelings. Moreover the fabrics influence positively the skin and organism due to the presence of the herbal plants extracts with antibacterial properties.

In the study the following plants were used, e.g.: French marigold *Tagetes* species L., Madder *Rubia tinctorum* L., Dyer's greenweed *Genista tintoria* L, Weld *Reseda luteola* L., Dyer's camomile *Anthemis tinctoria* L., Dyer's coreopsis *Coreopsis tinctoria* L., Coreopsis *Coreopsis grandiflora* L.**,** Woad *Isatis tinctoria* L. Indigo *Indigofera tinctoria* and others.

RESULTS AND CONCLUSIONS

- The wide palette of colours on naturally dyed linen fabrics was obtained
- The elaborated dyeing method enables to get some diversified colours and shades from the same plant
- Several samples confirmed good resistance of colours to washing, light, and sweat
- In our research we are interested in eco technology, in natural dyeing and creation of modern, ecological textile products
- The aim of the Institute's research was to create ecological clothing with the best textile, physiological, wellness and high comfort parameters
- Linen naturally dyed knitted fabrics show anti-bacterial activity, do not collect electrostatic charges, do not cause skin irritations or allergic reactions – they create the microclimate best for human skin.
- Colours of naturally dyed fabrics add to the linen fabrics new esthetics value.
- Ecological, beautiful colours of naturally dyed fabrics provide the added value, including the new esthetics one.
- Such knitted linen fabrics cretae a new source of materials for the designers of ecological apparels.

Natural dyestuffs as connection between the world of history, culture and technical applications. Promotion of historical methods by INF&MP

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Abstract

For the last ten years the research program on natural dyestuffs has been carried out in the Institute of Natural Fibres&Medicinal Plants in Poznan. The research has been based on historical sources and laboratory trials. Approximately 50 dyestuffs of plant origin were tested in this period for possible application in natural raw materials. The project is carried out by **Laboratory of Natural Dyeing** in cooperation with herbal companies. In 2003 the Experimental Farm of the Institute of Natural Fibres started a plantation of dyeing plants. The dyeing garden is supposed to be the center of experiments and training programs both presenting traditional methods of dyeing and promoting creation of totally natural fabrics.
Since 1998 the laboratory of Natural Dyeing –"Natural Art" has carried out studies linked with promotion of natural dyeing techniques.

These works have led to participation in numerous interactive events, exhibitions in museums and workshops, Fairs, Festivals of Art and Science, designed for various social groups including designers, students and children.

Fig.1 Exhibition of linen 3D fabrics and presentations of natural dyestuffs from the collection of Natural Dyeing Laboratory INF&MP in Archaeological Museum , Poznan, 2012

The workshops and exhibitions featured lectures on:

- historical dyeing techniques,
- dyeing techniques in general
- dyeing plants
- division into three colour groups: yellow, red and blue
- raw materials e.g. flax, wool and silk

The laboratory runs studies on obtaining different colours on fabrics, testing colour fastness, testing various mordants, washing, light and UV resistance.
The objective of the our activity is development of fabric patterns with ecological parameters, designing patterns for artistic and pro-healthy fabrics.
The paper presents the results of dyeing experiments on textiles like: linen, hemp, cotton and silk. The main aim of the research is to reactivate old and often forgotten dyeing methods, testing of dyes for their durability to weather factors, testing of their efficiency and developing our own dyeing technique for use on the natural fabrics and finally comparing these techniques.

Dye identification can provide information on where and how historic and archaeological textiles were made. This information, together with data from trade archives and the design and textile knowledge may determine its provenance, authenticity as well as original faded colour. One of the main subjects of the program Laboratory of Natural Dyeing is creation of a colour card for natural fibres, introduction of cultivated plants for dyeing and promotion of our result in modern textile design.

