DHA 26

26th Meeting of Dyes in History and Archaeology
Vienna - Austria
7th - 10th of November 2007

UNIVERSITY OF APPLIED ARTS VIENNA
ARTEC DEPARTMENT ARCHAEOMETRY

NATURHISTORISCHES MUSEUM

instituut collectie nederland

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ONDERZOEK CULTUREEL ERFGOED SCHAP

Dyes in History and Archaeology

Dyes in History and Archaeology (DHA), an international group of experts with multi-disciplinary background, meets every year, since 1982, to discuss chemical, analytical, biological, historical and technological aspects of natural and synthetic dyestuffs.
More information on this and preceding DHA meetings and publications can be found at http://www.chriscooksey.demon.co.uk/dha/meetings.html

26th Meeting of Dyes in History and Archaeology

The 26th Meeting of Dyes in History and Archaeology (DHA 26) takes place from the 7th - 10th of November 2007 in Vienna, Austria.

The meeting will be jointly organised by the University of Applied Arts Vienna, Department Archaeometry; the Natural History Museum Vienna, Prehistoric Department and the Netherlands Institute for Cultural Heritage, Amsterdam.

On Wednesday the 7th of November, previous to the 26th DHA Meeting, a conference on 'New strategies for natural dyestuffs analysis in art objects' is held at the University of Applied Arts Vienna. It is organized by the ORMYLIA Art Diagnosis Centre in Ormylia, Greece and the Netherlands Institute for Cultural Heritage, Amsterdam within the EC project EU-ARTECH - Access, Research and Technology for the conservation of the European Cultural Heritage.

In the evening of the 7th of November a welcome reception takes place at the University of Applied Arts Vienna including the opening of the exhibition 'Textiles intermedia' and the presentation of the book 'Natural Dyes - Sources, Tradition, Technology and Science' by Dominique Cardon.

The lecture and poster sessions will be held at the Natural History Museum Vienna, on Thursday the 8th and Friday the 9th of November 2007. Especially for the participants of the conference 'Dyed prehistoric textiles from Hallstatt' are exhibited and blue printing of the Austrian workshop Koó and the new art technique Bacteriography is demonstrated.

On Saturday the 11th of November guided tours are arranged to the Kunsthistorisches Museum Wien / Treasury and the MAK Austrian Museum of Applied Arts/Contemporary Art.

For the organizing committee
AProf. Mag. Dr. Regina Hofmann-de Keijzer
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PATRONAGE

Dr. Michael Häupl, Lord Mayor of Vienna

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CONFERENCE COMMITTEE

Dr. Gerald Bast, Rector of the University of Applied Arts Vienna
Univ.-Prof. Dr. Bernd Lötsch, General Director of the Natural History Museum Vienna
Henriëtte van der Linden, Director of the Netherlands Institute for Cultural Heritage, Amsterdam

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ORGANIZING COMMITTEE

AProf. Mag. Dr. Regina Hofmann-de Keijzer, University of Applied Arts Vienna
Hans Reschreiter, Natural History Museum Vienna
Dr. Ing. Maarten R. van Bommel, Netherlands Institute for Cultural Heritage, Amsterdam
Ing. Matthijs de Keijzer, Netherlands Institute for Cultural Heritage, Amsterdam

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CO-OPERATING INSTITUTIONS

University of Applied Arts Vienna, Institute of Art and Technology
Head: o. Univ-Prof. Dr. Alfred Vendl

University of Applied Arts Vienna, Institute of Art and Technology,
Department of Archaeometry
Head: ao. Univ.-Prof. Dipl.-Ing. Dr. Bernhard Pichler

Natural History Museum Vienna, Prehistoric Department
Head: Dr. Anton Kern

Netherlands Institute for Cultural Heritage, Research Department
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Head: Caspar M. Laffree, Deputy Director

University of Applied Arts Vienna,
Department of Textiles - Free, Applied and Experimental Artistic Design
Head: Univ.-Prof. Mag. art. Barbara Putz-Plecko, Deputy Rector

University of Applied Arts Vienna,
Institute of Fine and Media Arts, Department of Graphics
o. Univ.-Prof. Mag. art. Sigbert Schenk, Chairman of the Senate

University of Applied Arts Vienna, Public Relations
Mag. Anja Seipenbusch-Hufschmied

University of Applied Arts Vienna, Event Support
Christian Schneider

Natural History Museum Vienna, PR & Marketing
Ingrid Viehberger

EXHIBITIONS - FILM - BACTERIOGRAPHY - VISITS

UNIVERSITY OF APPLIED ARTS VIENNA
Exhibition Centre Heiligenkreuzerhof
Schönlaterngasse 5 and Grashofgasse 3, 1010 Vienna

EXHIBITION - TEXTILES INTERMEDIA
Projects of the Textile Department
Head: Univ.-Prof. Mag. art. Barbara Putz-Plecko

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NATURAL HISTORY MUSEUM VIENNA
Burgring 7, 1010 Vienna

EXHIBITION - DYED PREHISTORIC TEXTILES FROM HALLSTATT
by Mag. Dr. Karina Grömer, Hans Reschreiter and
AProf. Mag. Dr. Regina Hofmann-de Keijzer

HERSTELLUNG VON BLAUDRUCK - PRODUCTION OF BLUE RESIST PRINTS
Film in memoriam Josef Koó
Scientific author: Dr. Iris Barbara Graefe

PRESENTATION OF BLUE RESIST PRINTS
Joseph Koó

BACTERIOGRAPHY - MULTIORGANISMIC ART PAINTING
Erich Schopf

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KUNSTHISTORISCHES MUSEUM VIENNA, TREASURY
Hofburg, Schweizerhof, 1010 Vienna

THE CORONATION ROBES
Guided Tour
Dr. Katja Schmitz-von Ledebur
Dr. Ing. Maarten R. van Bommel

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MAK AUSTRIAN MUSEUM OF APPLIED ARTS / CONTEMPORARY ART
Stubenring 5, 1010 Vienna

THE TEXTILE COLLECTIONS OF THE MAK
Guided Tour
Dr. Angela Völker

26th Meeting of Dyes in History and Archaeology
Vienna, 7th - 10th of November 2007

di:'angewandte
UNIVERSITY OF APPLIED ARTS VIENNA
ARTEC DEPARTMENT ARCHAEOMETRY

NATURHISTORISCHES MUSEUM

instituut collectie nederland

PROGRAMME

Wednesday, 7th of November 2007

UNIVERSITY OF APPLIED ARTS VIENNA
EXHIBITION CENTRE HEILIGENKREUZER HOF
Entrance: Schönlaterngasse 5 and Grashofgasse 3, 1010 Vienna
House number 8, 1st floor and house number 7, Sala terrena

09:30 - 17:00 **EU-ARTECH Meeting**
New strategies for natural dyestuffs analysis in art objects

15:00 - 18:00 **Registration of the DHA participants**

18:00 **Welcome reception for the DHA participants**
Part 1: Drinks and snacks

19:00 **Part 2: Welcoming speeches**
Dr. Gerald Bast, Rector of the University of Applied Arts Vienna
AProf. Dr. Regina Hofmann-de Keijzer, DHA organizing committee

Book presentation
Dr. Jan Wouters and **James Black**
Natural Dyes - Sources, Tradition, Technology and Science
by **Dr. Dominique Cardon**

19:30 - 21:00 **Part 3: Exhibition 'Textiles intermedia'**

Opening of the exhibition 'Textiles intermedia'
Univ.-Prof. Mag. art. Barbara Putz-Plecko
Deputy Rector of the University of Applied Arts Vienna

20:00 - 21:00 **Part 4: Book autographing**
Natural Dyes - Sources, Tradition, Technology and Science
by **Dr. Dominique Cardon**

Thursday, 8th and Friday, 9th of November 2007

NATURAL HISTORY MUSEUM VIENNA
Burgring 7, 1010 Vienna

Thursday, 8th of November 2007

08:30 - 09:30	**Registration and coffee:** Entrance Hall and room 15
08:30 - 09:30	**Affixing of the posters:** room 15
09:30 - 10:00	**Welcoming speeches:** lecture room, Kinosaal Representative of the City of Vienna **Univ.-Prof. Dr. Bernd Lötsch**, General Director of the Natural History Museum Vienna **Dr. Gerald Bast**, Rector of the University of Applied Arts Vienna **Henriëtte van der Linden**, Director of the Netherlands Institute for Cultural Heritage, Amsterdam
10:00 - 12:00	**Session 1:** lecture room, Kinosaal **Chair: Maarten van Bommel**
10:00 - 10:20	**Regina Hofmann-de Keijzer, Karina Grömer, Maarten van Bommel, Ineke Joosten, Hans Reschreiter and Helga Mautendorfer** *Hallstatt textiles – the oldest dyed textiles found in Austria*
10:20 - 10:40	**Maria Jaõa Melo, Ana Claro, Isa Rodrigues, Meredith Montague and Richard Newman** *The color of Andean textiles from the MFA collection*
10:40 - 11:00	**Ilaria Degano and Maria Perla Colombini** *Dyestuff identification in pre-Peruvian archaeological textiles*
11:00 - 11:20	**Fanny Bessard** *Medieval dyers' workshops in the Hippodrome of Jerash (Jordan)*
11:20 - 11:40	**Katarzyna Lech, Maria Puchalska, Elżbieta Rosłoniec and Maciej Jarosz** *Mass spectrometric and liquid chromatographic investigation of historical fabrics from the collection of the National Museum in Warsaw*
11:40 - 12:00	**Discussion**
12:00 - 13:30	**Lunch:** room 15 **Posters and film 'In memoriam Josef Koó':** room 15 **Presentation of blue resist prints by Joseph Koó:** room 15 **Bacteriography - multiorganismic art painting:** room 15 **Exhibition 'Dyed prehistoric textiles from Hallstatt':** room 14

13:30 - 15:00	**<u>Session 2</u>:** lecture room, Kinosaal **Chair: Maria Jaõa Melo**
13:30 - 13:50	**Zvi Koren** *Color analyses of some unusual textiles from ancient Israel*
13:50 - 14:10	**Christoph Krekel, Stella Eichner and Karin Geißinger** *De edera et lacca* **–** *Identification of a medieval colorant made from Ivy*
14.10 - 14:30	**Masanori Sato** *Identification of vegetable blue dyestuff "Trichotomine*"
14:30 - 14:50	**Gundula Voss** *Preparation and properties of polymers with indigo units*
14:50 - 15:00	**Discussion**
15:00 - 15:30	**Tea and coffee break:** room 15 **Posters and film 'In memoriam Josef Koó':** room 15 **Presentation of blue resist prints by Joseph Koó:** room 15 **Exhibition 'Dyed prehistoric textiles from Hallstatt':** room 14
15:30 - 17:45	**<u>Session 3</u>:** lecture room, Kinosaal **Chair: Regina Hofmann-de Keijzer**
15:30 - 15:50	**John Edmonds** *Imperial Purple, dye and pigment*
15:50 - 16:10	**Irving Ziderman and Liraz Larush-Asraf** *Biochemistry of Murex trunculus dyes*
16:10 - 16:30	**Karen Diadick Casselman and Takako Terada** *Murex and Orchil methods and technique: part 1*
16:30 - 16:50	**Bernard Verhille** *HESBAYE and tinctorial plants (1200-1400)*
16:50 - 17:10	**Riikka Räisänen** *"Let us go for blue, sisters, for madder, brides!"* **–** *Dyes and dyeing in the Finnish Karelia*
17:10 - 17:30	**Brian Davies** *William Morris and the discharge of indigo*
17:30 - 17:45	**Discussion**
19:30 - 24:00	**Gala dinner** Hall under the Dome of the Natural History Museum Vienna. Excursion to enjoy the view on Vienna from the museum's rooftop.

Friday, 9th of November 2007

09:00	**The Natural History Museum Vienna opens**
09:15 - 10:45	**Session 4:** lecture room, Kinosaal **Chair: Jan Wouters**
09:15 - 09:35	**Chris Cooksey, Ioannis Karapanagiotis, Sophia Sotiropoulou, Evangelia Varella, Euphoria Tsatsaroni, Friedrich Sauter, Leopold Puchinger, Ziad Al-Saad, Omar Abdel-Kareem, Rachid Benslimane, Noureddine Chenfour, Emre Dölen, Recep Karadag, Georg Kremer, Uta Williams, Mahmoud Alawi and Mohammad Mubarak** *Investigation, revival and optimisation of traditional Mediterranean colouring technology for the conservation of the cultural heritage*
09:35 - 09:55	**Omar Abdel-Kareem and Ziad Al-Saad** *Preparing of artificial aged dyed textile samples simulated to museum dyed textiles*
09:55 - 10:15	**Leopold Puchinger, Friedrich Sauter and Evangelia Varella** *The effect of some mordant dyes on the fibre net of textiles*
10:15 - 10:35	**Recep Karadag, Emre Dolen and Turkan Yurdun** *Identification of dyestuffs in some 17th century silk skullcaps by liquid chromatography with diode array detection in the Topkapi Palace Museum collection*
10:35 - 10:45	**Discussion**
10:45 - 11:15	**Coffee and tea break:** room 15 **Posters and film 'In memoriam Josef Koó':** room 15 **Presentation of blue resist prints by Joseph Koó:** room 15 **Exhibition 'Dyed prehistoric textiles from Hallstatt':** room 14
11:15 - 12:30	**Session 5:** lecture room, Kinosaal **Chair: Christopher Cooksey**
11:15 - 11:35	**Micaella Sousa, Maria Jaõa Melo, A. J. Parola, P. J. T. Morris, H. S. Rzepa and J. Seixas de Melo** *More secrets of Perkin's Mauveine dye revealed*
11:35 - 11:55	**Maarten van Bommel, Ineke Joosten, Han Neevel, Jaap Boonstra and Paul Bruys** *Faded flowers, analysis of modern marquetry applied on 17th and 18th century Dutch furniture*
11:55 - 12:15	**Matthijs de Keijzer, Maarten van Bommel and Regina Hofmann-de Keijzer** *The early synthetic organic dyestuffs: The Yellows*
12:15 - 12:30	**Discussion**

