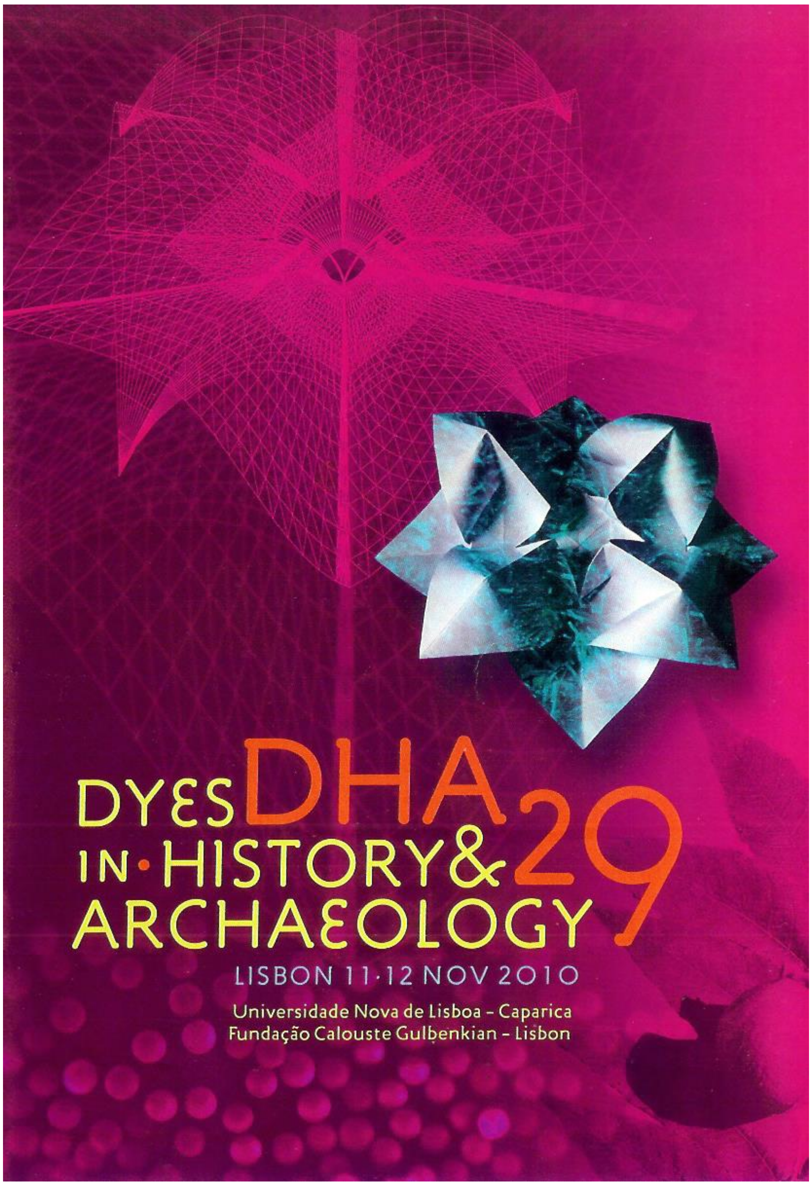
DYES IN HISTORY AND ARCHAEOLOGY 29
LISBON, 11–12 NOVEMBER 2010



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Abstracts of papers and posters

Dyes in History and Archaeology 29, Lisbon, 11–12 November 2010

A visit to the Museu Nacional de Arte Antiga took place the day before the meeting (10 November) and it was followed by an optional visit to Évora and Portalegre on Saturday, 13 November 2010.

List of papers presented

11 November 2010, Auditório da Biblioteca Faculdade de Ciéncias e Tecnologia, Campus Caparica, Universidade Nova de Lisboa

Chika Mouri and Richard Laursen, 'Kihachijō, an unusual, traditional Japanese yellow dye'.

Vanessa Habib, 'Dyeing and printing in Edinburgh in the Age of Enlightenment: the manufacturing interests of Andrew Fletcher of Saltoun, 1692–1766'.

Nicolas Garnier, Dominique Cardon, Xavier Machuron-Mandard and Oliver Vigneau, 'Mass spectrometry versus Raman microspectrometry: a comparative approach for the investigation of True Purple and imitations'.

Agnieszka Leśkiewicz-Laudy, Dariusz Ruszkowski, Livia Rajpert, Adam Jagielski and Aleksandra Skłodowska, 'Microbial decolourization and degradation of natural red dyes extracted from genuine silk velours in Wilanów Museum-Palace'.

Zvi C. Koren, 'New findings of the biblical *argaman* purple dyes at Masada: an HPLC-PDA multicomponent study'.

Irina Petroviciu, Ileana Cretu, Ina Vanden Berghe, Andrei Medvedovici and Florin Albu, 'LC-MS and LC-MS/MS dye analysis on textiles and parchment documents from Romanian collections'.

Rosemary Baker, 'The public perception of synthetic textile dyes in England in the late nineteenth century'.

Cristina Montagner, Mauro Bacci, Susanna Bracci, Rachel Freeman and Marcello Picollo, '*The Dyeing of Paper in the Pulp*: handbook in the past, database in the present'.

Cátia Souto, Micaela Sousa, Ana Dias and M. Conceição Oliveira, 'Characterisation of early synthetic dyes by HPLC-DAD-ESI/MS^n'.

Katarzyna Lech and Maciej Jarosz, 'LC-ESI MS/MS study of pre-Columbian Peruvian textiles from the State Ethnographic Museum in Warsaw'.

Matthijs de Keijzer, Maarten van Bommel, Regina Hofmann-de Keijzer and Regina Knaller, 'Indigo carmine: favored but fading'.

12 November 2010, Auditório 3, Fondação Calouste Gulbenkian Lisboa

Ana Manhita, Teresa Pacheco, António Candeias Teresa Ferreira and Cristina Barrocas Dias, 'Material study on historical Portuguese Arraiolos tapestries (17th–19th century period)'.

Estrella Sanz, Angela Arteaga, Maria Antonia García and Carmen Cámara, 'Characterization of natural and synthetic dyes employed in the manufacture of Chinese garment pieces by LC-DAD and LC-DAD-QTOF'.

Yoshiko Sasaki and Ken Sasaki, 'ESI mass spectrometric analysis of the early synthetic dyes'.

Lore G. Troalen, Alison N. Hulme, Hamish McNab, Jim Tate, Helen Hughes and David Howell, 'English "Sheldon" tapestry workshop in the mid-16th century: characterisation and provenance through PDA-HPLC analysis'.

Alessia Andreotti, Maria Perla Colombini and Ilaria Degano, 'The identification of the organic painting materials in Andrea Mantegna's *Pala di San Zeno*'.

Jan Wouters, Cecily Grzywacz and Ana Claro, 'Safflower (*Carthamus tinctorius* L.). History of use in China; ancient and present-day preparation technologies; a new identification strategy'.

Jens Bartoll, 'Silk in the Prussian royal palaces: dye and pigment analysis'.

Krista Vajanto and Riikka Räisänen, 'Folklore red in Finland'.

Isabella Whitworth, 'The orchil trail: from Portugal and Angola'.

List of posters

A poster snapshot session was held on 11 November in the Auditório da Biblioteca Faculdade de Ciéncias e Tecnologia, Campus Caparica, Universidade Nova de Lisboa, during which each poster was presented briefly. The full poster session was held on 12 November 2010 at the Fondação Calouste Gulbenkian Lisboa.

A.O. Adetuyi, T.L. Akomolafe, S.A. Adefegha, C.S. Odeyemi, G. Oboh and A.V. Popoola, 'Photovoltaic, antioxidant and neuroprotective potentials of some natural dyes of tropical Africa'.

Jeyhun Eminli and Khaqani Almamedov, 'Similarity and variation in painting motifs of the Eneolithic and Antique pottery of Azerbaijan'.

A. Baran, E. Mrozek and M. Baranska, 'Application of vibrational spectroscopy for detection of luteolin and its complexes with Al(III)'.

Emre Dölen and Serap Ayaz, 'Determining stability constants of kermesic acid and flavokermesic acid complexes with aluminium(III) by potentiometric method'.

Lina Falcão, Maria Eduarda M. Araújo and Pedro D. Vaz, 'Study of nineteenth century green morocco leather upholstery'.

L. Tobias, S. Salvador, A.Manhita, H. Vargas, I. Ribeiro, A. Candeias, D. Teixeira, C. Barrocas Dias and T. Ferreira, 'The color hue and photostability of wool dyed with plants traditionally used in Alentejo region'.

Art Néss Proaño Gaibor, Jo Kirby Atkinson, Maarten van Bommel, David Peggie, Ina Vanden Berghe, Ioannis Karapanagiotis, Sophia Sotiropoulou, Thibaut Deviese, Catherine Higgit, Costanza Miliani, Heike Stege, Mark Richter and Susanna Bracci, 'Collecting botanical sources: Joint research on organic pigments and dyestuffs'.

Thibaut Deviese, Catherine Higgitt, Janet Ambers, Jo Kirby and St John Simpson, 'Study of pink colorant residues in archaeological ceramics from Kush and Siraf, two sites on the Persian Gulf'.

Thibaut Deviese, Catherine Higgitt, Ioannis Karapanagiotis, Jo Kirby, Maarten van Bommel and Ina Vanden Berghe, 'Review of extraction methods for the characterisation by HPLC of organic colorants in textiles and pigments in cultural heritage objects'.

Katarzyna Lech and Maciej Jarosz, '1930 Spring color palette of Lyon Dyers' Guild – tandem mass spectrometry in identification of early synthetic dyes'.

Emine Torgan, Recep Karadag and Turkan Yurdun, 'Dyestuffs examination of *Quercus infectoria* and *Quercus ithaburensis* by the fermentation'.

Marie Marquet and Dominique Cardon, ‘The Rainbow project: a collaborative platform and online database on natural dyes and textile fibres’.

F. Franco, J. Lucas, R. Miguel, A. Manich, D. Cayuela and J. Carvalho, ‘The environmental sustainability era: a dyeing study of the wool/PLA blend’.

Leopold Puchinger, Ioannis Karapanagiotis, Dimitrios Mantzouris and Martin Puchinger, ‘Dyeing materials used for a Mediterranean carpet and a traditional Greek child costume around 1900’.

Raquel Rondão, J. Sergio Seixas de Melo, Jorge Parola and Maria J. Melo, ‘Indigo – one molecule, three forms, numerous applications’.

Masako Saito and Nobuko Kajitani, ‘The Color Standards Reference of natural dyes: Reds on Silk’.

Masako Saito and Nobuko Kajitani, ‘Thirteenth-century Sicilian lampas silk’.

R. Santos, J. Hallett, M.M. Sousa, Maria P. Cruz and N. Leal, ‘The mystery of three Persian carpets’.

Katarzyna Schmidt-Przewozna, ‘Revitalization of technology of natural dyeing in Polish double warp textiles’.

Maarten van Bommel and Jo Kirby, ‘Creating colours: the making of dyed textiles and organic pigments’.