The effect of searching for colours is used in design of modern tapestries, where the main raw materials used are linen and hemp. Those materials require a different mordant preparation for using natural dyes. The natural world is an inspiration in creation of artistic tapestries and fabrics.
Interactive activities of the laboratory brought in great interest in natural dyeing techniques and multifaceted issues connected with it among scientists, artists and the industry.

SILK DYEING AND LAKE PIGMENTS OBTAINING FROM *Helichrysum arenarium* AND THEIR ANALYSIS

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ABSTRACT

Natural organic lake pigments were producted in various colours from *Helichrysum arenarium.* At the same time silk fabrics were mordanted with different mordants and dyed with same plant. $Fe(SO_4)_2.7H_2O$; $SnCl_2.2H_2O$; $KAl(SO_4)_2.12H_2O$ and $Ca(NO_3)_2$ metal compounds were used when pigments were obtaining, Silk fabrics were mordanted with different metal mordants. The fabrics were dyed with same percent *Helichrysum arenarium*. During the dyeing, dye extracts samples were taken from dyeing bath each twenty minutes. Dye extacts, dyed silk fabrics and obtained lake pigments were hydrolyzed with a hydrochloric acid/ methanol/ water (2:1:1; v/v/v) mixture. A reversed-phase high-performance liquid chromatography with diode-array detection was utilized for the identification of dyed fabrics, plant extracts and obtained lake pigments. Colouring compounds in the dye extracts, dyed fabrics and obtained lake pigments were compared. The microstructure and chemical homogeneity of obtained natural lake pigments and dyed silk fabrics were analysed by scanning electronmicroscopy equipped with energy dispersion spectroscopy. Lastly, colour measurements were taken of both dyed silk fabrics and obtained lake pigments by CIEL*a*b* spectrophotometer/colorimeter.

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Purple dyeing with strawberry tree and alkanna according to the Classical recipes: insights in the dye content of this particular vegetable purple dyeing recipe

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In the Papyrus Graecus Holmiensis 97, a prescription is given to obtain purple by the use of the natural dye source indicated by the Greek term "κόμαρι", while also the Leyden Papyrus X 89 mentions a recipe for dyeing with both alkanna (*Alkanna tinctoria* Tausch. (L.)) and ""κόμαρι". The study of the classical sources and actual knowledge of the chemical composition of dyes, combined with practical dye experiments based on the old recipes, resulted in the attribution of the term "κομαρι" to the use of the strawberry tree (*Arbutus unedo* L.). This was presented last year at the DHA 31 conference in Antwerp [1].

More insight in the dye content of these dyeings was obtained by recent analyses of the wool samples dyed with the leaves and branches or either the unripe fruit of the strawberry tree alone or in combination with alkanna. The samples were analysed with high performance liquid chromatography and photo diode array detection after soft extraction of the dyes from the fibres.
Dyeing with the leaves and young branches of strawberry tree results in a yellowish shade, while combined with alkanna, a brown colour is obtained. The unripe fruit of strawberry makes a pale pink colour while by a second dyeing with alkanna a very nice pink/purple shade was produced.
The use of the leaves/young branches of strawberry tree results in the presence of multiple flavonoids such as morin, rutin, quercetin and kampferol, while the fruit is rich in tannin, with ellagic acid is the major compound found together with minor amounts of rutin, morin and quercetin.
HPLC analysis of the combined dyeings gives the combination of the strawberry tree dye compounds with the naphthaquinone alkannin and alkannin derivatives.
Main differences in dye content between the brown colour obtained by strawberry tree leaves/branches and alkanna dyeing, and the nice pink/purple shade obtained after dyeing with strawberry fruit and alkanna, are: (1) the higher relative content of the alkanna dye compounds compared to these from strawberry in the purple sample, (2) as well as the total significant lower dye content of the latter.

The actual study aims to stress the attention to this particular dyeing procedure mentioned in Classical literature as alternative to the more known contemporary methods using molluscs, lichen dyes or madder and indigo/woad combinations, and to characterise the dye compounds, markers for identification.

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