12:30 - 13:30	**Lunch:** room 15 **Posters and film 'In memoriam Josef Koó':** room 15 **Presentation of blue resist prints by Joseph Koó:** room 15 **Bacteriography - multiorganismic art painting:** room 15 **Exhibition 'Dyed prehistoric textiles from Hallstatt':** room 14
13:30 - 15:00	**Session 6:** lecture room, Kinosaal **Chair: Cecily Grzywacz**
13:30 - 13:50	**Cindy Connelly Ryan and Mary Baker** *Determining display conditions for the Waldseemüller world map: lightfastness testing in an anoxic environment*
13:50 - 14.10	**Han Neevel** *Optimisation of the micro-destructive light fastness tester, the "µ-Fado"*
14:10 - 14:30	**Barbara Błyskal** *Indigo dyeing and bio-deterioration of a woollen textile*
14:30 - 14.50	**Yassin Zidan, Harby Ezz Eldeen Hassan and Kh. El-Nagar** Aging behavior of silk dyed fabric with safflower dye
14:50 - 15:00	**Discussion**
15: 00 - 15:30	**Tea and coffee break:** room 15 **Posters and film 'In memoriam Josef Koó':** room 15 **Presentation of blue resist prints by Joseph Koó:** room 15 **Exhibition 'Dyed prehistoric textiles from Hallstatt':** room 14
15:30 - 17:30	**Session 7:** lecture room, Kinosaal **Chair: Jo Kirby**
15:30 - 15:50	**Anne-Marei Hacke and Chris Carr** *Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) analysis of natural dyestuffs*
15:50 - 16:10	**Richard Laursen and Xian Zhang** *On the detection and significance of glycosides in natural dyes*
16:10 - 16:30	**Nobuko Shibayama, Elena Phipps, Lucy Commoner and Mark Wypyski** *Investigation of dyed rabbit hair in a 16th-17th century colonial Latin American textile*
16:30 - 16:50	**Heinrich Piening and Peter Kopp** *A renaissance colour plate revealed. Lost colours of the Renaissance - unexpected results from a masterpiece of Renaissance marquetry*
16:50 - 17:10	**Yoshiko Sasaki and Ken Sasaki** *Non-destructive dye analysis for Japanese historical textiles at 17th C*
17:10 - 17:30	**Discussion and closing session**

18:30	**Viennese Heurige: Departure of the busses** Natural History Museum Vienna Burgring 7, 1010 Vienna
19:00	**Arrival at the Viennese Heurige** Peter Bernreiter, Amtsstraße 24-26, 1210 Vienna
22:30	**Departure of the 1st bus** to the centre of Vienna
23:00	**Departure of the 2nd bus** to the centre of Vienna

<u>Saturday, 10th of November 2007</u>

POST - CONFERENCE VISITS TO MUSEUMS

1st group 10:00 - 11:00 **2nd group** 11:00 - 12:00	**The Coronation Robes** Kunsthistorisches Museum Vienna, Treasury Hofburg, Schweizerhof, 1010 Vienna Guided tour by **Dr. Katja Schmitz-von Ledebur**, Kunsthistorisches Museum Vienna, Treasury and **Dr. Ing. Maarten R. van Bommel**, Netherlands Institute for Cultural Heritage, Amsterdam **Limitation to 25 participants (each group)**
1st group 14:00 - 15:00 **2nd group** 15:00 - 16:00	**The Textile Collections of the MAK** MAK Austrian Museum of Applied Arts / Contemporary Art Stubenring 5, 1010 Vienna Guided tour by **Dr. Angela Völker**, MAK Austrian Museum of Applied Arts / Contemporary Art **Limitation to 25 participants (each group)**

<u>Thursday, 8th - Sunday, 11th of November 2007</u>

Natural History Museum Vienna
Burgring 7, 1010 Vienna

Free entrance for the DHA participants

<u>Saturday, 10th of November 2007</u>

MAK Austrian Museum of Applied Arts / Contemporary Art
Stubenring 5, 1010 Vienna

Free entrance

Hallstatt textiles – the oldest dyed textiles found in Austria

Regina Hofmann-de Keijzer[1], Karina Grömer[2], Maarten van Bommel[3], Ineke Joosten[3], Hans Reschreiter[4] and Helga Mautendorfer[5]

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Abstract

In 1997 the Hallstatt region in Upper Austria was granted UNESCO World Heritage status in recognition of the importance of the archaeological sites, together with the distinctive flora and fauna. Hallstatt is famous for its salt production already in prehistoric times. According to radiocarbon dating, intensive mining for rock salt began at the latest in the Bronze Age (15th century BC). The wealth brought by the salt trade is evident in the grave goods found in the cemetery, which gave its name to an entire phase of prehistoric European culture - the Hallstatt Period (Iron Age, 800-400 BC). Due to the impregnation by the salt, the constant climate in the mine, protection from light and low temperature, organic materials as textiles, leather, fur and wood survived more than 3000 years. From 1849 till 2006 more than 550 textile fragments, mainly consisting of wool, have been found in the Bronze and Iron Age salt mines. They feature a wide variety of textures, patterns, seams, hems, stitches and colours.

The results of the dyestuff analysis on Iron Age textile fragments were discussed during the 23th Annual Meeting of Dyes in History and Archaeology in Montpellier (2004), the Symposium on Hallstatt Textiles in Hallstatt (2004)[1] and the 15th Triennial Meeting of ICOM-CC in The Hague (2005).[2]

To investigate the colours of Bronze Age fragments high performance liquid chromatography combined with photo diode array detection was used for the identification of the dyestuffs and SEM-EDS for the analysis of chemical elements. These analyses showed that in the Hallstatt textiles dyeing processes can be identified since the Bronze Age. Vat dyeing was known as well as dyeing with tannins and yellow and red mordant dyes. The dyes found in the Bronze Age fragments will be compared to those from the later Hallstatt period. Differences between the Bronze and Iron Age textile techniques can be explained by the technological improvement that obviously took place between these periods or by different functions. Relations between the dyeing of the textiles, the spinning, weaving and sewing techniques and the possibly former use of these textiles will be discussed as well as the question why many of the fragments show an olive-green colour.

References

1 HOFMANN - DE KEIJZER, R., VAN BOMMEL, M.R., JOOSTEN, I.: *Dyestuff and element analysis on textiles from the prehistoric salt mine of Hallstatt*. In: Peter Bichler, Karina Grömer, Regina Hofmann-de Keijzer, Anton Kern und Hans Reschreiter (Eds.): *Hallstatt Textiles - Technical Analysis, Scientific Investigation and Experiment on Iron Age Textiles*. BAR - British Archaeological Reports, International Series 1351, Oxford, Archaeopress, 2005, pp. 55-72.
2 HOFMANN - DE KEIJZER, R., VAN BOMMEL, M.R., JOOSTEN, I., RESCHREITER, H., GRÖMER, K., MAUTENDORFER, H., HARTL., A., MORELLI, M.: *Ancient textiles - recent knowledge. A multidisciplinary research project on textile fragments from the prehistoric salt mine of Hallstatt*. ICOM-CC 15th Triennial Meeting, The Hague, 2005, London, James & James, pp. 920-926.

The colour of Andean textiles from the *MFA* collection

Maria Jaõa Melo[1,2,3], Ana Claro[2,3], Isa Rodrigues[3], Meredith Montague[1] and Richard Newman[1]

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Abstract

Textiles and more specifically cloth production was central to Andean culture [1]. The role played by fibers was unique when compared to other civilizations, engineering problems were solved with fiber technology as in Inca suspension bridges, community ties were woven with the help of textiles, and the dramatic events of life, such as birth and dead, were celebrated with them; as emphasized by Lechtman [1] "The very technology of cloth production was central to (…) making sense of the world; so were the textiles themselves." As a cultural and historic record, Andean textiles "form the longest continuous textile record in world history" [2] and in the archeological sites of the Andean coast, namely of Paracas, characterized for their aridity, a surprisingly large number of fabrics were preserved, spanning from about 3000 B.C. to the present.

The superb colors of ancient Andean textiles from the *MFA* collection will be discussed, and the dyes used for their production characterized together with the mordant ions necessary to complex them to the fiber. The use of *Relbunium* plants and cochineal insects to obtain red colors and shades will be compared to the results published by Wouters and Rosario-Chirinos [3]. The dyes were extracted using recently developed mild methods [4,5] and characterized by HPLC coupled with diode array UV-Vis detector (HPLC-DAD) and MS (HPLC-DAD-MS). Moreover the results of the application of microfluorescence spectroscopy for the detection of purpurin will be also presented.

References

[1] H. Lechtman, "The Andean world" in Andean Art at Dumbarton oaks", E. H. Boone *ed.*, Dumbarton Oaks Research Library & Collection,1996.
[2] "To Weave for the sun: ancient Andean textiles in the Museum of Fine Arts, Boston", R. Stone-Miller *ed.,* Thames and Hudson, 1992.
[3] J. Wouters, N. Rosario-Chirinos, *J. Am. Inst. Cons*., 31 (1992) 237-255.
[4] *a)* X. Zhang, R. Boytner, J. L. Cabrera, R. Laursen, *Anal. Chem*., 79 (2007) 1575-1582; *b)* Zhang, X., Laursen, R. A., *Anal. Chem*. 77 (2005) 2022-2025.
[5] Guinot, P., Andary, C., "Molecules involved in the dyeing process with flavonoids", *Dyes in History and Archaeology* **25** (2006).

Dyestuff identification in pre-Peruvian archaeological textiles

Ilaria Degano and Maria Perla Colombini

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Abstract

Identification and characterisation of organic materials in archaeological objects, such as natural dyes, is a fascinating field of modern archaeology and archaeometry. Studying these materials allows art historians as well as anthropologists and archaeologists to obtain information on the original appearance of handiworks, on their function and use. The study of funerary objects may help to characterise the context of the burial by giving important insights not only on the social rank of the dead, but also on cultural and religious traditions in general. Aspects of economic, social and cultural history can be revealed through the characterisation of the dyes used for the textiles: even if direct evidence of colouration on textile artefacts is not readily visible in most cases due to degradation, charring, mineralization, etc, the identification of the colouring matters employed to dye the textiles used in mortuary contexts can provide tangible evidence of past life ways. Recognising colouring matters in old textiles is difficult not only due to the poor light fastness of some molecular markers and to the complexity of the degradation processes, which are not yet completely unveiled, but also to the wide range of substances used for dyeing purposes (the main chromophores in natural dyes are flavonoids, anthraquinones, tannins and indigoids, but carotenoids and anthocyanines were employed as well).

Several physical and chemical methodologies can be used for the characterisation of organic dyes. Particularly, this paper deals with the application of micro destructive chromatographic and mass spectrometric techniques, namely HPLC-UV/Vis, GC-MS and DE-MS, to determine flavonoids, anthraquinones, tannins and indigoid components in fibres. The method allows the easy identification of a dyestuff by the detection of the molecular markers surviving in old textiles and reproduced in fresh materials under accelerated ageing. A number of textile samples were collected from a set of Andean mummies conserved at the Musei Civici di Reggio Emilia, Italy, collected in 1884 from the necropolis of Ancòn, 30 Km North of Lima. The anthropological study of the mummies was really challenging due to the lack of grave goods; some coloured yarns and textile fragments were collected from the cerimonial clothes and subjected to chemical analysis in order to characterise the dyeing palette employed in the funerary site. Moreover, some samples consisting of red-coloured hair fibres belonging to three different mummies were examined for revealing the nature of the dye employed. The most significant results obtained by the analysis of selected samples will be presented.

Medieval dyers' workshops in the Hippodrome of Jerash (Jordan)

Fanny Bessard

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Abstract

I will present at the « Dyes in History and Archaeology » conference the findings of the excavations that I carried out last April in the Dyers' workshops of the hippodrome of Jerash (Jordan), along with the architect O. Callot (CNRS) and ©Abd Al-Majîd Mujalli, the president of the Jerash Archaeological Project. The dyers' workshops were never studied in depth before. They were cursorily cleared of the rubble in the 1980's and 1990's by the archaeologists I. Kehrberg and A. Ostrasz[1].

The dyers' workshops, situated in chambers W6, W9, W11, W14, and W15 of the hippodrome, have the main characteristics of the Byzantine dyers' workshops found in nearby Gaza[2] and the *Macellum* of Jerash[3]. They all have basins and vats which were used to clean fibres and fabrics of sandstone, greasy depositis or dye resistant pectins and for dyeing purposes. Since there is no hearth we can assume that the dyes used must have been vat dyes, in particular indigo, traces of which were recovered. Moreover, according to ceramic and numismatic evidence, the dyers' workshops of the hippodrome of Jerash can be dated to the first half of the 8th century A.D., that is during the first Arabo-Muslim dynasty, called the Umayyads. Given the high similarity of the five dyeing workshops in the hippodrome of Jerash, it is undoubtless that they were the effect of a coordinated action by the state or by local authorities, rather than being merely the result of individual undertakings. Thus, the analysis of the remains of the hippodrome's dyeing workshops, in the light of narrative sources, yields new and worthy information about the artisanal techniques used in textiles' dyeing in the East. In addition, the workshops testify to the thriving activity of an old Byzantine town like Jerash, even after the muslim conquest of the Near-East, and up to the earthquake of 131 H./748 A.D.[4].

References

1 KEHRBERG (I.) & OSTRASZ (A.), « A History of Occupational Changes at the Site of the Hippodrome of Gerasa », *SHAJ*, 6, 1997, p. 167-173.
2 OVADIAH (A.), « Excavations in the Area of the Ancient Synagogue at Gaza (Preliminary Report) », *Israel Exploration Journal*, 19/4, 1969, p. 193-198.
3 MARTIN-BUENO (M.) & USCATESCU (A.), « The Macellum of Gerasa (Jerash, Jordan): From a Market Place to an Industrial Area », *BASOR*, 307, 1997, p. 67-88.
4 RUSSEL (K. W.), « The Earthquake Chonology of Palestine and Northwest Arabia from the 2nd through the Mid-8th Century A. D. », *BASOR*, 260, 1985, p. 37-59.

Mass spectrometric and liquid chromatographic investigation of historical fabrics from the collection of the National Museum in Warsaw

Katarzyna Lech[1], Maria Puchalska[2], Elżbieta Rosłoniec[3] and Maciej Jarosz[1]

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Abstract

In conservation of historical textiles dyed with natural dyestuffs, preliminary chemical examination plays very important role. The amount of a sample taken from a fabric has to be as small as possible. It creates a serious challenge for analysts. For such analyses, sensitive and selective methods are necessary, especially for identification of substances responsible for colour of textiles, both organic – colouring matters and inorganic – mordanting ions. Moreover, many textiles are decorated by metal wefts and information dealing to composition of ornamental threads could be essential for conservators.

Identification of individual dyestuffs usually necessitates use of instrumental analytical techniques. Most of dyestuffs contain more than one colouring matter, and methods used for their characterization must include separation steps. When high performance liquid chromatography, HPLC, was used for the detection of separated compounds mainly UV-VIS spectrophotometry was recommended. However, new possibilities are offered by mass spectrometry providing information dealing to structure of each colour component of natural dyestuff.