Dyes in History and Archaeology 29
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PAPERS

Kihachijō, an Unusual, Traditional Japanese Yellow Dye

Chika Mouri[1] and Richard Laursen[2]

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2. Department of Chemistry, Boston University, Boston, MA. USA

Since at least the Edo period (1615-1868) and to the current day in Japan, the inhabitants of Hachijō Island south of Tokyo have specialized in the dyeing of silk threads and weaving them to produce distinctive yellow, red-brown and black textiles used primarily for the production of kimonos (http://www.youtube.com/watch?v=VRfqG2hX3Og). The most famous of the colors is 'kihachijō,' which means, literally, the 'yellow of Hachijō,' and is obtained from extracts of the grass, *Arthraxon hispidus*. The use of this plant as a dyestuff was described as early as the Warring States period (480-222 B.C.), and as the medicine, "Jin-cao," used for curing skin troubles, in "Shen-nong-ben-cao-jing," China's oldest treatise on medicinal plants. In the ancient literature of China and Japan, two grasses, *Miscanthus tinctorius* (Chinese dyeing grass, or "kariyasu") and *A. hispidus* are mentioned, sometimes interchangeably, as sources of yellow dyes. For example, a textile dyed by *M. tinctorius* was found in the 6th century Fujinoki tomb in Japan. Descriptions of *M. tinctorius* and/or *A. hispidus* can be been found in "Shosoin-monjo" documents stored in Shosoin and dating from the 8th century, " Engishiki" laws and regulations of the 10th century Imperial Court of Japan, as well as in many documents about dyeing methods in the Edo period. Analysis of extracts of *A. hispidus*, of fabric from Hachijō, and also of extracts of Chinese dyeing grass, *M. tinctorius*, by HPLC with diode array and mass spectrometric detection reveals not only that the dye profiles of *A. hispidus* and *M. tinctorius* are similar, but also that they are very complex. Furthermore, at least 80% of the yellow constituents seem to be heretofore unreported, acid-stable flavonoid C-glycosides. So far, the only reported C-glycoside dyes have been red carminic acid and its relatives found in cochineal and other scale insects. The use of dyeing grasses seems to be unique to East Asia.

Dyeing and Printing in Edinburgh in the Age of Enlightenment: The Manufacturing Interests of Andrew Fletcher of Saltoun, 1692-1766

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Andrew Fletcher of Saltoun, Lord Justice Clerk,nephew of the Scottish patriot Andrew Fletcher was appointed one of the Commissioners for Improving Scottish Fisheries and Manufactures after the Union of the Scottish and English Parliaments in 1707. He was the friend and political agent of Archibald 3rd Duke of Argyll. During his career Scotland modernised more quickly than any other European country. On his two estates near Edinburgh, at Saltoun and Brunstane, he directed experiments on a huge range of activities connected with the wool and linen manufacture, including dyeing and bleaching. He consulted with the leading Scottish chemists of the day and encouraged the setting up of highly organised bleachfields and printfields. At Gorgie printfield, on the Water of Leith close to Edinburgh, linen and cotton could be dyed with indigo or madder, printed with wood blocks and pencilled and later printed with copper plates. On the Brunstane estate Fletcher employed James Patterson, a scarlet dyer who had worked in London, for dyeing Scottish woollen cloth. Fletcher's close friendship with the Duke of Argyll who had created the estate of Whitton near London and was a serious botanist and scientist meant that new scientific ideas moved easily between London and Edinburgh. Andrew Fletcher and his colleagues were active in the manufacture of oil of vitriol, the cultivation of madder and the mining of alum, all resources previously imported to Scotland. In the first half of the 18thC the Scottish nation embraced industrial change and often led it through the effort and interest of enlightened patrons such as Fletcher. Described as a man who kept every scrap of paper addressed to him, Andrew Fletcher's huge and valuable archive in the Saltoun Mss in the National Library of Scotland enable us to follow in detail many of his manufacturing and scientific plans.

Mass Spectrometry versus Raman Microspectrometry: A Comparative Approach for the Investigation of True Purple and Imitations

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A new non-invasive method was implemented for the characterisation of natural dyes.

The detection and identification of natural dyes residues from ancient textiles has been the subject of two complementary approaches:

- invasive methods needing sampling and extraction of dyeing molecules and their analysis by separative and/or structural techniques (LC-DAD and LC-MS),
- non-invasive methods giving a global spectrum (Raman spectrometry, fluorimetry).

Part of the debate surrounds the ability of the methods to uniquely identify original dyes, without any sampling or by taking the smallest fibre as possible. Another is the opposition between the classical extraction performed with conc. HCl, and the use of much elaborated procedures using chelating and dissociating agents, in order to extract biomarkers without any degradation or structural modification as the hydrolysis of glycosyl group from flavanoids.

Desorption electrospray ionisation mass spectrometry (DESI-MS) offers the potential to directly analyse dyes bound to the surface of artefacts. The method permits desorption of analytes under ambient conditions directly from a wide range of surfaces with little or no sample preparation. This has already led to its application in a range of areas, including forensic analysis of trace levels of narcotic drugs. It does not require destruction of the artefact (e.g. by taking a sample or dissolution) and can work in concert with other methods (in a further development, it would be followed by sampling and classical study by LC or µLC×LC, at a precise location).

Here we report the development of the DESI-MS methodology for the characterisation of Purple and its imitation. Dyeing baths, deposits of dyeing bath on different textiles and dyed textiles with the same dyeing baths, were analysed, in order to evaluate the potential of DESI-MS for the extraction of dyeing markers. The DESI-MS interface was fitted to an Orbitrap high resolution mass spectrometer, allowing the determination of exact mass of each detected biomarker. A range of intact dyeing agents were identified from:

- True Purple from Muricids
- Red and blue botanical sources used for imitating purple: superposition of indigo and modified madder purpurine-rich (or wild madder), *Osnoma* sp. and lichens

The collected data will allow the identification of the principal markers of each species. The potential applications to dyes characterisation of this new analytical tool are discussed, in comparison to Raman microspectrometry.

Microbial Decolourization and Degradation of Natural Red Dyes Extracted from Genuine Silk Velours in Wilanów Museum-Palace

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Wilanów Museum-Palace is a baroque royal residence, situated in the south of Warsaw (Poland). The wall decorations in patterned silk velvet (1710-1730) in the Genoan style, placed in King's Apartments, are one of the most spectacular, baroque interiors in Europe.

This study was focused on identification microbial contamination of the silk surfaces and the dye degradation in dyed silk fibres. Therefore the genuine velvets were examined and samples of dyes extracted from silk fibres were tested. The separation and identification of ancient red dyestuffs' constituents was performed by HPLC technique with the PDA (UV-Vis) and ESI-MS detection. Three natural red dyes: carminic acid, alizarin and purrpurin were extracted from the red silk threads. The presence of three proteolitic bacteria from genus *Bacillus* (*B. cereus, B. vallismortis, B. subtilis* –identified by 16S rRNA gene sequencing) were able to hydrolyse the silk fibres as well as to decolorize red dyes from the threads. Two experiments were carried out to check the ability of bacterial isolates to decolorization and degradation of dyes extracted from the textiles. The use of natural dyes as an only source of carbon and energy by isolates was tested in the first experiment. It was shown, that isolated bacteria were able to grow in medium with natural dyes as energy and carbon source. The growth was supported even by trace amount of yeast extract. *B. cereus* formed strongly dyed flocks in liquid medium with purpurin and alizarin. This phenomenon may be explained dye spots occurrence in some points of textiles. The rate and efficiency of dyes biodegradation was examined in the second experiment. Chemically pure standards of red dyestuffs, identical with natural ones were used as substrates for bacterial isolates.

Bacterial growth rate (cfu), pH changes, UV-Vis spectrum, microscopic and macroscopic observations were examined during bacterial growth. Concentration of dyes was measured using HPLC technique. It was shown, that all tested bacterial strains were able to decolorize/degrade choosen red dyes. The rate of alizarin and carminic acids degradation in all cultures was higher than in sterile control. Chemical degradation of purpurin was observed in sterile control and the difference in the rate of degradation of purpurin was clearly visible in *B. valismortis* culture only.

To this time moulds only were considered as microorganisms responsible for silk threads decomposition, as well as direct and indirect dyes degradation. Our studies present a great role of bacteria in these processes. According to obtained results, bacteria from genus *Bacillus* are able to utilize red dyes direct on historic textiles with high efficiency and this process is supported by silk protein hydrolysis.

New Findings of the Biblical Argaman Purple Dyes at Masada: an HPLC-PDA Multicomponent Study

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Nearly 2,000 years ago, the Jewish-Roman historian Josephus Flavius described the tragic events that befell those rebels fighting against the Roman occupation of Judea. Particularly poignant in his writings is the depiction of the last vestiges of fighters who took refuge atop the fortified palace of Masada built a century earlier by King Herod. In Josephus' narrative, as the Roman artmy was besieging the rebels' fortified positions with the final assault bein imminent, almost a thousand combatants and their families committed mass suicide rather than being taken captive by the Romans. This agonizing and controversial action, the fantastic palace remnants, and Masada's last stand against Rome has catapulted this site to be one of the most important in ancient Israel. Consequently, artifacts discovered from that site have not only historical and archaeological significance, but also convey personal and emotional ties to that time in history.

Textiles are one of the most personal of artifacts associated with the people who used them, and certainly the Masada artifacts are no exception. Masada presents a classic case study of the methods in which the ancients of the Roman Period produced purple-dyed textiles. The well-known examples of producing "fake" purple by means of vegetal and insect sources are well-documented and have been previously discussed at last year's DHA28 in Poznan, Poland.

This talk will highlight the latest research and discoveries pertaining to the use of real molluskan purple dyes found in a number of Masada textiles. These findings are surprising as previously only one such purple-dyed textile was discovered, which belonged to the 1st century BCE King Herod himself (1, 2). The possible ownership of these prestigious purple textiles is still a mystery and will be discussed. Based on the multicomponent chemial fingerprinting of the dyes by means of HPLC-PDA analyses, the main (if not the sole) Muricidae source for all the dyes investigated was the Hexaplex (= Murex) trunculus sea snail species. The various purple colors of these ancient textiles can be ascaribed to the variety of colors referred to in the Bible as Argaman – a "Priestly Purple" woolen dyeing.

(1) Koren Z.C. 2006. Color My World: A Personal Scientific Odyssey into the Art of Ancient Dyes. In A. Stephens and R. Walden (editors), For the Sake of Humanity: Essays in Honour of Clemens Nathan, Martinus Nijhoff – Brill Academic Publishers, Leiden, Netherlands, pp. 155-189.

(2) Koren Z.C. 1997. The Unprecedented Discovery of The Royal Purple Dye on the Two Thousand Year-Old Royal Masada Textile. American Institute for Conservation, The Textile Specialty Group Postprints, Volume 7, pp. 23-34.

LC-MS and LC-MS/MS Dye Analysis on Textiles and Parchment Documents from Romanian Collections

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In the last years an analytical protocol for the identification of natural dyes in historic textiles by LC-MS was developed within a joint research between MNIR/CCIS and the Department of Analytical Chemistry in the Faculty of Chemistry, University of Bucharest. This new approach, based on data collected on standard dyes and dyed fibers, progresively uses the MS and MS/MS features to identify and confirm the individual dyes extracted from very low amounts of fibers.

In this study the results obtained by applying this analytical protocol to the characterisation and identification of dyes and biological sources in textiles and parchment documents are presented as compared data previously reported within the same research group. Dyes in various 19th century textiles from South-East Europe and Asia Minor, preserved in the National Art Museum of Romania, are compared with those obtained on Romanian ethnographical textiles. Analysis on silk threads used to connect seals in 15th c. parchment documents (from the National Museal Complex Bucovina, Suceava) are discussed as compared with the results reported on religious embroideries from the same period.

The Public Perception of Synthetic Textile Dyes in England in the Late Nineteenth Century

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William Morris (1834-1896) and William Henry Perkin (1838-1907) were close contemporaries but had very different attitudes to textile dyeing which exemplify the dichotomy in late nineteenth century England between the Arts and Crafts movement and the application of science in increasing industrialisation. It is well-known that Morris championed the use of natural dyes for his textile productions whereas Perkin was the first to manufacture a textile dye from coal tar. Morris gained wide public fame during his lifetime, partly due to his political activism as well as his design work. In contrast, Perkin did receive recognition of his achievements but only among the newly emerging scientific community (even though he received a knighthood) not among the general public.

Indeed, the public reception of the new synthetic dyes in England was ambiguous. Their attitude varied from fascination to fear. There were many social changes taking place at this time including an increase in the volume of the popular press. This gave a vehicle for the popularisation of science and this paper analyses these sources for evidence of the attitudes to the new synthetic dyes ranging from the didactic through fascination to condemnatory. The 1862 London International Exhibition was an ideal platform for promoting the new dyes and was widely reported in a range of different types of publication.

Despite early optimism and predictions that England would be the main supplier of textile dyes to the world, the lead in the field was soon taken by Germany. Many reasons for this were advanced at the time including the taxation and free trade policies of the English Government, patent law and national character. Lack of adequate scientific education was also cited at the time and formed the basis of calls for reforms in this area. The response to this is explored through the case study of the Yorkshire College of Science and the teaching of dyeing there. The differences between the education systems in Germany and England and the contrasts in the development of the dye industries in the two countries show that Germany was more competent to exploit the new technologies and build an efficient industrial base.

The Dyeing of Paper in the Pulp: Handbook in the Past, Database in the Present

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The Dyeing of Paper in the Pulp is an handbook for papermakers, containing 408 samples of dyed paper, published by Interessen-Gemeinschaft (I.G.) Farbenindustrie in 1925. This book is an important source of information about materials and techniques used to produce coloured papers at the beginning of the 20th century. The I.G. Farbenindustrie, a German conglomerate of dyestuff companies such as Agfa, Casella, BASF, Bayer, etc., was one of most prominent factories for chemical products in the world and before the First World War had an almost complete monopoly, at least in Europe, on the production of dyes.

The development of analytical methodologies to be applied directly *in situ* on the dyed paper-fibers objects is strongly recommended. Often, these techniques are the only permitted to be performed on works of art by curators and conservators.

The characterization of the 82 samples in *The Dyeing of Paper in the Pulp* was performed by means of UV-Vis-IR Fibre Optic Reflectance Spectroscopy (FORS). The dyes belonged to different groups of compounds, such as azo, acridine, anthraquinone, azine, diphenylmethane, indigoid, methine, nitro, quinoline, thiazine, triphenylmethane, sulphur, and xanthene classes. The analysis of these samples by FORS gives a further contribute in the study of these specific papermaker products that so far have not been deeply investigated by non-invasive analytical techniques.

The samples were divided into eight groups depending on their predominant hues calculated from the acquired spectra according to the Commission Internationale de l'Eclairage (CIE); within each group it was also possible to obtain information about the chemical structure of the dyes by analysing the shape of the reflectance spectra.

In the present communication the definition of a UV-Vis-NIR reflectance spectral database and the potentiality of FORS for the characterisation of synthetic dyes will be presented.

Characterisation of Early Synthetic Dyes by HPLC-DAD-ESI/MS^n

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A detailed identification and characterisation of 62 early synthetic dyes from the Smithsonian´s Helmut Schweppe Collection using high performance liquid chromatography with diode array detection and coupled with electrospray tandem mass spectrometry was performed in order to develop a database for early synthetic dyes mostly used in historical textiles.

It was previously reported a HPLC-DAD elution method using MeOH and TEAA (triethylammonium acetate, 3 mM) as mobile phase that was successfully applied in the separation of dyes with sulphonic groups as well as dyes with other functional groups namely nitro, carboxylic, etc. [1]

We report herein, the structural characterisation of the 62 early synthetic dyes using multiple-stage tandem mass spectrometry (MS^n). The negative-ion ESI mode was used for anionic dyes with (poly)sulphonated and/or (poly)sulfated groups whereas non-ionic or cationic dyes were analysed in the positive-ion ESI mode yielding $[M+H]^+$ or molecular adducts in the mass spectra. The detailed interpretation of tandem mass spectra enables the correlation between the effects of the functional groups on fragmentation behaviour.

The analytical protocol and the database were successfully applied to the identification of samples collected from a Persian Carpet T107 from the beginning of 20th century from Gulbenkian Museum.

(1) M. M. Sousa, M. Ballard, J. Giaccai, C. Grzywacz 'Analysis of Early Synthetic Dyes with HPLC-DAD-MS and FTIR', Dyes in History and Archaeology 28, Poznan, Poland, 2009.

Acknowledgements

We wish to thank the Museum Conservation Institute (Smithsonian Institution) for having granted us the early synthetic dyes Schweppe's collection. We thank Maria Fernanda Passos Leite from Calouste Gulbenkian Museum (Lisbon) for the access to the Persian Carpet T107 samples.

This work is part of the Project *Unveiling the secrets of molecules with colour and history*, POCI/QUI-QUI/099388/2008. We acknowledge Fundação para a Ciência e Tecnologia for financial support under the scope of the Portuguese MS Network (IST-Node) - Project REDE/1502/REM/2005.

LC-ESI MS/MS Study of Pre-Columbian Peruvian Textiles from the State Ethnographic Museum in Warsaw

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Pre-Columbian cultures had been developing in South America until they were conquered or strongly influenced by the Europeans. One of the main South American territories, the ancient Peru, for thousands of years was inhabited by successive great indigenous civilizations, such as Chavin, Paracas, Nazca, Chimú and Chancay. In the 15th century, most of the contemporary cultures joined the Incas, thus forming the largest empire in pre-Columbian America, which was dismantled after the Spanish conquest in 1532. Nowadays, textiles remained of all these cultures are one of the best known art works. They include embroidery works, elaborate gauzes, mesh-like openworks, paint-decorated fabrics, tapestries and rag dolls. The most popular decorative motifs were deities, mythological creatures, birds, snakes, large cats and monkeys, as well as geometric designs and checkerboard patterns in various colors. A full palette of hues was obtained by the use of available native dyes, such as cochineal, indigo, annatto, madder-like plants of the *Relbunium* and *Galium* species, logwood, brazilwood and old fustic. A diversity of applied preparations shows how high the level of Peruvian civilizations was.

Most of dyestuffs contain more than one coloring matter, so analytical methods used for their identification must include separation steps. The use of high performance liquid chromatography (HPLC) allows separating many compounds from different organic dyestuff groups: anthraquinones, flavones, anthocyanins, carotenoids or indigoids. They can be identified with the use of spectrophotometric (UV-Vis) or tandem mass spectrometric (MS/MS) detection. Both techniques are useful in dyes analysis; however, MS detectors, more sensitive and selective than the UV-Vis ones, provide information also about the structure of each color component.

HPLC–UV-Vis–ESI MS/MS method was developed for the analysis of natural colorants present in pre-Columbian textiles. Among examined objects were woolen and cotton fabrics from Paracas (750 B.C. - 100 A.D.), Chimú (850-1450 A.D.), Chancay (1200 - 1450 A.D.), Chuquibamba (1200 - 1450 A.D.) and Inca (1200 - 1532 A.D.) cultures. Obtained results allowed identification of extracted color compounds and formulation of hypothesis concerning used dyestuffs. They enabled comparison of materials used by different cultures and verification of historical knowledge of the analyzed textiles.

Indigo Carmine: Favored but Fading

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Around 1850 textiles were mostly dyed with natural organic dyes. Their use changed in the second half of the 19th century, due to the introduction of synthetic organics. Before that time pigments and half synthetic organics, like Prussian blue, indigo carmine, picric acid, pittacal and murexide, were used in the textile industry.

For the ICN-project 'early synthetic organic dyestuffs', an intense study on indigo carmine has been undertaken; the lecture will focus on this acid blue dye. The history, chemical constitution, names, production and the analysis will be discussed. In addition, dyeing recipes and the use as a textile dye will be presented.

The history is studied by the original historical sources, included the patent literature. The lawyer Johann Christian Barth (* around 1700, † 1759) at Groβenhain in Saxony, Germany, discovered a blue dye by treating natural indigo with concentrated sulphuric acid in 1743. He named it 'Sächsisch Blau' after his native region. For this invention he received the title Kurfürstlich-Sächsischer Bergrat (Counsellor) in 1746. The wool-dyers of Norwich bought the secret and it was patented in England in 1748. In 1754 it was renamed in indigo carmine. Other synonyms and obsolete names are indigo extract, intense blue, murabba, Saxe blue, Saxon blue, Chymick and chemick blue. In the last quarter of the 18th century and the first half of the 19th century the use as a dye is often mentioned in dye books.

A new episode for indigo carmine starts with the discovery and industrial production of synthetic indigo in the last decades of the 19th century. German patents from 1890 till 1903 prove that it was produced and even in sample books from one German dye factory, dated 1922, indigo carmine was used for dyeing wool, silk and leather.

Indigo carmine is still used as a colorant for food, pharmaceuticals, and cosmetics.

Indigo carmine is an acid dye and will dye wool and silk directly from an aqueous solution producing bluish-green colours. The dyestuff is dissolved in water to which alum and cream of tartar might be added and wool is dyed at boiling temperature. The properties of indigo carmine are poor: the fastness to light compared to indigo is much reduced and the colour changes from blue to green to yellowish. Also the fastness to washing is low; it is soluble in water.

Indigo carmine belongs to the class of acid dyes. Analysis can be done by means of HPLC-PDA using a gradient of water, methanol and tertiary butyl ammonium hydroxide, a technique especially developed for the analysis of acid dyes.

Analysis on many textile objects from the last quarter of the 18th century till the first quarter of the 20th century shows that indigo carmine was used for nearly two centuries after its invention.

Material Study on Historical Portuguese Arraiolos Tapestries (17th-19th Century Period)

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Arraiolos tapestries are probably one of the richest artistic Portuguese expressions in terms of textile heritage. These wool embroidery tapestries were produced in the south of Portugal from the late 1600s, beginning to appear listed in the Portuguese aristocratic household inventories in the 17th century. The tapestries are made with an embroidery of wool worked on a canvas (usually flax or hemp). Dating historical Arraiolos tapestries is a difficult task and it is nowadays done usually based solely in stylistic details.

Material studies on Arraiolos tapestries from the 17th to the 19th centuries belonging to the National Museum of Ancient Art (MNAA) have been performed in order to obtain a time scale of materials usage in the production of the Arraiolos tapestries. Samples taken from the historic tapestries were used for mordant analysis and natural dyes identification.