For the analysis of historical fabrics, the original HPLC-UV-VIS-ESI MS method has been developed. It allows to identify colour compounds of various chemical origins: anthraquinones, flavonoids or indigoids. Metal threads were analysed using scanning electron microscopy (SEM-EDS). The obtained results were confirmed by inductively coupled plasma mass spectrometry (ICP MS).

Two fabrics from the collection of the National Museum in Warsaw (Poland) were examined. Both have originated in 14^{th}-16^{th} centuries and have been richly ornamented by metal threads and braids. The results obtained by HPLC–UV-VIS–ESI MS method allowed to learn that they were dyed with different dyestuffs. The colouring matters in red threads were identified in one of them as carminic acid and in the second one – as alizarin and purpurin. In both textiles in blue threads indigotin was found. Analysis performed by ICP MS allowed to recognize nature of mordants used for the dyeing. Composition of metal wefts was evaluated by SEM-EDS and confirmed by ICP MS. The obtained results can help to verify hypothesis concerning origin of both examined textiles.

Colour analyses of some unusual textiles from ancient Israel

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Abstract

After more than a decade of analyses of archaeological textiles excavated from ancient Israel and environs, an amazing rainbow of colours has been discovered on the dyeings. The know-how associated with the chemical and technological advancements of the ancient dyers and weavers humbles those of us moderns involved in modern chemical research.

As many of these textiles were excavated in the Judean Desert outside of Jerusalem, the dry climatic conditions there have shielded the organic artefacts from detrimental weathering effects over thousands of years. Many of these dyeings are as vibrant today as they were when first created, so much so, that they look like they were dyed only yesterday instead of a few millennia ago.

The talk will discuss some of the more unusual textile dyeings that were analyzed by this author. These historically important dyeings represent rare dyes, interesting dye combinations, and (to the author’s knowledge) the oldest dyeing yet discovered. The textiles that will be discussed include (in reverse chronological order):

Byzantine Blue of 7th century CE ’En Boqeq on the Dead Sea
The Dual Reds of Byzantine ’En Boqeq: Madder and Cochineal
The Bar-Kokhba Rebels’ 2nd century CE Purple Fleece at the Cave of Letters
Masada Zealots’ 1st century CE Madder Reds and Purples
Nabatean Kermes of 2.000-year old ’En Rahel
Royal Herodian Purple at 1st century BCE Masada
Beni Hasan 4.000-year old Pharaonic Blues
6.000-Year Old Cave of the Warrior/Hunter Burial Shroud

De edera et lacca – Identification of a medieval colorant made from Ivy

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Abstract

In a few medieval manuscripts the production of a red *lacca* is described, a gum or a resin supposed to have been extracted from *hedera* (ivy) by piercing the stem of the plant in March. By cooking in water or urine, the gum becomes blood red and could directly be used to dye leather or parchment without using a binder or a metal salt (*parcia* colour). If baking a mixture with flour and vinegar or urine, a red, quite costly colorant is got which was used by illuminators. This colour was called *sinopis de mellana*, a name presumably deriving from Sinope earth mentioned by Plini. In addition, in German apothecaries *Taxae* from the 16th to 19th centuries and in other trade sources a gum from ivy (*gummi hedera*) can be found, perhaps used for pharmaceutical purposes.

Since the times of Eastlake and Merrifield these recipes are well known and several authors describe their fruitless attempts “sticking augurs in the spring time into the stems of everything that might have been this *hedera*”.[1] Since the recipes obviously do not work three solutions for this problem have been suggested: 1. The resinous juice appears in the warm countries only (Merrifield) 2. The plant name is fault (Thompson) 3. The red *lacca* is not produced from any gum but from the blue ivy berries that appear in March, too (Brachert).

In 2005-2007 a red, brittle resinous product was found at old injuries on stems of strong ivy plants (*Hedera helix* L.) in various parks and gardens in Stuttgart. This resin is insoluble in every organic solvent, in water, in acids and in leaches. As a similar product is described in some trade sources (e.g. Pomet) and old encyclopaedia (e.g. Krünitz), it is most likely that the resin is to be identified as *Gummi hedera* from the *Taxae* but not as the dye from the recipes. Cutting the stems of the plants where *Gummi hedera* was found in the month of March, a pale opaque juice exudes which becomes more and more thick and reddish coloured when left at the air. As main component *falcarinole* (1,9-heptadecadien-4,6-diin-3-ole) was identified by GC/MS, NMR and FTIR. This compound polymerises at air. Finally the red *Gummi hedera* is got. The red colorant could not be extracted from the polymer.

Cooking it with water or urine, the secretion of the ivy stems becomes orange coloured and thicker. It is easy to paint with this product directly on leather or parchment, where it forms a brownish orange and insoluble coating. However, if not cooked long enough, an oily court is formed around the paint. While the colorant is easy to handle, stable against water and mechanical abrasion as well as completely flexible, the *parcia* colour is perfectly suited for dyeing leathers like for gloves or covers of books, as it is mentioned in the medieval recipes. Baking the secretion of ivy together with flour and urine or vinegar forms a reddish brown crust which reminds of dried blood. Painting with this product together with gum arabic as binder, a pale orange paint layer is formed which might be taken for yellow ochre on first sight. Although this colorant is not very attractive, it is most likely that it is the *sinopis de mellana* from the recipes.

Reference

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Identification of vegetable blue dyestuff “Trichotomine”

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Abstract

The blue dyestuff Trichotomine is extracted from the blue seed of *Clerodendrum trichotomum* (family: Verbenacce, genus: *Clerodendrum*, spece: *C. trichotomum*). This plant is rather popular in Japan, China and Korea. In ancient Japan, the name of *Clerodendrum trichotomum*” (called “Kusagi” in Japanese, literally means “Bad Smell Tree”) was first cited in “Engisiki” of 10th century A.D. Since then, “Kusagi” has been used as a dyestuff for dyeing “Asagiiro” (light-blue indigo-like color). However, it is needless to say that the most important dyestuff for blue color is indigo throughout the world. In Japan, no detailed researchs on “Kusagi” or dyestuff "Trichotomine” has been performed until now. The molecular structure of Trichotomine was however analyzed about twenty years ago by Japanese researcher Y. Hirata and his collaborators using x-ray crystallographic analysis.[1]

As for archaeological textile fabrics in Japan, there was no clear evidence for the existence of textile fabrics dyed with Trichotomine until now. We are intended to study the spectroscopic characteristics of Trichotomine solution and of silk fabrics dyed with Trichotomine.

Trichotomine solution was prepared by dissolving crashed seeds of “Kusagi” in pure water or in methanol. Visible transmission spectrum showed absorption maxima at 661 nm and 611 nm. The surface reflectance spectrum of silk fabrics dyed with Trichotomine showed absorption maxima at 630 nm and 680 nm. The fluorescence spectrum of Trichotomine aqueous solution was measured by three-dimensional fluorescence spectrophotometer. Obtained contour map showed the maximum emission intensity at Ex.354 nm and Em.444 nm. These results are not able to directly compare with that of Indigo, because Indigo is not soluble in polar solvent like water or methanol. However, there is some fundamental difference in chemical characteristics between Trichotomine and Indigo. Trichtomine has two absorption peaks in visible region, whereas Indigo shows one absorption peak. Both dyestuffs show similar fluorescence contour. However, the emission maximum of “Kusagi” in aqueous solution is at a little longer wavelength compared with that of Indigo.

Among our collection of excavated textile fragments, there are a few samples suspected as Trichotomine dyeing. We are continuing the study to find clear spectroscopic evidence for the identification of Trichotomine used for dyeing excavated historic textile fragments.

Reference

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Preparation and properties of polymers with indigo units

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Abstract

The blue natural dye indigo 1 was used by humans for thousands of years for couloring fabric and other materials. Indigo and other compounds (so called vat dyes) are applied to fabric in their water soluble, reduced form (vat or leuco form), and then oxidized to the insoluble dye stuffs. We have prepared and investigated two polymers of the basic molecule 1: the 5,5'-polyindigo 2 and another polymer 3, bridged in 5,5'-positions by methylene groups. Both compounds 2 [1] and 3 [2] are vat dyes too. They have been synthesized more than 100 years ago without recognizing their polymeric structure.
The traditional route of obtaining monomeric indigo 1 is the oxidation of indoxyl in an alkaline solution with air. We used the same approach, but starting with 5,5'-bridged bis-indoxyl derivatives. Using diluted solutions and ethanol as co-solvent, the alkali was added sequentially in small aliquots - a prerequisite to control polymerization towards long, reproducible chains. Interestingly, the final reaction mixtures were clear solutions without the expected precipitates of the indigo polymers. From these alkaline solutions (green for 2 and blue for 3) the polymers finally were precipitated with acids.

In present times the polymers 2 and 3 have drawn attention due to their properties as so-called functional dyes with other applications than for colouring: For example, 2 has semi-conducting properties [3], and 3 was claimed to be the first pure organic ferromagnetic compound [4].

It is generally accepted that the building blocks of 2 and 3 have indigo structure [3,4]. However, investigations on chemical and physical characteristics of the macromolecules were frustrated by difficulties in obtaining reproducible and well-defined products. Typically, the syntheses of the polymers did result in non-homogenous mixtures, and poor solubility in a number of solvents did complicate sufficient purification and investigation of certain properties. The IR spectra suggest, that the polymers are not constructed merely by the repetition of conventional coplanar trans-indigo units, they point to additional hydrogen bonds and irregular fragments. Little is known about the real structure of the indigo building blocks within the macromolecules.

We set out to synthesize pure polymers 2 and 3 with reproducible and defined structures and chain length. The goal was to elucidate the real constitution of the indigo units within the polymeric chains, to study the properties of the polymers using spectroscopic and other physical methods, and to determine their molecular masses. We compared the products 2 and 3 under equitable conditions to come to conclusions by inference. The molecular weight of the polymers was established. The structures were clarified and the ferromagnetism of 3 was confirmed.

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Imperial Purple, dye and pigment

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Abstract

Imperial purple came in two forms like indigo, an insoluble pigment or a soluble dye. Both had their applications in the past. Only the dye presented technical difficulty which restricted the art to a limited number of skilled dyers. The sack of Constantinople in 1453 marked the end of murex purple in all its forms. This paper addresses the issue how and why this technology ceased so completely including its use for religious or profane purposes. Only now with the aid of modern science can we resurrect the technology.

Biochemistry of *Murex trunculus* dyes

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Abstract

The ancient craft of purple dyeing with Mediterranean shellfish has been re-established in Israel for textiles and in France for painting, using the banded dye-murex *Murex trunculus* [*M.tr.*].

All the other species of purple snails give a single colour - Tyrian Purple, which is essentially the dyestuff 6,6'-dibromoindigotin [DBI], and they require initial exposure to sunlight for the dye formation reaction to occur. In contrast to those species, *M.tr.* is unique in that individuals from the same catch typically yield different colours that can be shades of purple, violet or blue; also, exposure to sunlight is not necessary. Its unique ability to give a bluish shade of purple indicates that *M.tr.* was the source of *Tekhelet* violet ["biblical Blue"], the classical Hyacinthine Purple.

The different colours obtained from *M.tr.* specimens are a reflection of the dyestuff composition, which is essentially a mixture of three colorants in different proportions: indigotin [a blue], DBI [purple] and monobromo-indigotin [MBI]. These three colorants are formed in chemical reactions among two colourless natural precursor chemicals, respectively based upon indoxyl and bromo-indoxyl.

Previous studies have attempted to attribute the colour variability of *M.tr.* dyeings to a supposed difference in the natural distribution of the indoxyl and bromo-indoxyl precursors between the male and female snails. In the current presentation, this hypothesis will be critically reevaluated.

The colour of synthetic MBI is violet, but, when heated to 60 ºC, it undergoes an irreversible thermochromic transition to blue. This phenomenon accounts for the tinctorial lability of *M.tr.* purple-colored dyeings to become blue on heating.

The instrumental techniques used so far to study the thermochromism of MBI have not yielded significant findings. New studies using differential scanning calorimetry have not yet furnished meaningful results. In an attempt to study MBI by Raman spectrometry, the sample exhibited luminescence and disintegrated in the heat of the laser beam.

Murex and orchil methods and technique: part 1

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Abstract

The present investigation into murex and orchil methods is motivated by historical literature references to mollusc and lichen dye combinations which were a standard technology for dyeing wool and silk in both the ancient and medieval periods. As both molluscs (murex) and lichens (orchil) yield various shades of purple, why would they have been used together? Was there an economic or an aesthetic advantage? This research based on *Rapona venosa* (murex) and *Lasallia* and *Umbilicaria* spp. (a vernacular version of orchil) substantiates numerous classical and more recent references to these combined mollusc and lichen dyes. Our results on a variety of fibres indicate that murex and orchil, when used in combination, create deeper colours than when either dye is used alone.

HESBAYE and tinctorial plants (1200-1400)

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Abstract

As was said last year at the DHA 25, England and parts of Scotland were the main importing markets for tinctorial plants from different countries. Imports from what is now mainly Belgium began at the end of the 14th century from two neighbouring regions, Hesbaye and the county of Jülich (near Köln). Hesbaye lies south-east of Brussels and north of the Meuse between Namur and Liege and had already been producing tinctorial plants for many years. Its region of production lies between the left bank of the Meuse river and many right bank tributaries of the Schelde.

Woad had been produced in Hesbaye for dyeing purposes since the beginning of the 13th century. Many woad producing sites have been attested for the period 1230-1275.

Andre Joris published an interesting series of articles about the existence of woad mills in north east Namur, and then in the Hesbaye area. Hesbaye in fact was included in three political regions: the County of Namur, the Principality of Liège and the Duchy of Brabant.

Because of its geographical situation, Hesbaye had good access to the cloth-producing regions of Flanders, Brabant and the northern Low Countries through river and road communications. Since the publication of the research of Andre Joris in 1955-1964, new elements of analysis have made it possible to widen this field of research to include other tinctorial plants such as madder and weld.

Detailed analysis of the evolution of consumer markets and trading towns for tinctorial plants would help the understanding of the evolution of the production of these plants and pigments in rural areas. We intend to demonstrate the link between these three economic actors. A close study of the way the cloth industry developed in the Artois and the Low Countries and of the different types of cloth produced there, describes a changing picture of geographic and economic decline and development as well as variations in the quantities of consumption of the three main tinctorial plants produced in northern Europe. Other exceptional pigments such as grain, brasil or purple from Mediterranean markets are also attested.