Before dye analysis, chromophores were extracted from the wool fibers using an EDTA/DMF procedure (1). Dye chromophore identification was done by LC-DAD-ESI-MS. Mordant identification was done by SEM-EDX, while metal ion semi-quantification was achieved by ICP-MS.

As expected, alum was found to be the most commonly used mordant, but iron, copper and zinc were also found in the samples. Interestingly, even in the blue samples, Al was always detected suggesting a pre-mordantation procedure for all the used wool.

Historical sources (2,3) report the use of weld, surge flax, indigo, brazilwood and logwood as natural dyes. Nevertheless, LC-DAD-MS analyses of the wool extracts detected also the presence of madder, cochineal and *Morinda* spp.

Only few historical recipes describe the procedures used to obtain different color hues (2,3). However, the analyses done suggested that more combinations of dyes and mordants have actually been employed. For example, brown hues were reportedly obtained only by the use of natural brown wool, but the gathered data showed that they were also obtained by dyeing white wool with iron salt and weld or brownish wool with alum and weld.

Color degradation is also extensively observed in the historical tapestries. In several embroidery areas that now present a yellowish color, red and yellow chromophores were detected suggesting that an orange hue was initially intended. The indigo dye has a very photostable chromophore being historically used to produce green hues with weld. Nowadays, analyses showed that some blue embroidery areas were originally intended to be green as the remains of yellow chromophores have also been detected in those samples.

The study performed of the Arraiolos tapestries contributed to improve the overall knowledge of the Arraiolos industry, complementing the few historical written sources available.

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Acknowledgements

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Characterization of Natural and Synthetic Dyes Employed in the Manufacture of Chinese Garment Pieces by LC-DAD and LC-DAD-QTOF

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The Spanish Cultural Heritage Institute (IPCE) receives numerous historical textiles from museums and excavations for their restoration, technical analysis and identification of the dyestuffs employed in their manufacture. In this work, we present the results obtained in the characterization of dyes found in seven Chinese garment pieces: a theatre costume, a nuptial tunic, a chi-fu, child shoes, pair of trousers, a jacket and a belt. These pieces came from the Museum of Arts and Design in Madrid. They were dated between 1700 and 1900, the period of the Qing Dynasty, which was the last ruling dynasty in China.

In a first study, the samples were analyzed by liquid chromatography coupled to a diode array detector (LC-DAD). Dyes identified in the pieces under study were clearly correlated with two important features, their oriental origin and date of manufacture that makes them a particularly complex matrix. Thus, on the one hand, the natural dyes found, such as indigo, brazilwood, curcuma, Asian berberin yellow dye, pagoda tree and safflower, are characteristic for Asia and the Middle East. Moreover, a dark blue dye detected deserved special attention. It presented indirubin content higher than indigotin, which up to our knowledge has not been observed before for any dyestuffs from historical textiles. This finding agrees in turn with the composition of certain indigo plants from Southeast Asia, which are used in traditional Chinese medicine. On the other hand, the chronology of these pieces covered the transition period between the exclusive use of natural dyes and the widespread introduction of synthetic ones during the late 19th century. Therefore, some early synthetic dyes such as picric acid were also detected. However, several dyes of these samples could not be clearly identified due to lack of suitable reference dyes and to the intrinsic unspecificness of DAD detectors. Identifying single components in this complex matrix demands a higher discriminating detector. Consequently, in a second part of this study, selected samples were analysed by LC-DAD-QTOF (liquid chromatography tandem diode array-quadrupole-time of flight mass spectrometry) in order to improve identification power.

The QTOF's combination of MS/MS structural information and excellent mass accuracy are used to both confirm the presence of a compound and provide the ultimate in confident identification of unknown components in a single analytical run. Making use of this technique, additional dyes such as fuchsine or victoria blue B could be unequivocally identified.

ESI Mass Spectrometric Analysis of the Early Synthetic Dyes

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Identification of dyes by electrospray ionizaton mass spectrometry (ESI-MS) have been investigated. ESI-MS Analysis of the dyestuff used in 17th Century Mughal Carpets had already reported (1,2). By the ESI-MS analysis, acid red 88 (Fast Red A) gave only deprotonated molecular ion $[M-H]^-$ in a low concentration corresponding to the extract from 0.01mg of dyed cloth. Structural isomers of dyestuffs with a same molecular composition were easily discriminated by the application of MSMS method targeted on the molecular mass. The MSMS analysis gave characteristic product ions attributed to the neutral losses of small molecules such as SO_3, SO_2, and C=O, and two patterns of bond fission, NH-N of hydrazon form and/or C-N bond fission of azo form for azo dyes which were effective for structural identification of regio-isomers. Polysulfonated acid dyes gave multi-valent ions in addition to the mono-valent ion, and the MSMS method was also effective for discrimination of regio-isomers.

To confirm ESI-MS combining with MSMS method was suitable, this method has been applied for dyestuff identification of textile fragments (AN. 2520) related to "Memorial Notebook of Textiles for Prince Chichibu's Coming-of Age Ceremonial Costumes" (AN. 2517) which were stored in Kyoto Institute of Technology. Dyestuff used for AN. 2517 (also AN. 2520) are recorded in "Dyeing specification" attached to AN.2517. ESI-MS and MSMS analysis of red fragment, AN. 2520-1, gave four molecular mass. MSMS analysis targeted for the ion of *m/z* 352 reveals characteristic fragment ions for acid yellow 36 (Metanil Yellow), which was according to the "Dyeing Specifications". MSMS spectra targeted on *m/z* 227 and 435 were almost identical with those of acid red 26 (Ponceau 2R), but quite different from those of acid red 8 (Palatine Scarlet A) which was described in the "Dyeing Specifications".

ESI-MS of purple fragments, AN.2520-8,-10,-11 were determined to be dyed by a mixture of acid orange 7 (Orange II), acid yellow 36 (Metanil Yellow), and acid red 88 (Fast Red A), according to the "Dyeing Specifications" of the AN2517-6 and -16. Other, purple fragments, AN2520-18, 20 were determined to be dyed by a mixture of acid orange 7 (Orange II) and acid green 9 (Neptune Green SGX) as described in the "Dyeing Specifications" for AN2517-1 or -3. The black fragment AN.2520-4 dyed by acid black 4B in the "Dyeing Specification" , was determined to be dyed by a mixture of acid black 1 (Naphthol blue black) and acid orange 7 (Orange II).

Thus, ESI-MS and MSMS methods were found to be quite effective for identification of early synthetic dyes of traditional textiles.

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English "Sheldon" Tapestry Workshop in the Mid-16th century: Characterisation and Provenance through PDA-HPLC Analysis

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This paper presents a recent study of a group of mid-16th century English tapestries attributed to the Sheldon workshop at Barcheston in Warwickshire, through the identification of fibres and dyestuffs using PDA-HPLC analysis.

The term "Sheldon" has, until recently been applied to early English tapestries and mainly refers to large tapestry maps representing the English countryside, key examples today being part of the Bodleian collection in Oxford and the Victoria and Albert Museum in London. The assumption was that there was only this one workshop in England in the mid-16th century, at Barcheston, Warwickshire. However, this theory is now being reassessed in favour of a more complex situation, with the possibility of other weavers' workshops in London and migration of tapestry weavers from Brussels or France to work in English workshops.(1,2)

In order to understand better the characteristics of these tapestries, we studied a group of 19 small tapestries in the Burrell Collection in Glasgow, the home of the largest public collection of English Sheldon tapestries. The large majority of these tapestries are relatively small in size (50 by 50 cm) - have a colour palette mainly based on yellow, orange and green hues and represent biblical scenes, mainly based on the story of Susannah and the Elders. In order to compare these tapestries with secure "Sheldon" pieces, we extended our technical investigation to two of the large Sheldon tapestry maps preserved in the Bodleian collection.

Natural dyestuffs including weld, dyer's greenweed, madder, *Galium* species and indigo were identified using High Performance Liquid Chromatography coupled to Photo Diode Array Detector (PDA-HPLC), by comparing the chromatogram profiles of main and minor components to those obtained from references samples.(3) Special interest was given to the identification of the flavonoid-based dyestuffs particularly by determining the ratios of luteolin, apigenin and chrysoeriol compounds for the weld samples and luteolin, genistein, apigenin and diosmetin for the dyer's greenweed samples. These ratios provided information about the degree of fading of the tapestries.(4,5)

Finally, early synthetic dyes, corresponding to early restorations, were also investigated and discussed in relation to possible historical conservation work.(6) While there are records of conservators being employed to maintain and restore tapestries there is little documentary information, prior to the late 20th century, on the work that they carried out.

This study provides new information on this unique group of English tapestries, with the characterisation of the range of dyestuffs used in England in the mid 16th century. These results were compared to previous studies of contemporary continental tapestries and highlighted differences in the dye/fibre choice which may indicate characteristic practices of the Sheldon workshop.(5,7) In addition it provides new information about the extent of restoration though the identification of the fibres dyed with synthetic dyes dating from the mid-19th century.

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The Identification of the Organic Painting Materials in Andrea Mantegna's *Pala di San Zeno*

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The Pala di San Zeno by Andrea Mantegna (second half of 15th century) has recently been the focus of an important restoration at the Opificio delle Pietre Dure (Florence). The restoration was included in a protocol, entailing a massive diagnostic campaign, aimed not only at characterising the general state of conservation of the painting prior to cleaning and restoration, but also at gaining information on the painting techniques and the materials used by Mantegna.

The diagnostic campaign was mainly based on non invasive analyses: photographic and spectrophotometric techniques were applied to study the state of preservation of the painting layer and to highlight the underdrawings. XRF and FORS analyses proved fundamental for characterising the pigments; FORS analyses also gave some suggestions on the presence of organic lakes (1).

According to the non invasive measurements, a thoughtful sampling was planned: thus, micro samples were collected in order to prepare suitable cross sections to study the stratigraphy of the paint layers (2) and for the analysis of the organic components.

The present work reports the results achieved by using chromatographic techniques in order to gain a complete overview of the painting technique. In detail, gas-chromatographic/mass spectrometric analyses highlighted the use of egg as the binding medium. The analysis of organic dyes performed by liquid-chromatographic/diode array detector allowed for determining the presence of diverse red lakes and a yellow lake. In particular, the shining paintstrokes were characterised by the presence of lakes: kermes lake for brilliant red, kermes mixed with woad and a yellow flavonoid dye (a quercetin-based dye) for violet and a luteolin-based dye (most probably *arzica* lake) for a luminous yellow.

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Safflower (*Carthamus tinctorius* L.). History of Use in China; Ancient and Present-Day Preparation Technologies; a New Identification Strategy

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The earliest period of the use of safflower (*Carthamus tinctorius* L., *hóng huā)* in China is not exactly known and is subject to some debate, opposing legend and tangible evidence. The latter refers to written sources such as the *Materia Medica* of the Tang Dynasty (618-907 CE); the description of the farming of safflower in the *Qimin yaoshu* (535 CE); a drawing and description of the safflower plant reproduced from the original *Ching-Shih Chêng Lei Pei-Chi Pên Tshao*, the most important history text of the Song Dynasty (960-1279 CE), written in 1082; and the documented use of safflower for the red dye of dragon robes, as early as the Song Dynasty (960-1279). It may be generally assumed that the introduction of safflower in China, probably via Persia, can hardly be older than the third or fourth century, under the (Western) Jin Dynasty (265-317 CE).
Safflower contains both a yellow and a red dye. The main red dye component is carthamin (C.I. Natural Red 26; C.I. 75140) that can be extracted in water at alkaline pH, after removal of water-soluble safflower yellow. For the development of identification strategies, historically relevant reference materials of safflower dyed yarns, pigment, paint and cosmetic rouge were prepared in the laboratory. Four publications were used to gather information for these preparations. The first two were studies of the *Qimin Yaoshu* (535 CE); the third was a manual on traditional dyeing with natural dyes in Japan, considered of interest to compare present-day, but traditional, Japanese practice with ancient Chinese knowledge; the fourth publication was Berthollet's *Elements of the art of dyeing and bleaching*, representing Western technology in a period when the use of safflower was widespread in the West.
Safflower red was prepared by extracting safflower petals at alkaline pH, after the preliminary removal of water-soluble safflower yellow. Alkaline extracts were used to prepare dyed silk, wool, cotton and paper, to precipitate the pigment, to prepare paint and to produce the antique Chinese cosmetic rouge. All reference samples were analyzed with HPLC-PDA-MS after colorant was removed from its substrate by both a harsh and mild acid hydrolysis method. In addition to the red colorant carthamin, four colorless components were found to be markers for safflower. The latter components were characterized by their retention times, UV-VIS spectra and mass spectra and were given the codes Ct1,

Ct2, Ct3 and Ct4. Experiments on references clearly indicated that these Ct components, unlike carthamin, withstood as well harsh acid hydrolysis as light-induced accelerated ageing, and that they could be found even in a completely faded wool sample. This made them excellent markers to identify safflower red, even in discolored historical samples or in samples that must be treated in a way that destroys carthamin.

Silk in The Prussian Royal Palaces: Dye and Pigment Analysis

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Berlin became an important centre of silk manufacturing during the regency of Frederic II in the second half of the 18th century. In particular the interiors of the Prussian palaces used to be decorated with luxurious silk. Until today, many of these silk textiles such as damasks, colourful figured fabrics, painted or printed objects are still preserved and can be seen in the palaces of Sanssouci Park in Potsdam and of Charlottenburg Palace Garden in Berlin.

The Prussian Palaces and Gardens Foundation Berlin-Brandenburg is presently preparing a catalogue of these textiles. A team of art historians, restorers, and scientists is studying more than fifty silk objects.

One of the major aims of the research is to characterise the dyes and pigments used in the Prussian silk fabrication. To what extent were the materials mentioned in the historical sources used in Berlin and Potsdam in practice? Do they differ from materials used in other countries? Other questions of interest concern the state of preservation, for example fading effects, as well as the relative dating of the objects.

X-ray fluorescence spectroscopy is being used to study the mordants of the dyeing and the inorganic pigments in painted silk. Optical spectroscopy in reflection mode is being applied as another non-destructive method. Although this method alone is usually not sufficient for the identification of a colorant, it can, however, be applied for the selection of representative samples for further analyses with liquid chromatography (HPLC-PDA). Reference samples were dyed on silk according to historical recipes.

The main sources of dyes in the silk decorations of the Prussian palaces so fare identified are: cochineal, brazilwood, safflower, weld, orchil and indigo. The investigations also show that the fading of colours is often a result of the usage of light sensitive colorants from brazilwood and safflower. The identification of early synthetic dyes proves to be helpful to distinguish between original wall decorations from the 18th century and later copies.

Folklore Red in Finland

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The aim of our research is to enhance the knowledge of the Finnish dyeing tradition and the dye plants and dyeing methods used locally. This paper presents findings concerning the red dyes. We have collected data from the archives of folklore and made dyeing experiments. Later our aim is to do dye analyses of the historical textiles.

We have gathered Information about the traditional natural dyes and dyeing processes from the archives of the Finnish Literature Society and the National Board of Antiquities. These archives contain queries that have been collected by several different collectors dated to the beginning of the 20th century. The national romantic period, from the end of the 19th century till the beginning of the 20th century, inspired the Finnish scholars to collect information about the folk art and native culture. When travelling around Finland they got familiar with the traditional handwork and techniques. They collected textile samples and a great part of the costume collections of the museums are from that period.

At the time when the queries were done, the transition from using only natural dyes was changing to the wider use of synthetic dyes. The synthetic dyes were obtained from travelling sellers or from the market places at the biggest towns. Natural dyes were collected from local areas: forests, meadows and road sides. The information of the queries shows that rural people were well aware what plants to collect for dyeing.

In the traditional textiles and folk costumes the predominant colours were red, blue and white (undyed), but also black, green, brown and yellow can be found. For example the head ribbons of the maidens were usually red in colour, whereas the accessories like mittens, vests and scarves were of red, white and blue yarns.

According to the query data the most common dye plants for the red colour were the bedstraws *Galium boreale, G. album* and *G. verum*. The roots were collected with a special tool, the so called "*matarahakku"*, a bedstraw hack. Sometimes the roots of *Potentilla erecta* were mixed with the roots of the bedstraws. Both the mordanting and the fermentation methods were known. Alum was bought from travelling sellers, but sometimes a substitute for it was made from *Lycopodium* plants. With the *Lycopodium* it was also possible to ferment the dye bath.

In addition to bedstraws red or reddish colours were obtained from barks of buckthorn (*Rhamnus frangula)*, alder *(Alunus sp.)*, birch *(Betula sp.)* and willow *(Salix sp.)*. The dyeing methods with the barks are not explained in details, but boiling with copper or iron sulphate is mentioned. In some cases birch ash lye was added to achieve the wished red colour. The lichen *Parmelia saxatilis* is mentioned to produce a reddish-brownish colour. The lichen was widely used because the dyeing process needed no mordant.

Our experiments show that with a fermentation method it is possible to obtain bright red colours in low temperatures and without the usage of alum mordant.

The Orchil Trail: from Portugal and Angola

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This paper will outline the continuing study of a rediscovered archive relating to Leeds dye manufacturers Wood & Bedford. It follows from the research presented to the DHA Conference in Poland in 2009, which related to the trade in orchil lichen from Ecuador and elsewhere in South America.

Relentless demand for orchil lichen in the mid nineteenth century drove traders and speculators to explore ever-widening sources of supply. This next phase of study has been continued through many letters and accounts written by John Wilby, the Portugal-based agent of the Leeds company. Originally from a Yorkshire family, Wilby operated through Lisbon.

Wilby's letters and records reveal the day-to-day issues affecting the buying and selling of orchil from the Portuguese colonies and the secrecy in which deals were made in order to profit from a new source. They also record the fascinating story of Francisco Rodrigues Batalha, a Lisbon merchant. Batalha was both persistent and imaginative and co-opted sea-captains trading along the West African coast to search for dye lichens wherever they put into port. Through his efforts a hitherto unknown and abundant source of dyestuff was discovered in Angola and a new trade developed. "Angola Weed", as it came to be known, was especially valued for its rich dye content. Batalha made – and being a speculator, apparently lost – a fortune dealing in the lucrative dyestuff.

Eminent botanists of the time involved in taxonomy of lichen and other species also feature in this paper. Associated documents from the archive illustrate the efforts that were made by dedicated chemist James Bedford to identify many of the lichens in use for orchil production at the dyeworks in Leeds.

The documents include a correspondence regarding identification of the richly productive variety traded to England from Angola.

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POSTERS

Photovoltaic, Antioxidant and Neuroprotective Potentials of some Natural Dyes of Tropical Africa

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Natural and organic dyes and pigments Chemistry has opening its frontiers to many facets of life, playing a major role in the development of chemical industries, application to medicine, security, food, cosmetics, textile and information technology (1). The presentation will give an overview of work done in our group in the direction of harnessing/identify the potentials of the locally available natural dyes of Tropical Africa, viz-a-viz their sensitizing action and health roles (2). The present study focused on the photovoltaic, antioxidant and proctective effects of some natural dyes on cyclophosphamide induced oxidative stress in rat's brain (3). A wide range of dyeing plants was screened for both phytotherapeutic agents and technological uses. Some of which are *Zanthoxylum zanthoxyloides* (stem), *Parkia filicoidea* (fruit husk), *Pterocarpus erinaceous* (heartwood) and *Harungana madagascariensis* (bark) with ethanol. The phytochemical screening and antioxidant activities includes total phenol content, free radical scavenging ability, reducing power, Fe^{2+} chelating ability and *in vitro* inhibition of lipid peroxidation in rat's brain. Then the protective effect of dietary inclusion of the dyes (0.5 & 1.0%) on cyclophosphamide (75 mg/kg of body weight) induced oxidative stress in rat's brain was assessed. The results of the study revealed that the dyes contained alkaloids, phleobatannin, anthraquinone, saponin, tannin and flavonoids (except *P. erinaceous*) (4,5); however, *H. madagascariensis* has the highest total phenol content(64.9%) free radical scavenging ability(97.6%), reducing power, Fe^{2+} chelating ability. *Z. zanthoxyloides* had the highest inhibition of Fe $^{2+}$ induced lipid peroxidation on rat's brain tissue (*in vitro*). Furthermore, the dietary inclusion of the dyes caused a dose dependent significant (P<0.05) decrease in the rat's brain malondialdehyde content, serum activities of aspartate aminotransferase, alanine amino-transferase, alkaline phosphatase and total bilirubin content. Hence, dietary inclusion of these natural dyes could prevent cyclophosphamide-induced oxidative stress.

In another study, some of the natural dyes (*Bixa orellana, Pterocarpus erinaceus, Sorghum candatum, and Zingber officinale*) were found to be good dye-sensitizers in T_i0_2 coated plate of a dye sensitized solar cell. (6). Isolations of the constituents of these tropical natural dyes revealed a lot of compounds ranging from oily substances (aliphatic alcohols) to crystal-like and coloured compounds. Some of which are known to have health benefits.

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Similarity and variation in painting motifs of the Eneolithic and Antique pottery of Azerbaijan

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The most ancient patterns of painted and dyed pottery in Azerbaijan belong to the eneolothic period. In Azerbaijan there were registered more than 150 eneolotihic monuments which in 43 of them have been discovered painted and dyed pottery. In the Early Bronze Age typical to the South Caucasus and Azerbaijan Kura-Araks archaeological culture was existed painted pottery. Afterwards, in the Middle Bronze Age there was appeared archaeological culture under the “dyed pottery culture” and passed four development stages. Between the Late Bronze Age and Early Iron Age producing the dyed pottery become less and stopped. From the mid of the 1st century BC the manufacturing of painted and dyed pottery developed more.
Despite the long distance between the eneolithic and antique periods, there were followed the similarity in the painting technology and motifs. In both periods’ monuments there were followed the impact of the Near East and Front Asia traditions.
In this paper we tried to analyze the technological methods and paint motifs separately for both periods and on the basis of similarity and distinction studied the genetic relation between them.

Application of Vibrational Spectroscopy for Detection of Luteolin and its Complexes with Al (III)

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The vibrational analysis of pigments and dyes has become very important and increasingly popular kind of analytical method. The main advantage of Raman and IR spectroscopy is small amount of sample need to be measured and the possibilities of in situ measurements so they are very useful in the area of art conservation. Additionally, vibrational spectroscopy was chosen in regard to its sensitivity in detection of any structural changes of the analyte.