Other elements which this study highlights are the existence of madder mills and weld cultivation which widens the field of study from woad alone. Woad nevertheless remains the dyeing matter for which there is, so far, the most information in medieval documents.

“Let us go for blue, sisters, for madder, brides!” – Dyes and dyeing in the Finnish Karelia

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Abstract

The women’s traditional handwork has been an important part of Karelian folk art until the recent times. Wool and linen have been treated for use in the households: cloth has been woven, socks and mittens have been knitted, and various kinds of textile objects have been decorated with embroidery. In Karelia women used dresses that were home made and richly embroidered with knowledge and patterns obtained from elderly women, mothers and grandmothers. These folk costumes represent the most primitive and unfashionable costumes in Finland when comparing cuts, fabrics and embroidery motifs. In Karelia folk costumes were in use till the latest and with elderly women even in the beginning of the 20^{th} century.

The yarns and fabrics were made from the very beginning by hand and dyeing was an essential part of the textile preparation process. There was a specific order for the different duties during the year. It was necessary to schedule the preparation process and take into account the seasons, growing period of linen and dye plants, the cold and dark winter, the light spring and summer etc. In the summer women collected plants to dye yarns. “In the spring she dyed yellow yarns, in the summer the reds, in the autumn the blues“, tell the traditional Withsuntide Festival songs, which the young maidens sang wandering along the lanes of the village.

The Karelian folk costumes are well known and they have been studied earlier by several researchers. However, the focus in these studies has been mainly on the appearance, materials and techniques of preparation. The aim of this research is to concentrate on dyes and dyeing techniques used in Karelia by applying research methods from several disciplines. This presentation highlights some of the aspects concerning the Karelian dyeing tradition. The research material is based on the literature, archives of folklore and interviews. Later, textiles of museum collections are studied and dye analysis are made from the chosen textile pieces.

William Morris and the discharge of Indigo

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Abstract

The Printers' Notes (1880-1885) of Morris & Co. are contemporary with the firm's move to Merton Abbey in 1881 and with the early production there of printed chintzes. A short handwritten bibliography of books consulted on dyeing is followed by notes of the proportions of indigo, copperas and lime used in vats by their authors. There is also an outline of the full (white) and half-discharge (light blue) procedures described by Persoz (1846) in which indigo dyed cloth is treated with 'bichrome' before being printed with a thick paste containing oxalic or citric acid, the principle being that acids cause chromates and dichromates to become strongly oxidizing and remove indigo from the printed areas.

While early suggestions appear in the notebook, precise details of the Morris & Co. procedures for creating decorated chintzes with an indigo background are recorded in the Merton Abbey Dyebook (1882-1891). 'Bichrome' was potassium dichromate, rendered strongly alkaline to prevent the premature formation of 'chromic acid'. Cloth padded with this was protected from light, avoiding photo-oxidation of indigo or of cellulose fibres. The printing paste, applied the next day and thickened with mixed gums and clay, contained oxalic acid with some sulfuric acid, and was strongly acidic. Its complete removal of indigo left a white design on a dark blue ground and was used alone for the first chintzes to be produced at Merton Abbey in 1882.

The next designs on the indigo-blue ground involved, in addition to this full discharge, a milder 'half-white' discharge to remove just some of the indigo to yield a lighter blue. The printing paste for this contained no sulfuric acid, but the oxalic acid solution was thickened with a mixture of gum and lime juice, containing citric acid. The Dyebook indicates the precision of these procedures; differences in the concentrations of acids used for the various patterns presumably related to the shade of the indigo-dyed fabric, but there are subtle running alterations, too, recorded in the recipes.

Particularly in the hands of Morris & Co., the ability to produce both white and light blue areas on a dark blue indigo ground was the very basis of designs created by the simplest of subsequent printing and dyeing procedures. White areas were converted to yellow, and light blue to green, by printing with mordant and steaming or dyeing with quercitron bark or with weld. When required for the designs based on indigo, red was printed before the yellow, usually by steaming with mordant and 'medium alizarine', while madder was the red dye for colourways based on red. Using different concentrations of mordant and dye, a range of reds and pinks could be produced which could then, where required, be converted to orange by yellow overprinting. In most designs, printing with mordant and dyeing with weld or bark was the last step, dyeing becoming the preferred method rather than steaming. Some designs, though, were provided extra richness by a final printing of detail with catechu.

Investigation, revival and optimisation of traditional Mediterranean colouring technology for the conservation of the cultural heritage

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Abstract

The goal of this contribution is to describe in brief the objectives, the activities and the current results of the MED-COLOUR-TECH (www.medcolourtech.org) project which is funded by the European Union (Contract No: 015406, 2006-2008, 6th FP) within the INCO-MPC framework. The objectives thus relate to the creation of a Euro-Mediterranean research area and target long-range sustainable development around the Mediterranean.

Colouring or painting with natural organic materials has been fundamental in art and intrinsic to the cultural identity of the Mediterranean area, since antiquity. The reconstruction and revival of traditional manufacturing processes for natural organic colorants, as well as of dyeing procedures or painting techniques is essential for the preservation of the Mediterranean cultural heritage.

The objectives of MED-COLOUR-TECH can be summarized as follows:

- Establishment of an analytical methodology for dyestuff/pigment identification on selected art objects of the cultural heritage of the Mediterranean area and formulation of corresponding recommendations on conservation.
- Systematic analysis and reconstruction of ancient colouring techniques, typical of civilizations developed in the Mediterranean area, to elucidate the local ancient colouring technology.
- Dissemination of natural organic pigments and corresponding colouring components, currently not available in the market, to the scientific community, interested target groups and general public.

The implementation plan of the project includes the following activities:

- Collection of historical data, sources of dyestuffs and art objects of the Mediterranean area.
- Production of colouring components (standards) of the dyestuffs of interest.
- Identification of natural organic dyes in art objects, using analytical techniques.
- Production and characterization of natural organic pigments based on ancient recipes.
- Optimisation and standardization of the production processes of natural organic pigments.
- Pilot (industrial) production of natural organic pigments.
- Recommendations for conservation strategies.
- Creation of an encyclopaedia for natural organic pigments of the Mediterranean area.

MED-COLOUR-TECH is expected to elucidate aspects of colouring technologies developed by several civilizations of the Mediterranean area leading ultimately to the formulation of a database which will include several important data such as: historical information, analytical results, recipes for dyeing and pigment production and recommendations for conservation of the artworks. More than 130 artworks will be studied including textiles, icons and mural paintings.

Preparing of artificial aged dyed textile samples simulated to museum dyed textiles

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Abstract

Natural historical dyed textiles are characterised by a high degree of variability of properties and therefore are rarely suitable for experimental research because variations in results can be attributed to the nature of specimens rather than the particular conservation treatment under investigation. In addition to the main aim of conservation researches is to preserve textile objects, so that the usage of ancient ones as experimental samples is prevented. For that this study is carried out to assess and evaluate behaviour and characterisation of dyed wool textile samples after degraded artificially. This evaluation is to investigate the possibility of preparing artificial deteriorated dyed textile samples simulated to deteriorated ancient textiles, to be used as experimental samples in historical textile conservation researches. In this study new wool textiles were dyed with 10 natural dyes common used in Mediterranean countries in the past time.

Different mordant were used in this study to produce different colours from each dye. The dyed wool samples were artificially aged by light for various periods. The changes in the color of dyed samples before and after aged by heat and light were observed visually compared with blue scale. Also the color components (parameters L, a, and b values were recorded. The changes in the parameters L, a, and b values (ΔL, Δa, and Δb) were calculated. Finally the total changes in the color differences (ΔE) were calculated. The results show that yellow dyes are the most sensitive tested dyes to light aging. Madder is most tested dyes fastness to light. The colors composite from tow dyes became other new colors after light aging such as green color became blue. This study informs that the colors that we see on historical textiles in the museum may be different than their original colors in the past in the moment of their production. The obtained results show that it is possible to prepare artificial experimental textile samples simulated to faded ancient ones. These artificial experimental samples can be used for conservation researches, and the practical training of textile conservators. However the exposure time required for preparing these samples depend on type of the dyes. Some of tested dyes such as madder needs about 80 hours and other dyes such as turmeric needs about 40 hours only.

The effect of some mordant dyes on the fibre net of textiles

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Abstract

Apart from other topics Med-Colour-Tech*, an multinational EU-project, deals with the research on ancient and medieval traditional recipes for dyeing textiles by natural organic colouring materials prepared from plants and animals. A great group of people like restorers, conservators and artistic weavers is very interested in the results of these old dyeing technologies, e.g. the colour index, wash and light fastness of such dyed textiles. The present investigations are dealing with the effect of mordant dyeing on the state of the supporting matrix (cellulose, keratin) of cotton and sheep´s wool. It was known from literature that wool is much more suitable for mordant dyeing as cotton. A selection from important mordant dyestuffs and their use with the mordants copper sulphate, potassium dichromate and alum has been proved by means of SEM/EDX (Scanning Electron Microscopy/ Energy-Dispersive X-Ray Spectroscopy).

Results

- In partially damaged sheep´s wool (keratin) the sharp contours of the roof-tiles on the fibre surface of intact material were less visible and parts of it began to break.

- Partially damaged cotton (cellulose) has a rough surface showing fibrillation and frayed contours compared to its healthy structureless reference material.

- Direct dyeing (without mordants) preserved a healthy cellulose fibre net of cotton, while the keratin skeleton of sheep´s wool was damaged if used either safflower and brazilwood as colouring materials.

- Mordanting of cotton with $CuSO_4$ did not influence the fibre structure, however $K_2Cr_2O_7$ caused a medium damage of the fibres with safflower, madder and cochineal as well as $KAl(SO_4)_2.12H_2O$ with madder.

- By mordanting of sheep´s wool in combination
  of $CuSO_4$ with saffron, turmeric, safflower, madder, cochineal and brazilwood slow
  of $K_2Cr_2O_7$ with saffron, turmeric madder and brazilwood slow, with cochineal high
  of $KAl(SO_4)_2.12H_2O$ with cochineal slow, with brazilwood high
  changes in fibre structure could be observed.

- By mordanting with $CuSO_4$ and dyeing with safflower the measured Cu percentage on the fibre surface of both textiles is twice as high as that with other dyestuffs.

* Studies were carried out within the EU-Project “INCO CT 2005 015406 MED-COLOUR-TECH”.

Identification of dyestuffs in some 17^{th} century silk skullcaps by liquid chromatography with diode array detection in the Topkapi Palace Museum collection

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Abstract

High performance liquid chromatography (HPLC) with diode-array detection (DAD) method was utilized for the identification of dyestuffs in some 17^{th} century silk skullcaps.

Reversed-phase HPLC with diode-array UV–Vis spectrophotometric detection has been used for identification of natural dyes in extracts from silk fibres of skullcap. The examined objects originate from 17^{th} century and belong to the collection of Topkapi Palace Museum in Istanbul. Extraction from fibres was carried out with HCl/methanol/ water (2:1:1) solution.

The most important natural red and yellow dyes were found in historical textiles. In this study, as the main individual chemical components of natural dyes, anthraquinone and flavonoids, including carminic acid, laccaic acid and luteolin were found.

Project funded by the European Community under the Sixth Framework Programme Integrating and strengthening the European research area Investigation, Revival and Optimization of Traditional Mediterranean Colouring Technology for the Conservation of the Cultural Haritage); INCO CT 2005 015406 MED-COLOUR-TECH.

More secrets of Perkin's Mauveine dye revealed

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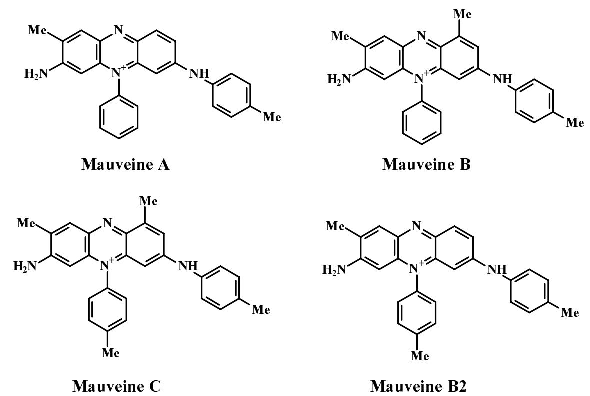
Abstract

It was 150 years ago that William Henry Perkin invented mauveine, a dye which is considered a landmark in the history of chemistry and the dye industry[1-4] . Before 1856, only a few dozen of dyes, all of natural sources, were known. Furthermore, the purple color was produced with thousands of tiny marine molluscs and that production almost lead to the first ecological disaster.

The accidental discovery of mauveine, when Perkin was trying to synthesize the anti-Malarial pharmaceutical quinine from coal-tar chemicals, launched the synthetic dye industry in Europe. The mauveine color which enchanted Empress Eugenie of France and Queen Victoria, was quickly outclassed by other synthetic dyes and bright new colours.

The structure for the mauveine dye had waited until to 1994[5] to be clarified, where it turned out to be a mixture of two compounds: Mauve A ($C_{26}H_{23}N_4^+$) and Mauve B ($C_{27}H_{25}N_4^+$) (scheme 1). These compounds were both different from the commonly accepted chemical structure of mauveine[5]. Mauve B2, an isomer compound of Mauve B, and Mauve C ($C_{28}H_{27}N_4^+$) (scheme 1) were recently identified in Perkin's Mauveine historical samples from the Science Museum in London[6].

A full characterization of Perkin's Mauveine historical samples by HPLC-DAD, ^{1}RMN, MS and FT-IR, including its inorganic counter-ions, will be presented. The importance of this knowledge to confirm the year of production of the museum samples will be discussed.



Scheme 1- Chemical Structures of Mauveine A, B, B2 and C.

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Faded flowers, analysis of modern marquetry applied on 17th and 18th century Dutch furniture

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Abstract

In the 19th century the decorative 17th century Dutch flower marquetry furniture became collectible once more. One did not stop at being satisfied with the genuine article but soon when stocks ran out the 'improvement' of hitherto undecorated pieces started to take place. To the extent that it is sometimes hard to distinguish between authentic 17th and 18th century marquetry and the additions of the late 19th - and early 20th century, even for trained specialists. It goes without saying the distinction between authentic original and altered object matters.

Art dealers and historians might therefore look at stylistic details, anachronisms in the depicted figures or unbalanced, cramped compositions, whereas conservators will try and pick up on technical details like the veneer thickness or wood species used. As some marquetry elements usually are artificially stained this might offer yet another viewing angle. The positive identification of modern colorants could serve as a valuable tool for the dating of the marquetry inlays. A complicating factor however is the often degraded state of the colorants in the today already severely faded marquetry. This research makes use of the fairly unique collection of unused marquetry elements originating from the stocks of an Amsterdam marquetry cutter J.L Miner, active between 1905-1927. Now it is kept as study material in the Rijksmuseum Amsterdam, the Netherlands Institute for Cultural Heritage and the Amsterdams Historisch Museum. The analysis performed on samples taken from this collection served as reference material which was subsequently compared with samples taken from marquetry on historic furniture.

As sampling can be problematic, the approach we choose was to first apply non-invasive techniques for first screening and sample selection. To identify the possibilities and limitations of the techniques, the first application was done on some left over materials from the late 19th century, early 20th century from a furniture restoration practice. It was known form historical sources that these materials were used in marquetry. A portable X-ray Fluorescence (XRF) was used to determine the inorganic elements present, while a portable Fibre Optic Reflectro Spectrometer (FORS) was used to collect reflectance from UV/VIS up to near infrared (NIR). Next, samples were taken used analysed by High Performance Liquid Chromatography coupled to Photo Diode Array detection (HPLC-PDA). In the second step marquetry of objects, suspected to be not original, was analysed.

The results of the analysis, and the possibilities and limitations of the technique used will be discussed during the presentation.

The early synthetic organic dyestuffs: The Yellows

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Abstract

In 2002 we started a project focussed on a selection of 65 well-known synthetic organics, covering all dye-classes from the period 1850-1900. The research project has two main aims. First: to collect historical information by studying the original historical literature sources, including the patent literature. Secondly: to evaluate present techniques and to develop new analytical methods for the identification of these dyes. The second part of the project is carried out in collaboration with the Royal Institute for Cultural Heritage (KIK/IRPA).

This lecture will focus on the important synthetic organic yellow dyes. Our selection of 65 synthetics contains eleven yellows and they can be divided mainly in two groups: the nitro dyes and the azo-dyes. The nitro dyes belong to the first known synthetic organic group, characterised by the presence of nitro (-NO_2) groups. Nitro dyes are not very common and the shade range is limited to brown, yellow, orange and green. Nitro dyes are prepared by the treatment of on especially phenols and naphthols by nitric acid.

The second group are the azo dyes, which are characterised by the presence of the -N=N- bond. In 1858 Johann Peter Griess discovered the diazo-reaction, which can be used for preparing acid dyes. These dyes are produced by coupling a diazonium salt with an activated aromatic molecule. Three yellow synthetics belong to other chemical groups. Auramine is a di-aryl methane dye, quinoline yellow is a quinophthalone colouring matter and fluorescein belongs to the chemical group of the hydroxy-phthaleins.

The yellow dyes on textiles show different light-fastnesses. The nitro dyes, picric acid, Martius yellow and Naphthol yellow S, have a poor light-fastness. They are strongly fading within several days and nearly completely faded in several weeks. The yellow azo-dyes discovered in the 1880s, such as metanil yellow, tartrazine yellow and brilliant yellow, show a much better light-fastness. So research, especially done by German dye factories, produced newer and better yellow synthetics with an increased light-fastness.

The history, the chemical constitution, the production and the names of the different dyestuffs will be presented. Additionally the identification of these dyes will be demonstrated by international case-studies on textile objects.

Name	C.I. Name	C.I. Number	Dye class	Discoverer(s)	Year of Discovery
Picric acid	Acid dye	10305	Nitro	P. Woulfe	1771
Martius yellow	Acid Yellow 24	10315	Nitro	R. Ganahl C.A. Martius	1856 1864
Fluorescein	Acid Yellow 73	45350	Hydroxy-phthalein	A. Baeyer	1871
Naphthol yellow S	Acid Yellow 2	10316	Nitro	H. Caro	1879
Metanil yellow	Acid Yellow 36	13065	Azo	C. Rumpff Hepp	1879 1882
Quinoline yellow	Acid Yellow 3	47005	Quino-phthalone	E. Jacobsen	1882
Auramine	Basic Yellow 2	41005	Di-aryl methane	A. Kern and H. Caro	1883
Tartrazine yellow	Acid Yellow 23	19140	Azo	H. Ziegler	1884
Brilliant yellow	Direct Yellow 4	24890	Azo	F. Bender	1886
Alizarine yellow GG	Mordant Yellow 1	14025	Azo	R. Nietzki	1887
Flavazin L	Acid Yellow 11	18820	Azo	C. Möllenhoff	1892

Determining display conditions for the Waldseemüller world map: lightfastness testing in an anoxic environment

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Abstract

The Library of Congress has recently acquired an important early 16th-century map, the only known surviving copy of the first printed map to show 'America' as a continent. Produced in 1507 by the cartographer Martin Waldseemüller, the map comprises 12 woodblock sheets which form a wall-sized display over 4' by 8'. A multi-year project has been undertaken to conserve and analyze the map and to prepare it for long term exhibition in an oxygen-free encasement.

An important facet of this project has been determining the light-sensitivity of the media on the map to establish light limits for display. Printed in a carbon-based ink, the map bears scholarly annotations by another 16th century cartographer in iron-gall ink and a red organic ink, which were suspected to be fugitive. Adhesive residues from binding and materials used in earlier conservation treatments also raised concern over their possible differential aging from the main areas of the paper. The anoxic environment will greatly slow deterioration of the paper, but its impact on the fading rates of these materials could not be predicted.

Lightfastness tests on a selection of known-composition colorants were carried out in air, argon, and humidified argon, using an accelerated micro-scale lightfastness test. Our results illustrate the contributions of humidity and oxygen to light damage for these colorants. However, the age and history of an object also affect its light sensitivity, and even where media can be confidently identified their behaviour cannot be predicted fully. Ultimately, lightfastness tests were carried out on the object itself in a humidified argon environment matching the conditions selected for its exhibit case, and projections have been made for the map's long-term stability on exhibition.

Optimisation of the micro-destructive light fastness tester, the "µ-Fado"

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Abstract

In the past, many artefacts have been exhibited without knowing their light stability and without monitoring light exposure. This has resulted in the loss of the original colour. The first lighting standards for exhibition, 50 lux for sensitive and 200 lux for less sensitive objects, defined by Thomson in 1961, were based on common sense of the levels needed for a good visual perception of the artwork and not on reliable light fastness data of the materials present [1]. Also, as light damage is cumulative, it is more appropriate to define a limit for the total exposure, rather than a light level.

Light fastness data of many dyes, mainly used for colouring textiles, have been published in the Colour Index [2]. Light fastness testing usually is carried out with artificial light sources on dummies. To use these data for predicting the behaviour of a dye or pigment on an artefact during exhibition, it is necessary to identify the dye or the pigment, as well as the materials around it, e.g. the substrate, as these have an influence on the light fastness. If no reliable data can be found in literature, time-consuming fading studies have to be conducted on dummies. To avoid this, the American researcher Paul Whitmore, developed a laboratory-built apparatus to directly conduct micro-destructive light-fastness measurements on the artefact [3]. A tiny area (~ 0.25 mm^2) on the artefact's surface is exposed to a high-intensity light beam from a xenon light source. The light is guided and focussed on the surface at an angle of 90º by an optical fibre, coupled to a lens system. The light, reflected from the surface, is captured by a second lens system, coupled to an optical fibre at an angle of 45º, and guided to a spectrophotometer. The latter measures the spectral reflectance curve of the material at pre-set time-intervals. The spectral data then are converted to CIEL*a*b colour space data and the colour change ΔE is calculated. A change of $\Delta E = 1.5$ is considered to be just perceptible to the human eye. A plot of □E against the light exposure (in lux hr) shows at which exposure value this so-called "just perceptible change" (j.p.c.) is reached.

Some essential improvements have been made to Whitmore's design, leading to easier focussing and a reproducible adjustment of the light intensity at the focal plan. Reciprocity law was checked by exposing the same sample to different light intensities and measuring the increase of spectral reflectance at the wavelength of maximum absorbance as a function of the received light exposure. Samples were prepared by plotting onto drawing paper aqueous solutions of synthetic dyes, commonly used in inks for writing and drawing. Results of light fastness testing of these samples will be presented, as well as some results of testing on inks on originals (postcards).

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Indigo dyeing and bio-deterioration of a woollen textile

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Abstract

The applications of natural dyes date back almost to the beginning of the history of humankind; and the textile dying was one of them. Indigo, called the king of colours and colour of kings, and, also, considered the oldest known to the man dye, was the most commonly used blue colouring substance in the world.

Indigo-dyed textiles can be severely damaged by microbes developing therein. They initiate a process known as bio-deterioration that can result in the lowering of the value or in the complete loss of cultural properties. Many factors impact the degree of textile bio-deterioration. Among them, there are: microbial metabolic products, i.e. enzymes, acids and pigments; chemical composition of material and the fact whether or not some auxiliary substances, as dyes, can be found in materials; moisture content and its accessibility to micro-organisms; history of an object and its age; local microclimate including the availability of oxygen and light, temperature and RH. From among all the groups of micro-organisms, fungi pose the biggest threat to art objects.

There are two key objectives of this study: to assess the effect fungi exert on the level and range of bio-deterioration of the woollen textile dyed using indigo; to determine the impact of micro-biological medium enriched by additional nutrients on the degree of microbial deterioration of the woollen textile.

The experiments under this study were conducted using a pure culture method. Micro-organisms applied were isolated from both the bio-deteriorated antique and the contemporary woollen textiles. The analysis of the range of bio-deterioration of indigo dyed woollen textile was performed with the use of several methods, such as: tensile strength and elongation tests, spectrophotometry, electron and light microscopy. The study showed that the fungi caused structural damage and colour changes to the textile dyed with indigo. Apart from the above, the research yielded some new and interesting findings referring to interactions occurring between the indigo dyed textile fibres and fungi.

Aging behaviour of silk dyed fabric with safflower dye

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Abstract

Many textile archaeologies from the different period in different museums in the world, such as the silk fabrics in the Islamic Art Museum in Cairo-Egypt, are coloured with the yellow safflower natural dye.

This study aimed at study the effect of different aging procedures such light, thermal and chemical aging procedures on silk dyeings with the safflower as a natural dye mordanted with different mordents e.g., alum $Al_2(NH_4)_2(SO_4)_4.24H_2O$, $FeCl_2$, $CuSO_4$, and $SbCl_2$-Tartaric acid. The dyeings were performed by the exhaustion method using a liquor ratio (LR) of 1:20. The silk aged dyeings were investigated for their surface morphology, colour parameters (CIELab). This study was carried out to establish the standard conditions of light, and temperature at which the archaeological textile objects can be maintained without any deterioration. The aged samples were also used for conservation objects 12014 and 12015 of the Ottoman age in the Islamic art museum, Egypt.

The CIE-Lab values of the dyeings were measured with a double beam Optimatch spectrophotometer (Macbeth-UK, sample diameter 10 mm). The colours are given in CIE Lab coordinates, L corresponding to the brightness (100 = white, 0 = black), a to the red–green coordinate (positive sign = red, negative sign = green) and b to the yellow–blue coordinate (positive sign = yellow, negative sign = blue).

The Spectrophotometer equipped with integrating sphere and calibrated by using the reflectance certified standard white tile (100% reflection).

Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) analysis of natural dyestuffs

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Abstract

Natural dyestuffs madder, cochineal, brazilwood, dyer's greenweed, weld and fustic and the tannins oak gall and alder bark were analysed by Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) in the form of dried films from dyebath solutions, dyebath solution applied to paper and dyed wool and silk fibres.
The study was undertaken in order to investigate the applicability of the ToF-SIMS technique for analysis of dyestuffs without extraction from the fibres. The analyses were largely successful on dried dyebath films and paper substrates; while the detection of dyes on textile substrates was in most cases unsuccessful due to dye location in the fibres.

Introduction

Dyestuff identification has received much attention in the field of conservation science and has reached the sophisticated level where not only dye classes can be distinguished but even their origin from different species of plants or animals of the same families. Today, the analytical method of choice is usually High Performance Liquid Chromatography (HPLC), often linked with a diode array detector. In addition to chromatography, various mass spectrometric techniques have been applied successfully for the identification of dyes. However, most techniques require the extraction of the dyestuff from the fibre using various solvents and extraction protocols. The extraction process itself may be destructive and is not always quantitative for all chromophores in a dye mixture. Solvents can cause partial destruction or chemical alteration of chromophores during the extraction process or storage. In recent years several researchers have investigated some mass spectrometric techniques that do not require extraction for the identification of dyestuffs. In this context the present study was undertaken to investigate the applicability of ToF-SIMS for the identification of some natural dyestuffs.

Conclusions

The study showed that several of the chromophores present in natural dyestuffs such as madder, dyer's greenweed, young fustic and weld can be identified by ToF-SIMS analysis of dried films of dyebaths and applied to a paper substrate. Analysis of brazilwood and cochineal were less distinct with the principal chromophore signals being of lower intensity than other peaks in the same mass region. Both Cs+ and Au1+ primary ion sources were shown to successfully desorb and ionise the chromophoric species from dyebath films.
Oak gall yielded peaks attributable to gallic acid and ellagic acid, known to be the principle building blocks of gallo tannins. This could be of use in the identification of inks on paper, which often consist of the combination of tannins with ferrous sulphate. However, no species containing Fe were identified. Indigo was identified on the surface of wool fibres while the detection of other dyes on wool and silk fibres failed. This may be due to the penetration of dyes into the bulk of the fibres, surface contamination or the inability to desorb and ionise the chromophoric species from wool and silk substrates under the applied analysis conditions.

On the detection and significance of glycosides in natural dyes

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Abstract

Many plant dyestuffs contain dyes or dye precursors that are glycosides. Depending on the situation, cleavage of the glycoside—that is, removal of a sugar—can be essential, desirable or detrimental, or it may have little effect. In the case of indigo, the blue colour can only form *after* conversion of a precursor molecule (often a glycoside) to indoxyl, which is further oxidized to the familiar blue dye. With ruberythric acid, found in species of madder, removal of the sugar moiety to form alizarin results in a dye with an absorption maximum of longer wavelength, i.e., a deeper red. In our own studies, we have found that glycosylation (or other substitution) of the 3-hydroxyl group of yellow flavonols such as quercetin, kaempferol or isorhamnetin, is essential to preserving lightfastness of the dye. The latter conclusion stems from the discovery that the yellow dyes in many old textiles are 3-*O*-glycosides of flavonols, for example, rutin, the 3-*O*-rutinoside of quercetin. A common source of rutin is the buds of the pagoda tree (*Sophora japonica*), which have been used for centuries in the Far East as a source of a yellow dye. To detect this and other glycosides, we developed a mild, non-hydrolytic method for extracting the dyes from textile fibers and analyzed the extracts by mass spectroscopy, which gives the exact mass of the molecule and therefore is very helpful in its identification.