The vibrational spectroscopy, especially Raman spectroscopy, is often used to study paintings or sculptures, however, analysis of organic dyes is still not popular in the profession of art conservators. The main reason of that are properties of natural dyes – they give a high fluorescence in the Raman spectra and are often biologically polluted.

Luteolin is a yellow flavonoid occurring in a few plant species i.e. *Reseda luteola.* It is considered to play an important role in the human body e.g. as an antioxidant and a free radical scavenger. This compound is also commonly known as a traditional dye used in the past, especially in Europe, Middle East and North Africa (1). The technology of dying requires using metal ions called mordants to fix and stabilize colorant on the textile. The most popular mordant was alum but other metal salt e.g. copper and iron were also used (2). Due to the interesting properties of this dye, the synthesis and then analysis of luteolin complexes with Al(III) was put as an aim of this research.

Several flavonoids were investigated by various spectroscopic techniques (3, 4), but vibrational analysis of luteolin has not been reported yet. The issue what is the chemistry of luteolin complexes has not been answered in contrast to other flavonoid compounds e.g. quercetin (3). Therefore in this work we demonstrate FT-Raman and FT-IR spectroscopy analysis of luteolin and its complexes with aluminum (III). It was supposed that luteolin can form different complexes depending on the ratio of metal:ligand, but according to our research only one form of complex is detected. Additionally, vibrational analysis of deprotonation process of this compound in respect to pH is carried out.

Moreover, analysis of art pigment based on natural luteolin and stem of *Reseda luteola* was carried out. An effort was made to detect luteolin or its complexes in the analyzed samples.

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Determining Stability Constants of Kermesic Acid and Flavokermesic Acid Complexes with Aluminium(III) by Potentiometric Method

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The insect that have been and are still used today as sources of red textiles dyes, paint, pigment, food and pharmaceutical colorants are all classified in the super family *Coccoidea* of the class *Homoptera*. Kermes insect (*Kermes vermilio*) is in that family of the *Coccoidea*. The dyestuff constituents of this insect are kermesic acid and flavokermesic acid.

The aluminium(III) salts were used as mordant in the dyeing process with natural dyes. In the other hand, most of the organic pigments are metal complexes. In this study first, the protonation constants of kermesic acid and flavokermesic acid were determined potentiometrically by Irving Rossotti method. The evaluated protonation constants for kermesic acid $\log K_1 = 5.58$, $\log K_2 = 3.72$, $\log K_3 = 2{,}45$, $\log K_4 = 1{,}92$ and the evaluated protonation constants for flavokermesic acid $\log K_1 = 4.74$, $\log K_2 = 3.72$, $\log K_3 = 2{,}54$ and $\log K_4 = 2.07$ at the 25 ^{0}C were found. The formation constants of aluminium(III) of kermesic acid and flavokermesic acid were determined by the same method. In this calculation, pK values of ligands were used as data. Stability constants were found for kermesic acid-aluminium(III) complex $\log K' = 6.14$ and for flavokermesic acid-aluminium(III) complex $\log K' = 7.77$ at the 25 ^{0}C. Conditional formation constants of complexes, under the assumption that only existance of OH^- ion as a second ligand in solution, were calculated. Also, from the conditional formation curve drawn for complexes, pH intervals where conditional formation constant reach a maximum was determined.

tudy of Nineteenth Century Green Morocco Leather Upholstery

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In the present study dark green morocco leather applied as wall and wing chairs covering material in the Princes wagon compartment, part of the Portuguese Royal train (Museu Nacional Ferroviário, Entroncamento, Portugal) which belonged to King Luis I of Portugal (1861-1889), was investigated by UV-Vis spectrophotometry and ATR-FTIR spectroscopy. Morocco leather is oak galls or sumac tanned goatskin, widely used for upholstery, bookbinding, footwear, gloving and other decorative artifacts. Commonly, this type of leather presents the grain layer (outer layer of the skin) dyed. Historic descriptions for the production of dark green leather include dyeing with a mixture of fustic and logwood [1] or barberry root and Saxon blue [2].

Dyestuffs in grain layer were extracted in hot acidified methanol as common procedure described for proteinaceous textile fibbers. For comparative purposes, sampling included historic non dyed morocco leather, also dated from the nineteenth century, and a non tanned skin, a parchment.

UV-Vis spectra of the dyed leather extract showed a band at 630 nm and a shoulder at 432 nm, which were absent in the acidic methanol extract of non dyed morocco leather, suggesting two dyes were used to form the green colour. Extracts were also analysed by ATR-FTIR, but only tanning and collagen protein materials were clearly identified.

In addition ATR-FTIR spectra were directly obtained from the samples surface. In this case, and by spectra comparative analysis, some bands not due to collagen or tanning materials could be identified, which can be assigned to dyestuff.

In this communication, UV-Vis and ATR-FTIR spectra are presented and results compared with literature data and discussed.

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The Color Hue and Photostability of Wool Dyed with Plants Traditionally Used in Alentejo Region

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The study of natural dyes is an important aspect in museum studies due to the prevalence of these materials in the collections worldwide. Textile conservators' major concerns include the sometimes unavoidable light degradation that causes color fading and hue changes on the collections. The scientific reasoning behind the differences in the chromophores photostability and the influence of the dyeing methodology and used materials on the photodegradation of the fiber colors is still mostly unknown.

In this work, *Ficus carica*, *Daphne gnidium,* and *Rosmarinus officinalis* were used together with alum and copper salt to dye wool samples. Authors performed a systematic study where the dye bath concentration was kept constant while the mordant chemical nature and concentration were changed. Two dyeing methods were used to dye the fibers: a pre-mordanting and a co-mordanting procedure.

Wool dyed samples were subjected to accelerated ageing studies under controlled conditions in order to evaluate the chromophore photodegradation. Analyses of the chromophore contents were performed before ageing and at different ageing times by LC-DAD-MS (liquid chromatography coupled with diode array and mass spectrometry). Colorimetric studies were performed on the samples before and after artificial accelerated ageing to assess the influence of the chromophores photodegradation on the fibers color changes. Analyses of the aluminum content on dyed fibers were performed by ICP-AES (inductively coupled plasma – atomic emission spectrometry) and the fiber copper contents were analyzed by atomic absorption spectroscopy (AAS). Morphological characterization and local X-rays microanalysis were carried out by SEM-EDS (scanning electron microscopy - energy dispersive X- ray spectrometry).

The results obtained indicate that the mordant concentration and dyeing procedure have a strong impact on the wool fibers final hue.

Chemical analysis on the fibers showed that the actual Al and Cu contents on the samples were much smaller when compared to what was available in the mordant bath. The relative amounts of the different compounds present in the plant dyeing baths are also distinct from those that are extracted from the dyed fibers, which partially explain the different fiber hues obtained in the dyeing conditions. Daphnetin derivatives can be used to unequivocally detect *Daphne gnidium* as dye source while psoralen and bergapten can be used to identify *Ficus carica*. Rosmarinic acid can be the marker for the use of *Rosmarinus officinalis*.

The artificial light ageing studies showed that the plant chromophores photostability was highly dependent on their chemical structure. The different rates at which their photodegradation proceeded resulted in fibers color fading and hue changes with light exposure.

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Collecting Botanical Sources: Joint Research on Organic Pigments and Dyestuffs

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One of the work packages of the CHARISMA project, which is being carried out under the European framework (FP7), is the development of innovative methodologies for laboratory research. The main concerns within this work package are natural dyes and organic pigments used in works of art and/or objects of cultural heritage. A better knowledge of these materials will help to improve the understanding of these works and also assist considerably in their conservation. We aim to create new, relevant information suitable for a better development of art technological research and conservation practices in ancient and in contemporary art.

For this task we are concentrating on two groups of dye plants which have been widely used in Europe since ancient times, growing wild or cultivated. The two groups consist of dye plants rich in red anthraquinone components, like madder, and those rich in yellow flavonoids, such as weld. Each group contains plants with a rather similar dyestuff profile, which could be sometimes confusing for the analyst.

It is known that the organic colorants in plants may be affected by environmental factors, so we are collecting specimens from as wide an area across Europe as possible to determine the significance of their geographical origin. It is important that the investigated specimens are identified correctly taxonomically, thus we are asking botanical gardens and nursery gardens for their help.

The plants we are studying are as follows:

Rubia tinctorum L.	(Madder)
Rubia peregrina L.	(Wild madder)
Galium verum L.	(Lady’s bedstraw)
Galium mollugo L.	(Hedge bedstraw)
Reseda luteola L.	(Weld)

Genista tinctoria L. (Dyer's broom)

Serratula tinctoria L. (Sawwort)

To unify the research analyses carried out by the participating institutions, two standard extraction protocols were developed, one for anthraquinone plants and one for flavonoid colouring plants. Several procedural quantitative extraction methods, in which time and temperature of extraction were varied, were tested in an experimental set of 4, 8 or 10 samples of madder root and flowering weld plant. All plants will be analysed on a qualitative and quantitative level using high performance liquid chromatography (HPLC). These standard extraction protocols will be available online.

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Study of Pink Colorant Residues in Archaeological Ceramics from Kush and Siraf, Two Sites on the Persian Gulf

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Excavations at two coastal sites on opposite sides of the Persian Gulf have yielded ceramic vessel and ground stone either containing or covered with residues of a pink pigment or colorant. Kush (modern-day Ras al-Khaimah, UAE) is a small tell on the Arabian peninsula with a recently excavated occupation sequence extending from the Sasanian to the early Islamic periods (i.e. c. fourth-early fourteenth centuries), with evidence for much later re-occupation into the seventeenth/eighteenth centuries. The coloured sherds have been found from a range of contexts from the eighth/-early ninth century onwards. The earliest sherds overlap chronologically with material of very similar appearance from Siraf on the opposite Iranian coastline. Between the ninth and eleventh centuries AD Siraf was the main centre of maritime trade in the Persian Gulf at a time when Indian Ocean trade underwent a dramatic expansion. The sherds from both sites appear to be from containers and the ground stone appears to have been used in processing but it is unclear whether the coloured residues are traces of pigment or are linked to dyeing.

A multi analytical approach has been used to identify the nature of the coloured residues. Initially, the samples were analysed by Raman spectroscopy which demonstrated that the residues, although of very similar appearance, are composed of different materials. Raman analyses demonstrated the presence of hematite in the Siraf sherds while for the Kush sherds from all contexts the pink residues corresponded to an organic pigment or colorant. Complementary analyses were performed by HPLC to identify the nature of the colorant. Using a soft extraction method (BF_3/MeOH), the resulting chromatograms show only one component corresponding to alizarin.

Reviewing the literature, the most probably source of a colorant containing only alizarin is chay root, although most written sources and surviving Indian chay-dyed textiles are rather later in date than the earliest Kush contexts (1). Chay (*Oldenlandia umbellata* L.) grows in India and Indonesia and was particularly extensively cultivated along the Coromandel Coast (eastern India) (2). There is however some confusion regarding the identification of the botanical source: further research reveals many names apparently corresponding to this dye plant and many different botanical sources apparently named chay. Many samples were collected from botanical gardens and in India in an attempt to obtain an authentic chay sample and to explore the range of potential botanical sources. The second step of this challenging study has been to identify the technique used to extract the colorant from roots in order to throw light on whether the vessel residues are the remains of a dyebath or a deliberately produced pigment.