For some time we were mystified by the fact that certain old textiles contained only rutin, while analysis of dried pagoda tree buds (the presumed dyestuff) contained both rutin and the aglycone, quercetin. However, information from a recent Japanese paper and from some 17th century Chinese sources indicates that pagoda tree buds contain an enzyme, rutinase, which can be inactivated by heat treatment - either boiling or roasting. In fact precisely the same technology has been used since at least the 8th century in China to make green tea: fresh tea leaves are heat-treated to inactivate the enzymes (oxidases) that will otherwise convert the leaves to black tea. We have subsequently found evidence for such enzymes (glycosidases) in other plant dyestuffs. This finding is particularly relevant for dyestuffs that contain 3-hydroxyflavones, e.g., quercetin, because these compounds undergo fairly rapid photooxidation (that is, they are unstable to light), whereas the 3-*O*-substituded derivatives are stable.

Thus enzymes intrinsic to various dyestuffs play key roles in the development of colours. No doubt early dyers understood that dyestuffs had to be processed in certain ways to get the desired results. However, they could not have known *why* certain processes worked better than others because enzymes were not characterized until the 20th century.

Investigation of dyed rabbit hair in a 16th-17th century colonial Latin American textile

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Abstract

An extraordinary 16th-17th century Latin American Colonial tapestry-woven textile composed of dyed rabbit hair and spun feathers, belonging to The Cooper-Hewitt, National Design Museum, Smithsonian Institution was the subject of a recent collaborative research project conducted by the authors. The unusual material and technical aspects of the textile called into question its former classification as Peruvian. Through an investigation of its fibers, dyes, and structural techniques, in combination with art historical research, the study informed a reclassification of the textile as originating in Mexico.[1] As very few Mexican textiles have been preserved from the period before the Conquest, or from the early Colonial era, the opportunity to examine the rare 16th-17th century textile enabled a study of the dyes, along with the fiber, spinning and weaving techniques used by the ancient people of Mexico, in the context of a Spanish Colonial aesthetic. The current paper will present the dye analysis conducted for this study.

Six different colored yarns from the tapestry - red, yellow, green, dark green, light green, and grey - were analyzed by high performance liquid chromatography using a photo-diode array detector. The results are listed below:

YARN COLOR	PROBABLE DYE IDENTIFICATION
Grey	Naturally pigmented animal fibers
Red	Cochineal (*Dactylopius coccus* Costa)
Dark green	*Caesalpinia* species
Yellow	Possibly *Cuscuta* species, *zacatlaxcalli* (the Nahuatl name)
Light green	Flavonoids (possibly glycosides of apigenin) - dye plant currently unknown
Green	Mixture of the same color components found in the yellow and light green yarn

The paper will present the outcome of the study, particularly on the dyes used in the textile and their identification, in context of the little-known Pre-Columbian and early Colonial Mexican traditions.

Reference

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A renaissance colour plate revealed.
Lost colours of the Renaissance - unexpected results from a masterpiece of Renaissance marquetry

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Abstract

Stained veneer with bright colours as blue, green, yellow and red is a most interesting element of designing marquetry at pieces of furniture and interior decoration during the centuries. Today it´s quite impossible to find an early historic wooden artwork in its original colours, because natural dyes are highly sensitive to light and begin to fade soon after a masterpiece has been completed. Traditional recipes, shown in historical tractates, give an idea of the use of colorants and technologies in these early times, but it is not easy to verify the use of dyestuff on stained veneer, expecially when we are in front of an intact surface and we do not want to damage it.

By using UV-VIS-absorption-spectrometry as a non destructive method of analysing colorants (pigments and dyestuffs)which allows also to identify low concentration or faded dyestuff, it was possible for the first time to identify the "palette of colorants" of two mannerist artists, who created one of the best maintained wooden marqueterie panels of the 16th century at the Hofkirche of Innsbruck.

The presentation will be split into two parts: in the first part the technical options of the analytical method will be described. The second part deals with the technical history of wood dyeing and examines specifically the renaissance colour palette of the "Fürstenchor", commissioned by Ferdinand II from Austria in the Hofkirche of Innsbruck.

Non-destructive dye analysis for Japanese historical textiles at 17th C

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Abstract

Non-destructive and micro sampling analyses are important for the spectroscopic characterization of natural dyestuffs of colored historical textiles. Especially, combination of visible reflectance and fluorescence spectra for dyestuff and ATR infra red spectra for material determinations were effective tools for non-destructive methods.

Here, we would like to introduce non-destructive method using visible and fluorescent spectra for determination of dyestuffs for a 17th century traditional textile “Uchishiki” (kimono fragment with print and embroidery) for determination of red, yellow and blue dyestuffs of the embroidery threads, and square patterns. Moreover, we also report infrared analysis for binding material determination in the blue and red stencil bound dot. The “UTISHIKI” was square rag sewed up the fragments of KIMONO, dedicated to the temple for use in the Buddhism Ceremony in Edo period in Japan.

Information of dyestuff used for the multi-dyeing easily were obtained by combining the fluorescence emission and excitation spectra. or example, armor cork tree as minor component was observed with safflower in the embroidery red thread in the excitation spectra. This observation was an indication of pre-dyeing of yellow dye in red dying by safflower. Yellow dyestuffs were easily discriminated by the excitation spectra of turmeric, armor cork tree, and Eulalia.

The bound dot was dyed into red and blue by brazilwood and indigo. The binding materials in the stencil dyeing were determined by ATR-IR spectra. In the blue dot, a spectrum was almost identical with that of typical dextrin, indicating usage of starch glue. In the red dot the spectrum was slightly different from that of the starch, but nearly identical with the spectra of glucomannose. Thus, it was found that the binding materials were changed by the color in the stencil dot.

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Investigation of artificially aged dyed textiles using High Performance Liquid Chromatography with Photodiode Array Detection (HPLC-PDA)

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Abstract

Identification of dyes in archaeological objects not only assists sometimes in their dating and locating their origins but also provides invaluable insights to the application of appropriate treatments during conservation and restoration work. It is often that identification of natural dyes can be done by compared unknown archaeological dyes with new known dyes. The aging process may cause changes in the chemical components of dyes that can cause that the comparison method not completely acquired to identify ancient dyes. So this study aims to detect and identify the chemical components present in extractors of dyes in textile fabrics before and after artificially light ageing. This study is carried out to assess and evaluate behaviour and characterisation of dyed wool textile samples after degraded artificially with light. This evaluation is to investigate and identify if there are any alteration in chemical composition of natural dyes after light aging. Also to assess if there are any new matters produced after light aging as results in deterioration products in dyes or textile fibre. In this study new natural wool textile fabrics were dyed with natural dyes common used in Mediterranean countries in the past time. The dyed wool samples were artificially aged by light. All dyed samples before and after aged by light were investigated using High Performance Liquid Chromatography with Photodiode Array Detection (HPLC-PDA).

King Midas's golden color chemistry

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Abstract

In the legend of King Midas, anything he touched turned to gold. Yet the 8th century B.C. Tumulus MM ("Midas Mound") of a great Phrygian king in Gordion, Turkey contained fine furniture, leather, bronze, and a little iron—but no gold. Textile fragments from the tomb were brought to the Smithsonian Museum Conservation Institute for fiber and dye identification in 2003.[1] Among the fragments were plain weave gold-colored textiles. They were examined initially with light microscopy and polarized light microscopy; the results seemed strange and implausible: what looked like fiber had no organic component. In other words, no fiber remained, only a gold-colored coating that conformed to the shape of the lost yarns and fabric. The coating was identified by energy dispersive X-ray spectroscopy (EDS) as containing 97% iron (by weight); the center of the fibers appeared hollow by scanning electron microscopy (SEM). Fourier transform infrared spectroscopy (FTIR) tentatively identified the coating as goethite ($\alpha FeOOH$), a pigment named after the German poet Goethe, but also known as yellow ochre. Near infrared spectroscopy (NIR) and Raman spectroscopy also matched the ancient coating with goethite. The identification of this crystalline form was subsequently confirmed by X-ray diffraction (XRD), using molybdenum $K\alpha$ radiation.

While the coating is clearly crystalline, or it would not be identifiable with XRD, it is a very fine crystalline structure, of uniform thickness, and even distribution. It is nothing like a pastel powder nor is there an organic binder, as there is with pigment printing. There is no interaction with the fiber, as in khaki. Instead, the appearance of the ancient coating matches the composition and SEM images of a modern, patented method to render woven fabric coated with iron oxides from an aqueous solution.[2] Yet the coating method resembles the classic dyeing of mordanted protein fabrics: aqueous solution, auxilaries, wetted out fabric, temperature gradually raised to 90° C and held for a period of time. The auxiliaries which would have been available in ancient times include urea, formic acid, and ammonium formate. The source colorant is a divalent iron oxide like Mohr's salt. The level of the pH will determine the final hue. Goethite, hematite, or magnetite can be produced (i.e. gold, orange, or brown colors). However, the fiber type of the fabric substrate is immaterial. Any fabric substrate is possible. King Midas's golden chemistry was bacteriostatic, lightfast, and protected the wearer from ultra violet light.[3] Elsewhere in the tomb, goethite coated yarns were striped with indigo, as identified by spot testing and FTIR. When a modern replica of goethite on linen was vatted with sodium dithionite a deep earthy colorfast green is produced—visually matching yet another small fragment in the tomb.

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Study of the dyes found in Early Iron Age Danish textile costume fragments, excavated from peat bogs

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Abstract

The study of the natural dyes is part of a two year Danish research program 'Textile and Costume from Bronze and Early Iron Ages in Danish Collections' (2006-2008). Denmark possesses a unique collection of prehistoric garments recovered from bogs and burials in all periods from the Bronze Age onwards. They provide an outstanding contribution to the understanding of the Scandinavian prehistoric textile and costume development. The majority of these Danish prehistoric costumes have been dated to the Bronze Age (1800-500 BC) and Early Iron Age (500 BC – 400 AD). About 180 archaeological textile samples, belonging to 47 textile finds, coming from 25 sites all over Denmark, are analyzed with HPLC-DAD to detect whether any dyes could be found, hence proving the use of dyed garments for costume figuration, and if so, to identify the biological dye sources. Apart from one grave find, all finds are situated in the bogs.

First results, using a dye extraction method with acidified methanol, showed that mainly flavonoid components were to be expected, and this only at trace level. In order to improve the sensitivity of the applied technique especially for flavonoids, a big part of the study was dedicated to evaluate other, recently published, mild extraction methods, giving higher extraction yields and preserving the glycosidic linkages (Zhang and Laursen 2005, Surowiec 2006) and an intern optimized method using ethyl acetate (KIK, unpublished). A table with the outcome of these tests performed on a small group of archaeological bog samples, will be shown on the poster. Whatever the applied extraction method, dye components could only be found at trace level and no glycosides could be detected. For some specific samples, more information on flavonoid dye components and derivates was found with one of the mild extraction methods from Zhang and Laursen, while the method of Surowiec, using a second extraction in dimethyl formamide, showed to be very interesting for indigoid dyes. Regarding the fact that for most samples, the detected aglycones (flavonoids and indigoids) also could be detected with the optimized method using acidified methanol followed by ethyl acetate, and that lichen dyes were only suggested by this method, the latter was selected for the analysis of the complete series of samples.

In a second part, an overview will be given from the dye components found in the complete series of the Iron Age textile fragments.

Dyes in Romanian archaeological textiles from Mirauti church 16th century

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Abstract

Textiles in Romanian collections have been mostly studied with respect to the weaving technologies used, decoration motifs or historic and artistic criteria.

A consortium made of LNCPC, KIK/IRPA and NAMR focused on medieval textiles (15th - 17th centuries) from the National Art Museum of Romania and Putna Monastery collections. Dyes in brocaded velvets used in the Princes' clothes and those in orthodox religious embroideries worked in the Byzantine style were reported. It was supposed from the results obtained that materials in brocaded velvets were of Western origin while those in religious embroideries of Oriental.

The present poster would bring more information about dye analysis on Romanian textiles, important for historians, art historians and scientists. This time we concentrate on archaeological items discovered in Suceava region, at Mirauti church, which say it was erected by Prince Dragos, in the 12th - 13th century. At the beginning of the 15th century became Metropolitan Church. In 1997, in the right hand side of the nave it was discovered a very well preserved oak coffin, dated from the 16th century. The funerary inventory contained a silk damask shroud, a golden painted floss silk shroud, a pillow, and splendid pieces of garments, including "drappi d'oro". Will these 25 new samplers bring more interesting information about the Romanian textiles and their provenience?

The Dyeing processes of the Nasca Culture in Peru - Identification of dyestuffs Realisation of standards to complete the database

Nathalie Boucherie[1] and Witold Nowik[2]

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2 Witold Nowik, Chromatography Department, LRMH (Laboratoire de Recherche des Monuments Historiques, Champs-sur-Marne, France).

Abstract

As part of our investigation into "The Dyeing processes of the Nasca Culture in Peru", topic of our dissertation for a Ph. D. in Archaeology under the direction of Pr. Dominique Cardon, we have came up against the problem of an incomplete database in HPLC about Precolombian dyestuffs.

Several studies have given information about Precolombian and traditional dyestuffs in South America but many more are still unknown, especially in regions where textile traditions have disappeared, as in the case of the Nasca region (coastal region south of Lima, Peru).

An important step in our research therefore was to complement the database with reliable references. To that effect, we have built up a collection of standards of yarn (mainly alpaca fiber but also cotton and wool*)* dyed with plants of the Nasca region and its surroundings. This constitutes the basic reference of our database: all data are precised, such as the botanical species of the dye source, the fibre substrate, the mordant.

At the epoch of the Nasca culture, relations between different regions of the Andean world are attested. It was therefore important to also include dyestuffs from others regions into our database.

Building a corpus of reliable dye references involved some considerable fieldwork, in order to obtain dyestuffs from the South Coast, and also from the Central and South Andean regions as well as some dye sources from the Amazonian jungle.

Ninety eight dye references were realized during this investigation.

Tattoos, carpets and felts - dyes from Daghestan collected in July 2007

Robert Chenciner and Magomedkhan Magomedkhanov

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Abstract

In July 2007 I was allowed to return to Daghestan after a 12 year interval. I worked with my long-term collaborator Dr Magomedkhan Magomedkhanov of the Russian Academy of Sciences Daghestan Scientific Centre who has been running a natural dye project for 10 years as a revival of the tradition which ceased about 1870. This is a development of the DHA 24 poster session in Liverpool in 2005.

From our ethno-botanical expeditions in Daghestan I brought back:

1. Examples of the best madder roots in the world, from the Derbent area, according to an 19th century French analysis
2. Walnut skin powder for black.
3. Cats' pears berries for purple tattoos and ink from a 3-metre high bush which grows in one cemetery in Gapshima village, unknown outside Gapshima in Daghestan
4. Alpine rhododendron scrub bushes for yellow and green which only grow above the woods over 3000 metres near Archi village. This plant is unknown outside Archi in Daghestan.

The first and last, as I am informed, make invigorating medicinal teas madder as a vulnary and rhododendron as a strained joint healer, and both also have aphrodisiac properties. Cats' pear berries are poisonous to eat.

Botanical specimens will be on show; also photographs of plants and a map. Also a carpet and a felt which use the dyes will be shown. We hope to have the 'new' plants 3. and 4. identified by RHS Kew, and to show the results of preliminary chemical analysis.

Comprehensive analysis of historical fabrics from the collection of National Museum in Warsaw

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Abstract

Liturgical vestments of Orthodox Church are very rare in the collection of the National Museum in Warsaw. The paper concerns two fabrics probably from the turn of 16th or the beginning of 17th century. The first was a donation of 1929 from the collector Jadwiga Bobińska. It presents Jesus Christ enthroned, with the Gospel in his left hand, blessing with the right one. There are inscriptions around the crosses flanking Christ's head, and on the side of the footrest, around the crosses flanking Christ's head, and on the side of the footrest, which are difficult to see and read due to the thread-bare condition of the fragment. The letters are Armenian. The figure of Christ is repeated twice on the surviving fragment (23x18 cm). It is a lampas-weave silk, with metal thread and patterning wefts in ivory, light red, green and blue.

The second fabric was purchased by the Museum in 1917 from a private collection. It is also lampas-weave silk, with a metal thread and patterning wefts in white, black and blue. It depicts Christ in liturgical vestment with hands raised in a blessing gesture wearing - the miter and the epitrachilion - within an oval medallion regularly repeated. Between the medallions are crosses with the white and blue Greek inscriptions ЇC XC an NK - Ιησούς Χριστός Νίκά. The fabric is a fragment (80 x 21 cm) of a liturgical vestment in the shape of the chasuble side column, sewn from the six smaller fragments. Due to the great amount of the gold thread the fabric was very precious. After destruction of original vestment (saccos) it was re-used probably in 18th century.

Even in their current condition, the fabrics show at first sight many similarities. Both come from liturgical vestments of orthodox churches, depicting a repeated motif of Christ. There are crosses and inscriptions on both of them. Colors are also similar – the basic warp is red and binding warp is white. Lampas weave and metal threads make the structure similar, too.

However, despite these similarities after a closer look the fabrics show some substantial differences. The first one concerns iconography - in the first fabric Christ is depicted as a Pantocrator on the throne, in the second as a priest in miter and saccos. Inscriptions are in different languages and the shapes of cross and nimbus are different. After the more detailed analysis one can see significant distinctions in the fabric construction and the properties of the threads used for warp and weft - for instance the first fabric is brocaded while in the second one the metal weft is applied as a patterning weft.

The above mentioned similarities and distinctions were the reason to undertake the comprehensive analysis of the fabrics. Except for the analysis of dyes and metal threads, which will be presented in a separate paper, the detailed analysis of the structure and technology of the fabrics, and the structure of the warp and weft threads was completed. On the basis of these analyses the visualization of weave pattern was made. We also made an attempt to computer-assisted reconstruction the original appearance of the fabrics. It resulted in partial identification of the fabrics and showed substantial distinction in manufacturing methods, suggesting different provenances of the fabrics. The paper will also present an iconographic and historical analysis of the fabrics on the basis of analogous examples from various museum collections.

A critical examination of methods for black dyeing

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Abstract

There are many methods which have been published for black dyeing. Some involve more than one dye e.g. indigo top dyed with madder but the majority are single black dyes. Many recipes involve iron compounds and tannins but there are different ways of getting the constituents onto the fibre. Examination of old recipes show that some involve the immersion of fibre into preformed black dyes, in some cases the fibre will already be impregnated with a tannin. The preformed black can be made using metal powder or by using iron salts. Other times two tannins will be applied sequentially. Maori methods involve the use of black muds which are rich in iron and which are applied to yarn already impregnated with tannin. This paper will consider mechanisms for dyeing and consider whether reduction of the iron(III)-tannin complex might play a part in the dyeing process.

The microbiology of the medieval woad vat

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Abstract

This poster illustrates the preparation of the woad vat and the fermentation involved. It explains the analysis of the indigo reducing bacteria and its identification.

Finally the poster explains the medieval procedure in modern terms and the future possible commercial applications.

The dyestuffs used in the royal Sicilian robes

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Abstract

This poster illustrates with samples the dyestuffs and mordants used in creating the Siclian Coronation robes of the 11/12th centuries AD. Photographs of the robes are attached to indicate the colours achieved. These robes are contemporary with the Bayeaux tapestry and illustrate the superb achievements of Byzantine craftsmanship.

Natural dyestuffs in Pre-Columbian art

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Abstract

The Art Diagnosis Laboratory of the National Autonomous University of Mexico has been working on Mexican dyes mentioned on XVI and XVII century documents, material analysis from pre-Columbian mural painting, preliminary studies on different XVI and XVII century codexes, and picking up information from traditional artisans from the states of Oaxaca and Michoacán that continue the use of local dyes for the production of their art work.

Our approach has been both experimental and theoretical, since the use of specific colorants is mentioned on historical documents, and the material analysis of mural painting and codex reveal the existence of many pigments of organic origin.

We aim to identify the material, and at the same time to establish an analytical protocol to identify the constituents of the dyes using non-destructive methods. We believe that the project must follow different investigation paths: Field work has proven that besides the classical colorants mentioned in the historical papers that come from the High-plateau of Mexico, the geographical richness of Mexico show us that there are many other unidentified colorants materials that are still in use.

On the other hand, the proper identification of the organic material is a known problem for most scientific conservators: the quantity and degradation of the historical samples, being an important issue. We have been experimenting with the different electromagnetic radiations in order to establish an efficient approach without the need of sampling.

Our experiments cover the production of artificial pigments, the measurement of original pigments in historical documents or works of art, and we are now starting with the generation of a material data base using different analytical apparatus, such as RAMAN, FTIR, IR reflectography, and UV photography.

We also are interested in promoting research related to the chemistry of the colorants, thus opening the investigation towards other uses and possibilities. For instance the non-pollutant use of dyes and mordents for the indigenous communities of today's Mexico, and thus, promote the study of the organic materials in grand scale in order to establish identification protocols and material standards.

Many collaborators have worked in this project: Sonia Ovarlez, studied the maya blue for her master degree in chemistry, University of Nice. The pre-Hispanic mural painting project, from the Aesthetic Research Institute, where the laboratory is located.

The non-destructive material analysis project carried out with José Luis Ruvalcaba, and the Anthropological and Historical National Library for the study of Codexes, and also the identification of organic pigments, presumably lakes used in the early colonial period. We have just started our first encounters with the Spanish group of CSIC, in order to establish a collaboration project by means of SERS- RAMAN. We are not able to give any conclusions so far, yet the problematic seems interesting enough to discuss with a group of experts in the field.

The analysis of Phtalocyanine pigments presence in paintings with aid of non-destructive method in situ

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Abstract

Phtalocyanine synthetic organic pigments (PhP) had appeared at the end of 1930's. They possessed unique artistic and technological peculiarities:

- They have very intensive green, blue or violet colours.
- They are insoluble in many liquids of paintings.
- They are extremely resistant to many aggressive natural factors, first of all, to action of light.

The painters immediately appreciated their values and began to use them as paint pigments already in the beginning of 1940's. The presence of the PhP in painting allows one:

1. To establish that a painting was created after the beginning of 1940's.
2. To reveal falsifications in the Russian Avant-Garde paintings (1900-1930) created after the beginning of 1940's.

So it was very important for painting's scientific research to encounter PhP in them «in situ» using non-destructive method, without of micro samples collection. It is possible now to obtain a portable commercial apparatus (120 x 62 x 20 mm) with the special effective sensor. This apparatus can indicate the presence or the absence of the PhP in many art monuments, first of all in paintings. If the apparatus' sensor contacts with any surface coloured with PhP one can hear a sharp acoustic signal. If PhP are absent in paint, no signal is audible.

First of all it was necessary to check if this apparatus can reveal the presence or the absence of PhP in much thicker paint layers of easel paintings. Especially for these purposes there were prepared model samples of paint layers. They contained 70 various green and blue PhP as well as the high content of organic binding media. The analysis of these model samples with an aid of portable apparatus provided the following results:

- The apparatus uttered an acoustic signal being put in contact with 95 % model samples containing studied PhP.
- In the same time the model samples containing other green and blue organic and inorganic pigments did not let out any sound.

The PhP model samples indication depended on the value of the minimal meaning of reflecting spectra in near infrared fields (1-10 microns). It was possible to detect the PhP when the value of the minimal meaning of reflecting spectra was 0,8. If other pigments were present in the paint layer, the possibility to reveal PhP depended on the sum value for the meaning of reflecting spectra in near infrared fields in this pigment mixture.

Imitating historical dyeing methods from the Hallstatt period - dyeing experiments with weld, indigo and oak bark

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Abstract

The results of the project Halltex 1 showed that the textiles from the prehistoric salt mine of Hallstatt in Upper Austria were dyed with plant and insect dyes.[1] In most of the analysed textiles the element copper was detected. Possible copper sources are copper containing mordants used in the ancient dyeing processes and/or the conditions under which the textile fragments were embedded in the "Heidengebirge" ("heathen rock"). In this area, naturally copper containing salt rock can be excluded. Therefore the broken off tips of bronze picks from the Hallstatt period (800-400 B.C.), which are found in the "Heidengebirge", are supposed to be the source of copper.

To find out how different mordanting and dyeing methods as well as the embedding conditions in the "Heidengebirge" influence the copper content in textiles, wool samples were dyed with plant dyes and buried in the "Heidengebirge". Analysis of the copper content before and after the embedding in the salt shall enable conclusions about the determining parameters.

The dyeing experiments should imitate dyeing procedures which possibly could have been used in the Hallstatt period. At the same time, the experiments should also meet the high requirements of modern methods of analysis: standardized test materials, standardized dyeing methods and avoidance of non definable influences during the dyeing process. The poster presented at the conference describes the dyeing methods and shows the dyeing results.

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Ganjifa: Rejuvenation of ancient card game of India

Suvarnareha Jadhav

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Abstract

Among India's immortal architectural and artistic legacies is a unique game of card, Ganjifa. While it is believed to be of Persian origin, it also features imprints of Dashavatara (ten reincarnations of Lord Vishnu), Rashis (planets), and other folklore, highly characteristic of Indian design, style, and artistry.

Brightly painted Ganjifa cards are made by bonding layers of cotton cloth with tamarind seed paste, coated with chalk and sun dried. Finally it is polished with a stone to make a smooth base for painting with natural dyes and pigments such as those produced from flowers, leaves, barks, roots, etc. The backside of the card is stiffened with lacquer to provide it the mechanical strength.

Ganjifa playing cards once well known in royal families all over India declined in popularity with the abolition of princely titles. However, about 350 years ago, after fleeing from the Portuguese regime, the Bhonsale royal family of Goa settled in Sawantwadi, (Southwest India), revived this card game. They brought several artisans well versed in woodcarving and painting who made their livelihood by supplying the royal family with handcrafted items. In the 1960s there were 45 artisan families practicing this art, though today, only six live in Sawantwadi. In this poster presentation we provide historical information including deducted mechanism of Ganjifa production and rejuvenated interest in this unique card game in modern India and elsewhere.

Surface Enhanced-Raman Spectroscopy (SERS) as an analytical tool in the detection and characterization of natural dyes employed in cultural heritage

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Abstract

The identification of dyes used in works of art is essential for dating, restoring and conserving artwork and for studying art history in general. There is a wide range of works focused on the analysis of inorganic pigments. In contrast, organic dyes have been less studied although natural pigments have been used as coloring materials in Cultural Heritage artworks throughout the history. Raman spectroscopy has been firmly established as an invaluable technique for the identification of materials found in works of art and Cultural Heritage. This noninvasive technique allows for the study of microscopic samples with great spatial resolution when a microscope is used as a sampling accessory. By means of SERS, the inherent limitations of Raman spectroscopy are readily overcome thanks to the use of nanostructured metal surfaces to enhance the signal and to quench the fluorescence at the same time. The intensity of the normally weak Raman scattering is increased by factors as large as 108 for compounds adsorbed onto a SERS substrate, allowing for trace-level detection[1].

The vast majority of organic coloring materials belong to the chemical classes of flavonoids (yellow), anthraquinones (red), and indigoids (blue). These dyes were largely used for textiles. The most widely used and traded flavonoid-containing yellow dyes in western Europe included *Reseda luteola* L. (weld), *Chlorophora tinctoria* Gaudich. (old fustic), *Genista tinctoria* L. (dyer's greenweed) and bark from *Quercus velutina* Lamk. (quercitron bark)[2,3]. In spite of the enormous importance of the flavonoid compounds, only few Raman studies applied to flavonoids have been published so far. Generally, only a limited number of Raman spectra of natural dyes are available in the literature[4]. In addition, few SERS studies have been published so far on flavonoids[5,6], although the SERS spectroscopy has been successfully applied to other natural dyes[1,7]. In this work a detailed vibrational characterization was accomplished for a group of flavonoids with related structure which varies depending on the presence of double bond and/or carbonyl group as well as on the number and position of substituted hydroxy groups. The first SERS experiments of reference samples were also done.

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Consolidation of degraded iron-tannate fibres on Maori waist garment - Puipui

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Abstract

The indigenous Maori people of New Zealand tradition wove garments from the fibres and leaves of *Phormium tenax* (New Zealand Flax). One of the dyes used to decorate these garments was a black iron-tannate complex which degrades and embrittles the *P. Tenax* substrate to which it is applied. As a result, various elements of the dyed garments are subject to loss of mechanical integrity and fracture. The treatment of a Piupiu waist garment of traditional Maori costume using a novel consolidant, zinc alginate, on degraded fibres that have been traditionally dyed with the black iron-tannate dye (an iron-containing mud known as paru and tannin treated substrate), *P. tenax* is presented. A “once only” approach is taken with limited handling, support, consolidation and attachment of broken waist garment lengths.