This poster present the results of the analyses of the archaeological and botanical samples and reviews the botanical data relating to the chay plant and the techniques used to extract dye from its roots.

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Review of Extraction Methods for the Characterisation by HPLC of Organic Colorants in Textiles and Pigments in Cultural Heritage Objects

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The unique nature and typically small size of samples, the effects of time and past treatment and the diverse range of potential biological sources make identification of the natural organic colorant source for dyes and pigments in cultural heritage contexts highly challenging. Selection of the most appropriate extraction method to solubilise the constituents of the colorant for HPLC analysis is a further problem. For samples from cultural heritage objects, extraction must not only dissolves the molecular constituents, but typically must free the colorant components from the fibre or dye–mordant complex (for textiles and other dyed materials), or from the pigment substrate and frequently also from an additional matrix (such as the paint binding medium).

A number of different extraction methods have been developed and applied to such samples: some have been optimised for particular colorant classes, or to allow highly quantitative extraction from tiny samples, or are designed for particular sample types (e.g. dyed textiles but not paint), etc. Natural organic colorants are complex mixtures of components, including both the basic colorant components (aglycones) and sugar derivatives of these components (glycosides). There is growing interest in so-called 'soft' extraction methods that preserve the glycoside content or other chemically labile components which can be highly informative of the biological source and/or dyeing or pigment-making technologies. Such approaches also allow a wider range of colorant classes to be explored. There is, however, a lack of knowledge about the advantages, limitations and wider applicability of the different extraction methods.

Within the European project CHARISMA (*Cultural Heritage Advanced Research Infrastructures: Synergy for a Multidisciplinary Approach to Conservation/Restoration*), five laboratories undertaking colorant research have reviewed the literature relating to the extraction of organic colorants in cultural heritage objects and are creating a database, to be made available to the scientific and heritage community, containing a standardised description of the protocols. The partners in this project have undertaken comparative studies of the different methods for a range of textile, pigment and paint standards in order to establish the advantages, limitations and applicability of the extraction methods. This poster presents the main protocols identified in the literature and the results of the comparative studies which demonstrate clearly the importance of the choice of extraction procedure. The ultimate aim is to develop an optimal extraction method (or sequence of steps) or selection of methods:

applicable to the widest range of colorant classes and to colorants applied to a range of supports/sample types and in a range of matrices or complexes;

permitting efficient and (semi-)quantitative extraction of components and which preserve all colorant components or specific markers, indicative of biological source or which are contained within a mixture of colorants, regardless of differences in chemical stability;

to permit researchers to select the most appropriate procedure to maximise the information that can be obtained by HPLC analysis of samples from unique cultural heritage objects.

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1930 Spring Color Palette of Lyon Dyers' Guild – Tandem Mass Spectrometry in Identification of Early Synthetic Dyes

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After the first synthetic dye had been discovered in 1856, the number of diverse synthesized dyes grew rapidly and the field soon became characteristic of inconsistent nomenclature. Hence, nowadays identification of these dyes poses many problems to researchers. These difficulties can be overcome with the use of mass spectrometry, which provides information on the structure of examined compounds.

The present study concerns identification of early yellow synthetic dyes from silk fibers taken from the 1930 spring color palette of the Lyon Dyers' Guild (La Chambre Syndicale des Teinturiers). Identification was based mainly on the MS/MS spectra obtained in the positive and negative ion modes of electrospray (ESI) or atmospheric pressure chemical (APCI) ionizations. Both the techniques were combined with high performance liquid chromatography (HPLC), which enabled separation of the analyzed compounds. Spectra registered for each of the examined synthetic dye allowed to identify their lost fragments, what in consequence made possible reconstruction of their molecular structure.

Due to the lack of standards, the reconstruction itself was based only on the fragment and the quasi-molecular ions, which is rather uncommon in the field of dyes analysis and means groping for the correct structure rather than proving signals presence by comparison with standards. The fragments lost from the examined dyes involved mainly SO_2, SO_3, CO_2, CO, NO_2 and C_2H_4.

Dyestuffs Examination of *Quercus infectoria* and *Quercus ithaburensis* by the Fermentation

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Gall oak *(Quercus infectoria* Olivier*)* and valonia oak *(Quercus ithaburensis* Decaisne*)* was extracted with water. The extractions were fermented in the room temperature. Fermented extractions of *Quercus infectoria* and *Quercus ithaburensis* were analyzed by HPLC-DAD every third days for three months. Same time silk brocades were dyed with the fermented extraction of *Quercus infectoria* and *Quercus ithaburensis* every third days for three months. Colours of dyed silk brocades were measured by CIELAB (Table 1) and the dyed silk brocades were analyzed by HPLC-DAD. Variation quantities of gallic acid, gallic acid derivatives, ellagic acid and ellagic acid derivatives were compared at direct fermented extraction and on dyed silk brocades every third days for three months. Quantity of gallic acid, gallic acid derivatives, ellagic acid and ellagic acid derivatives are seen table 2.

Table 1: Colours measurement of dyed silk brocades with *Quercus infectoria.*

Days	Unmordanted dyeing			Dyeing with alum mordanted			Dyeing and post mordanted with iron		
	L*	a*	b*	L*	a*	b*	L*	a*	b*
1	71.43	4.03	25.42	72.62	0.70	34.27	26.18	3.43	-0.50
4	70.95	4.24	27.38	72.22	1.54	35.30	22.90	2.58	-1.04
7	69.96	4.72	26.83	70.49	1.88	36.28	26.78	3.35	3.35
11	68.85	4.93	28.98	70.10	1.96	36.23	24.32	2.24	-0.08
14	68.33	68.33	29.17	68.18	2.34	36.85	25.99	2.60	1.52
18	69.06	5.06	28.82	69.00	2.46	37.65	24.05	1.75	0.54
21	67.61	5.49	29.61	69.53	1.82	38.13	31.63	3.16	4.96

Table 2: Variation quantities % of gallic acid, ellagic acid and other tannin derivatives are in the fermented *Quercus infectoria and Quercus ithaburensis.*

Days	Gallic acid (*Quercus infectoria*)	Gallic acid (*Quercus ithaburensis*)	Ellagic acid (*Quercus infectoria*)	Ellagic acid (*Quercus ithaburensis*)	Other total tannin derivatives (*Quercus infectoria*)	Other total tannin derivatives (*Quercus ithaburensis*)
1	8.194	3.494	38.529	49.790	37.168	30.660
7	9.934	4.306	41.507	24.746	19.525	10.031
14	33.246	9.228	21.660	65.902	26.473	19.328
18	18.264	7.798	11.841	67.283	-	8.435
21	4.816	5.422	39.329	68.718	-	-
32	-	-	28.205	63.881	-	-
35	-	-	26.573	62.436	21.826	19.627
45	-	-	27.366	65.748	30.762	19.229
56	-	-	38.747	65.830	11.811	18.976
59	-	-	39.899	70.097	12.882	20.093
67	-	-	42.570	71.043	10.897	16.624

Acknowledgment

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The Rainbow Project: A Collaborative Platform and Online Database on Natural Dyes and Textile Fibres

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The Rainbow Project aims at contributing to significant progress in research into natural dyes and textile history by providing a new tool and impetus for enlarged collaborations and worldwide sharing of information.

Identifying colorants, inventorying ancient and traditional textiles

Collecting and preserving traditional know-how and recipes

Sharing and publishing works on all fields connected with Natural Dyes

The software tool

The database / imagebank "Rainbow" proposes the conception of a powerful software tool, able to link together all relevant data on the uses of natural dyes in the different parts of the world. Data are organised in five different types of files, which correspond to the five components of the result of each request.

1. Identification and description file for Botanical and Zoological sources of Dyes and fibres
2. Recipe file containing historical and ethnographical recipes
3. Colorant file with analyses and referencial on chemical data
4. Textiles and artefacts COLLECTIONS database
5. Bibliography and sources

A tool for collaborations and syntheses

This tool makes it possible to select and analyse groups of data, by regions and civilisations, according to the raw materials used and to crosslink different types of information without losing track of their sources. In this way, RAINBOW opens new possibilities for synthetical work in a comparatist approach, in history, anthropology, linguistics, as well as in the study of the chemistry of colorants.

It is a tool for collaborations, making simultaneously accessible data coming from different research fields and resulting from the work of researchers based in different countries, thanks to the on-lining of the tool from a server. In an initial stage, the data gathered together in this way are extracted from the previous works of the members of the team, from their historical and field research. Other partners can get involved in the project for using or filling the database via internet, in a wiki manner. Conception of this project was started at the University of Lyon II, (UMR 56 49 / CIHAM) by Dr. Dominique CARDON's research team, Marie MARQUET (PhD student) worked on this tool together with Arnaud BELONOSCHKIN (computer programming), and they propose a detailed description and analysis of the future tool, partly programmed already. Data including results of the team's current research programs will be transferred into Rainbow as soon as the platform is created.

The Rainbow Project's purpose is to develop international collaborations and exchanges, and to offer a cooperative and collaborative tool, to be used by every personne involved in Natural dyes Study and practice.

The Environmental Sustainability Era: A Dyeing Study of the Wool/PLA Blend

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The fibres companies identified the consumer trends, are developing and presenting at the market fibres originating from renewable sources, biodegradable, anti-bacterial, able to operate on thermal regulation and water vapour permeability. Some of these fibres are still being introduced in the textile industry and, in some cases, in different areas of the fabrics and clothing. There is, thus, an important area of applied research related to, firstly, the development of wool fabrics blended with these fibres in order to obtain functionalities that optimize the performance in use and, secondly, the industrialization of the production processes of these fabrics.

Many biological materials can be incorporated into biodegradable polymers, being, the most commons, the starch and the fibres extracted from various plants. There has been, recently, an increasing interest in biodegradable polymeric materials used in packaging, agriculture, medicine, automotive, food industry and textiles and clothing. The polymers that form the basis of plastics materials are continually employed in areas of expansion. As a result, it has carried out much research on the modification of traditional materials to make them more environmentally friendly and on the development of new polymers from natural materials.

The poly-lactic acid (PLA) is a thermoplastic aliphatic polyester, biodegradable, with a straight chain that is obtained from renewable resources like corn. At the beginning, their use was limited to biomedical applications, such as sutures and drug delivery systems, due to its limited availability and high cost. Recently, efforts have been developed for its large scale production considering applications in packaging and textiles.

The factors that lead to the widespread use of PLA are the polyesters used (mainly PET) represent about 40% of world consumption of textiles, with a tendency to growth, the production of these polyesters be made from non-renewable fossil sources and, also, these polyesters are not biodegradable.

On the other hand, PLA has some negative characteristics, such as:

- Low fusion temperature (130-170 ° C) when compared with other synthetic fibres, leading to constraints on the fabrics heat setting and the clothes ironing;
- Poor resistance to alkalis, which causes a decrease in fibre strength after dyeing with disperse dyes, that are the suitable dyes for these fibres;
- Difficulties in obtaining dark colours in dyeing.