Tyrian Purple in Mycenaean wall paintings of the 13th century BC in Pylos, Greece

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Abstract

The aim of the present study is the investigation of organic dyes contained in paint details of fragmentary wall paintings from the “Palace of Nestor” at Pylos, Greece. The Mycenaean Palace is located on a low hill in western Messenia on the southwest coast of the Peloponnesus (Navarino bay) and is dated in the LH IIIB period (13th century BC).

Microsamples selected for this study were in the gamut of red – purple shades, providing indications for the presence of organic pigments. For that reason, indirubin, 6-bromoindigotin, 6’-bromoindirubin, 6-bromoindirubin, 6,6’-dibromoindigotin and 6,6’-dibromoindirubin were synthesized to be used, along with other commercially available compounds (e.g. indigotin, alizarin, purpurin etc.), as reference compounds for the FTIR and HPLC analysis. The indirubins and the substituted indigotins were synthesized, and purified, according to published procedures from the commercially available compounds; isatin, 6-bromoisatin, and 3-acetoxyindole.

Vibrational signatures, collected by FTIR revealed the presence of several indigoid compounds in purple paint details of the wall fragments providing evidence for the use of Tyrian Purple. In all samples of similar purple shades, 6,6’-dibromoindigotin and 6,6’-dibromoindirubin were clearly identified. In most cases, weaker spectral features were ascribable to other compounds such as indigotin, indirubin and 6-bromoindogotin. A proteinaceous material was detected in all paint samples, while characteristic bands of the carbonate group CO_3^{2-} indicated the presence of calcium carbonate in the form of calcite, not only in the ground, but, in the paint layer as well. In several spectra the form of aragonite was also detected. Finally, Egyptian blue was identified either in mixture with purple to give dark purple shades or as an underpaint of the pink-purple paint layer. Apart from conchylian purple, no other red organic pigments have been detected in the investigated samples.

An effort to apply HPLC-PDA for the detailed analysis of the organic colorants contained in the historical samples is currently under progress. Some samples have been already analyzed and seem to be in agreement with the FTIR data. We report, however, that extraction of the dye from the paint substrate appears to be not easy. Hot DMF, DMSO and pyridine were used to extract the organic colorants. However, the paint layer appeared to be unaffected even after extensive treatment with these chemicals which are good solvents for indigoid compounds. The liquid phase appeared to be colorless and indigoid compounds were detected as traces in the HPLC chromatogram. More aggressive chemicals (including acids) are currently tested to achieve dye extraction. More over, SEM-EDS experiments will be performed to gain a better understanding of both the microstructure of the paint layer and the chemical composition of the organic pigment.

Capillary electrophoresis versus liquid chromatography - alternative tools for identification of anthraquinone natural dyestuffs

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Abstract

Anthraquinones are important biogenic compounds, but they also were used as colouring matters for painting and textiles dyeing. Nowadays, analysis of these substances becomes much more easy and simple than in the past. Even very small amount of a sample can be used for analysis performed with use of highly selective and sensitive modern techniques. Reversed phase liquid chromatography (RPLC) with diode array detector DAD and electrospray mass spectrometer ESI MS are most often used for the identification of anthraquinone colouring components of natural dyestuffs. However, separation by capillary zone electrophoresis (CZE) coupled to these detectors also creates efficient tool for such analyses. This technique is simple and requires minimal sample volumes (to 50 nl), what is very important for the examination of works of art. Electrophoretic separation is performed thanks to different migration of solutes in an electric field. High electrical fields ensure short analysis time and high resolution.

For CE – DAD – ESI MS, electrospray mass spectrometer was found as much more appropriate detector in comparison to diode array one due to higher sensitivity (detection limits in the range 0.1 – 0.5 $\mu g \cdot ml^{-1}$) and selectivity. In case of RPLC separation, electrospray mass spectrometer offers detection limits in the range 0.03 – 0.09 $\mu g \cdot ml^{-1}$ for the examined compounds. The developed methods made possible univocally identify carminic acid, isoforms of laccaic acid, alizarin and purpurin as colouring matters in examined preparations of cochineal, lac-dye and madder, respectively. The presented methods allow fast, direct and straightforward identification of colouring components of natural dyes used in art and could be very helpful in restoration and conservation procedures.

Indigo in the Romanian tempera paintings, 15th -19th century

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Abstract

The paper presents our modest contribution in micro-chemical analyses made between 1967-2007 regarding tempera painting: icons and paintings made on Romanian wood churches. The research began more than 40 years ago, when Mr. Istudor, the first investigator of art object in the NMAR started to study this kind of objects and continued this job for the monuments. Since 1976, I continued this work in NMAR. Now, we are able to present our results, in a table format, with the name of icons, churches, period and location.

Indigo was found in 4 churches, one painted ceiling in a house in Sibiu from 15th century, and in 13 icons from 16th -19th century; the distribution of them is: Transilvania 10, Walachia - 6 and 2 in Moldavia (the old territory of Romania).

Ageing of natural red dyes – theoretical and experimental study

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Abstract

Natural dyes are organic compounds that are highly sensible to environmental conditions particularly due to photodegradation. Colour fading of textiles is a major concern to museums and conservators and therefore the study about the degradation mechanisms is a key issue for their adequate long-term conservation. Unlike most colours used in textile dyeing, red hues can be obtained both by animal and plant sources. Chemically red dyes are mainly substituted anthraquinones with the exception of brazilein obtained from Brazil wood. These dyes fade to yellow probably due to cleavage of the parent compound.

This work is part of a project (experimental and theoretical) that envisages the identification of the dyes and mordants used throughout the ages in the production of Arraiolos tapestries, one of the richest artistic Portuguese expressions in terms of textile production, and the establishment of the major factors (like mordant, humidity and light) that are responsible for the colour and fading of the natural dyes as well as for the degradation of the fibres.

In this work we present an experimental and theoretical study on red dyes that were used in the production of Arraiolos Tapestries. Wool fibers dyed with several natural red dyes were subjected to controlled accelerated ageing conditions. A temporal study was undertaken by sampling the dyed fibers at regular intervals. The fibers were analysed by colorimetry and the dyes were extracted by a previously optimized extraction procedure and analysed by LC-MS.

The molecular geometry of each free dye, degradation products and their dye-mordant complexes was optimized at DFT level using the Gaussian03 package [1] at DFT/B3LYP level. After each optimization, the electronic spectra of the free dye molecules, degradation products and mordant/dye complexes were calculated by TD-DFT [2] in order to identify the origin of the colours and characterize the influence of metal coordination on colour modifications. The results show a good agreement between theoretical predictions and experimental spectra of both original dye and degradation products. The theoretical results allowed a further insight on the electronic processes, which are responsible for their colour spectra.

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Some aspects on MS detection of dyes in historic textiles

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Abstract

Liquid Chromatography with UV-VIS (Dioden Array) Detection has proved to be a valuable tool in the identification of dyes in historic textiles, being successfully applied in laboratories all over the world for more than 20 years. However, development of Mass Spectrometry as detector in liquid chromatography opened a wide range of new applications. Several laboratories, mostly from the academic field, published contributions underlining the use of HPLC-MS both as a complementary technique to HPLC-DAD in the identification of dyes by the molecular ion detection (MS) and as a useful tool in structural studies of unknown dyes (MS^2… MS^n).

A collaborative effort between the National Research Institute for Conservation and Restoration (INCCR), Bucharest, Romania and University Bucharest, Faculty of Chemistry, Cathedra of Analytical Chemistry, with the support of LaborMed Pharma Laboratories, Bucharest, Romania was established in order to build an analytical protocol of natural dye analysis in historical textiles by HPLC with DAD and MS detection, based on the recent experience accumulated at European level within the Eu-Artech project.

The poster will include a discussion on MS^{2-} fragmentation of selected flavonoides and antraquinones on Ion Trap Mass Analyser compared with Triple Quadrupole and some comments resulted from the application of HPLC-DAD-MS (Ion Trap) in the analysis of dyes in historical textiles.

Characterization of purple from burials of the Roman period by Raman and DE-MS

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Abstract

The chemical analysis of residues of organic materials from archaeological burials is a precious source of information for archaeologists. Identifying the materials and collecting data on the treatments of these materials, allow us to reconstruct technology and funerary practises. A wide range of natural substances may be found in association with archaeological burials. Of these, organic colours are known to have been used extensively by ancient populations for dying textiles, as ingredients for cosmetics, balms and medications, and as symbolic materials.

This work describes an investigation of the chemical composition of violet organic dyes from two burials dated back to the third century AD and discovered in Naintré and Anché (France), respectively.

An analytical methodology, based on the use of complementary techniques, Raman spectroscopy and direct exposure-mass spectrometry (DE-MS), was developed for studying the samples collected from the two tombs. Reference molecules and materials were used to test the methodology and to build up spectroscopic and mass spectrometric databases.

Raman analysis performed on the samples collected from the tombs discovered in Naintré and Anché allowed us to provide evidence of some bands ascribable to purple. DE-MS analysis revealed the presence of 6,6'-dibromoindigo, monobromoindigo and indigotine allowing us to assess the occurrence of purple in all the samples.

The magic red and purple in natural colours and their UV barrier properties

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Abstract

The paper is a part of the study of red colours and shades obtained from natural sources and their UV barrier properties. Although most natural dyes come from plant sources, some of historically important dyes were derived from selfish and insects.

The presentation concerns research carried out as part of the research project concerned with the scientific basis of the cultivation of the natural dyeing plants and creation of the collection of data on existing natural dyes and production process.

The Institute of Natural Fibres has done research to compare the result of UPF protection on linen and silk samples dyed with natural dyes.

The transmission, absorption, and reflection of UV radiation are in turn dependent on the fibre, fabric construction (thickness and porosity) and finishing. Many dyes used in finishing process, absorb UVR. In this study were analyzed many shades of red and purple colour applied on silk and linen fabrics.

The results of our experiments will present the large variation in hue of red colour and the influence of finishing process on UV barrier properties. The examples used in illustrating this paper will show the range variations to be achived in examining the extracted from the: Madder *Rubia tinctorum* L., Saflower *Carthamus tinctoria* L., Indian Madder *Rubia cardifolia* L., Annato *Bixa orellana* L., Pomegranate *Punica granatum* L., Logwood *Haematoxylum campechianum* L., Sappanwood (red wood) *Calsapinia sappan* L. And insects dyes: *Kerria lacca Kerria laccae*, Cochineal *Coccus cacti* in the conjunction with a broad spectrum of alternative mordants.

In our experimental work we have obtained beautiful shades of red colour: light pink, pink, indian red, light coral, red, crimson, orchid, coral, hot pink, purple, magneta, violet.

Bacteriography - multiorganismic art painting

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Abstract

Bacteriopraphic paintings are created with living, colour-producing bacteria. The skill of the artist (bacteriopgrapher) consists of transposing his artistic ideas by painting with these initially invisible organisms which subsequently develop their colourful appearance.

The hidden and invisible “microorganismic objects of beauty” originating from air and water are thereby not only made visible but are also able to show all their inherent capabilities, for example, their own mobility, production of special strucures, light and shadow effects.

The artist (bacteriographer) is their director – quasi their conductor – the painting undercoat thereby functions as the “stage”.

Consequently, a bacteriographical painting is, as it were, an allegory on a play – it obtains through the art of its coming into being a completely special “bacterial charm”.

By fixation and application of a special topcoating, the formation process is ended and the finished “natural painting” (bacteriography) can be exhibited behind special glass (museum glass) just like a conventional painting.

Remarks

The artist is present on Thursday, 8th of November from 12.00 – 13.30 hrs. and on Friday, 9th of November 2007 from 12.30 – 13.30 hrs. During the above – mentioned times, original works of art of the bacteriographer Erich Schopf can be viewed.

Sex-specific Tyrian purple genesis and precursor distribution in the pallial gonoduct of Dicathais orbita (Neogastropoda: Muricidae)

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Abstract

Exploitation of Tyrian purple from hypobranchial gland secretions of muricids since antiquity has prompted much interest in its chemical composition. Nevertheless, there remains a paucity of information concerning the distribution of dye precursors in the reproductive system of the Muricidae and the biosynthetic routes leading to observed differences in pigmentation between male and females. In this study we have developed a method for simultaneous quantification of the dye precursors and pigments using HPLC-DAD coupled to ESI-MS. The ultimate dye precursor tyrindoxyl sulphate was detected for the first time using this technique and dominated DMF extracts of hypobranchial glands, female capsule, albumen and ingesting glands, and male prostate glands. Intermediate precursors, tyrindoxyl, tyrindoleninone and tyriverdin were also detected in female hypobranchial and capsule glands, along with the blue-purple pigment 6,6'-dibromoindigo. Male hypobranchial and prostate glands were found to contain the oxidation by-product 6-bromoisatin and the red-purple pigment 6,6'-dibromoindirubin. Multivariate analysis revealed statistically significant differences in the dye composition of male and female hypobranchial glands ($p = 0.002$). Together these findings provide the first evidence for sex-specific Tyrian purple genesis and the involvement of tyrindoxyl sulphate in muricid reproduction.

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Original Burgenland Indigo Prints Made by Hand

In former times, indigo print fabrics were used in Burgenland for clothes of everyday life and work. Our company (est. in 1921) is today one of the last businesses in Europe to use this traditional technique for printing fabrics and dyeing them with indigo.

The term indigo printing is not absolutely correct, as the fabric is not actually printed but rather dyed with indigo. The paste is applied onto the fabric using old wooden printing blocks and washed out again after dyeing. As a result, a pattern in white appears against a blue background.

Some of our printing blocks are more than 200 years old and carved in pear or lime tree wood. Brass pins are used to refine the patterns.

The recipe of the paste is the well-treasured secret of the indigo printer. Only a small number of written records have survived. Each printer has his own special recipe which is passed from generation to generation. But we can tell you this much: gum arabic and clay belong to the main ingredients.

Once printed, the fabrics (linen, cotton, silk) need to dry for approx. three weeks before they are dyed. The fabric is suspended on a round frame using small brass hooks. Tiny perforations on the hem of the fabric remain, which are typical of this mode of dyeing. Water, indigo and lime are the main ingredients of the dye bath.
Depending on the desired intensity of the blue hue, the dyeing procedure may take up to four hours. Subsequently, the paste is washed out and the fabric is dried in the open air.

Our speciality is making double-sided prints showing a different pattern on each side. These fabrics are handcrafted using an old rotary printing machine.

Today, our indigo prints once again enjoy great popularity. Although they are very labour-intensive, we take pleasure in our work and are continuously encouraged by our customers´ approval.

Sincerely,
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Photos on the front page:

Manuel Wandl: Der blaue Faden
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Blaudruckerei Koó: Blue resist print

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