In this research work is intended to contribute for solving some of these problems through technical procedures. Thus, it is proposed to redesign the dyeing/finishing processes for resolving these problems, namely using dyeing/finishing lower temperatures and changing the alkaline-reducer treatment, to be carried out after dyeing with disperse dyes, in order to limit the hydrolysis of these fibres. We study the dyeing process with two dyes and tree dyes, with monitored dye absorption in order to analyse the dye exhaustion and the sample colour, in wool/PLA blended fabrics.

Dyeing Materials Used for a Mediterranean Carpet and a Traditional Greek Child Costume Around 1900

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The "Austrian Museum of Folk Life and Folk Art" in Vienna as well as the "Museum of Ethnography" in Kittsee (Austria) are well-known for their unique collections about folk art and regional culture not only of Austria but also its neighbouring countries (former crownlands). In comparison to collections from other Europe these are the only museums which own an European perspective concerning the historical and present life-style and cultural statements of social and ethnic groups mainly in Europe.
Samples of two historical art objects were left to us from the curators of these two museums for analysis purposes of colouring materials applied to them during manufacturing process:

A Greece National Boy Costume made up of an overcoat, a fustanella (slip), a jacket, gaiters, a felt Fez with a tassel and shoes like velvet sewed with strings (blue as dominant dyeing material, Fez in red) and

A Kelim (flat-weaved carpet) stemming from Piroti (Serbia) with brown, yellow, red and blue colour elements.

The following chromatographic equipment was used for the identification of natural organic dyestuffs occurring in the sample materials:

An ultimate rapid separation liquid chromatograph (RSLC) combined with both a diode array detector (DAD) and a charged aerosol detector (CAD) but before applying this device dyestuff extraction was necessary and

A pyrolysis capillary gas chromatograph/mass spectrometer (Py-CGC/MS) suitable for direct measurement of textiles without time-consuming sample preparation.

In addition to these analyses scanning electron microscopy/X-ray microanalysis (SEM/EDX) was helpful to distinguish between anorganic and organic dyes.
Although the boy costume and the carpet were produced around 1900 only natural organic material like cochineal and indigoid dyestuffs was found and not – as could be expected for this time – synthetic dyeing substances.

Indigo – one Molecule, Three Forms, Numerous Applications

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Indigo, a molecule which has influenced mankind's history for several millennia, and is a chemical icon, still harbours mysteries. The more common leuco is the water-soluble form used in the dyeing processes, which when exposed to oxygen leads to the coloured neutral keto form. Dehydroindigo (DHI), the oxidized (and third) form of the blue indigo, has been the forgotten form of indigo.

Maya Blue is considered as the first fabricated organic (indigo)-inorganic (clay) hybrid, and is the source of blue of this ancient civilization. Its chemical structure, although puzzling until recently, seems to involve the incorporation of indigo into palygorskite or sepiolite clays. Indigo reveals a strong attachment to these clays and that, together with dehydroindigo, it penetrates more deeply (and is consequently more protected) into the channels of the clay.

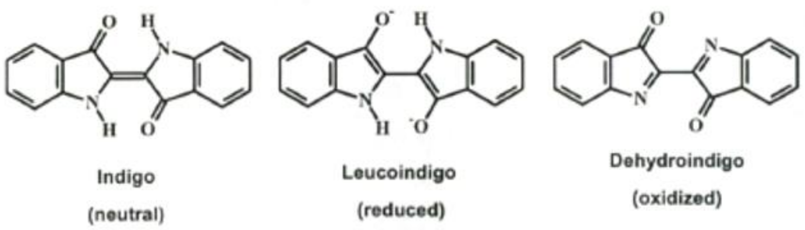

Figure 1. The three structures of indigo

This incorporation protects the organic dye, leading to outstanding stability which has made possible the preservation of the colour for centuries in paintings submitted to severe environment conditions, in particular those involving light (photodegradation). However, the mechanism leading to indigo's incorporation and its localization within the clay, i .e., if it is distributed in the surface or if it goes into the clay channels, or a distribution of these two, is still under debate. Incorporation in both clays and with different indigo derivatives was tested.

A comprehensive investigation of the electronic spectral and photophysical properties of the three forms of indigo, has been carried out in solution at 293 K. In marked contrast to what has been found for keto-indigo [4, 3], where the internal conversion channel dominates >99% of the excited state deactivation, or with the fully reduced leuco-indigo [2], where fluorescence, internal conversion, and si nglet -to-triplet intersystem crossing coexist, in the case of DHI [1] in toluene and benzene, the dominant excited state deactivation channel involves the triplet state.

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The *Color Standards Reference* of Natural Dyes: Reds on Silk

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In the course of routine management of museum textile collections preserving age-old dyed colors from further fading by light and altering by pH actions, museum professionals—conservators, collection managers, and curators alike—must routinely estimate, with their naked eyes and educated memories, their possible original colors and probable types of dye sources. In performing the task, a set of reference samples of dyed colors in history is an essential tool to have, without depending solely on perceptions. Such reference samples showing an intrinsic color that is accompanied by prepared light- and chemically-altered colors have however not been available.

In this project, as reference standards, color alterations by effect of light were tried on a set of eight red-color-dyed silks. Since combination of silk and red dyes, some fade reactively while others slowly, is the most common and identifiable target in planning length and strength of exposure to gallery lighting of museum textiles in exhibitions.

The eight red-dye/silk standards were prepared in the manner of graduated color chart: each sample is composed of large unexposed original color area with the smaller blocks of four faded colors. The size of references prepared is each in 7 cm x 12 cm individual rectangle for handy use of the purpose. In making, seven lengths of eight silk fabrics were mordanted with alum, and dyed with seven natural red dyes: dyer's madder, Chinese madder, Indian madder, cochineal, lac, safflower, and sappanwood. The eighth length dyed with cochineal was mordanted with tin. The eight dyed silk lengths were cut into the rectangles, and in groups, each sample was exposed to controlled xenon light using Suga FAL-25AX. The exposure hours were variegated with 20, 60, 200, and 400 hours to achieve visibly identifiable four graduated colors. The colors were recorded by measuring by a color meter, Macbeth CE-7000, and expressed by H V/C, and ΔE was calculated between the original and each faded shade. The charts show the original and four different stages of faded color and the light fastness of these seven natural red dyes. The basic record of prepared colors accompanies the samples.

We hope the *Color Standards Reference*: Reds on Silk will assist interested professional's visual estimation of colors in museum textiles by comparing with the standards in juxtaposition under various artificial lights and ultra-violet ray to visualize differences in extrapolating fading-related color development, estimation for source of dyes, possible original shades, controlled exposure to gallery lighting, and selective sample preparation for further instrumental dye analysis.

Thirteenth-Century Sicilian Lampas Silk

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The Medieval Age Sicilians in the early thirteenth century left distinguished architecture and extraordinary craftwork surpassing the other Mediterranean cultures of the time. Abreast with the architectural and craftwork legacies, a small number of exquisite silk textile items made of loom weaving, tablet-weaving, and embroidery dedicated to Christian churches, today in church treasures and museum collections, astound us. Since no records were left that describes the production, our discussions on them remain solely analysis of examples in fortuitous encounter. Six examples of loom products in nine fragments from the collection of the Metropolitan Museum of Art (New York), and one fragment in a private collection are under our examination.

All the six silk textiles are in the identical structure of a lampas weave (combination of two structures interconnected): warp-faced plain weave and weft-faced plain weave. It is composed of:

Ground structure (warp-faced plain-weave): a set of heavier warp (two sub-elements per warp combined) and a set of finer weft;

Pattern structure (weft-faced plain-weave): a set of finer warp and a set of one heavier continuous pattern weft with one metallic and one or two silk discontinuous substitutions.

At least five types of yarns were thus used in each textile.

Of them, only those quantitatively sufficient samples of silk and metallic yarns were planned to be subjected to instrumentation for dyes and metallic component of metallic yarns, and so far few samples have been analyzed.

Dyes

In one textile, red discontinuous pattern weft was dyed of kermes; in another, ground structure's heavier warp was of kermes and the finer weft was of madder. All green warps and wefts yielded luteolin and indigotin. Regarding luteolin, the HPLC chromatogram showed characteristics of other components of weld so that in Sicily, presumably weld was the source of yellow. Blue was presumably woad. (Auxiliary dyeing agents are planned for examination.)

Component of Gilt Metallic Weft Yarn

There are two types of metallic weft yarns composed of metallic strips wound around silk core thread used sporadically for enhancement of design. With five of the six textiles, metallic strips were composed of membrane as substrate that was gilt by adhering gold leaf, then cut into strips. X-ray fluorescence shows, in ratio, the gold leaf contains more gold than copper. With one of the six textiles, it is gilt metal with less gold than copper cut into strips. All of them have never been subjected to water or washing. They have been completely tarnished and slightly fallen off, and could detach further if abraded.

The Mystery of Three Persian Carpets

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In the 1950s, three Persian Carpets were acquired to furnish the Palace of the Dukes of Bragança (Guimarães). At that time, they were understood to be 19th-century, possibly Turkish, carpets. In 2007 they were “rediscovered” and identified as being important ‘Salting’ carpets; the largest collection outside the Topkapi Saray (Istanbul). For more than a century, both the provenance and chronology of the ‘Salting’ group have been the source of considerable debate. At the end of the 19th century, they were believed to have been made in 16th-century Tabriz (Iran) and were recognized to be similar to a large group of well-preserved prayer rugs, with brilliant colours, in the Topkapi. However, their presence in Istanbul encouraged subsequent authors, such as Tattersall (1931) and Erdmann (1941), among others, to claim they were 18th- or 19th-century Turkish rugs, and possibly even forgeries of classical Persian carpets.

The research presented in this poster takes an interdisciplinary approach to these problems. Detailed characterization of the materials present in the carpets was performed using different methods. The dyes were identified using high performance liquid chromatography with diode array detector (HPLC-DAD), as well as mass spectrometry (when necessary); the mordants were analyzed by inductively coupled plasma with atomic emission spectrometry (ICP-AES), among others. Carbon 14 was also used for dating. With the results obtained it was possible with relative certainty to propose a 16th- or 17th-century date and a Persian provenance for the three carpets.

Revitalization of Technology of Natural Dyeing in Polish Double Warp Textiles

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Double-warp textiles are some of the most interesting and original phenomena in Polish folk art. Such fabrics are found in North-East Poland. The design is based on geometric figures, usually two-coloured, with repeats that are traditional for this part of the country. The oldest fabrics were dyed with natural dyes such as indigo, cochineal, madder, buckthorn and oak bark or preserved the natural colour of wool (white, grey, brown, black). They were made by professional as well as rural weavers in Mazury Lake District, near Elk and Olecko and date back to 18th century. Polish museums have collected more than a thousand of such double-warp fabrics what consititutes large material for studies. In 20th century Eleonora Plutynska and Zofia Tomrie played an important role in saving this dying weaving technique and the technique of using natural dyestuffs. The tradition of this archaic technique, which has been almost completely forgotten in Europe is nowadays cultivated by weavers from Janow. The Institute of Natural Fibres and Medicinal Plants has conducted natural dyeing workshops for a group of weavers in Podlasie Region. The reconstruction of dyeing with the following dyestuffs was made: cochineal, madder, weld, buckthorn bark, reseda, elder, dyer's greenweed, tansy, chestnut, oak, alder, birch, and galas. These actions are an essential part of the project to reactivate the old weaving techniques in their cultural environment.

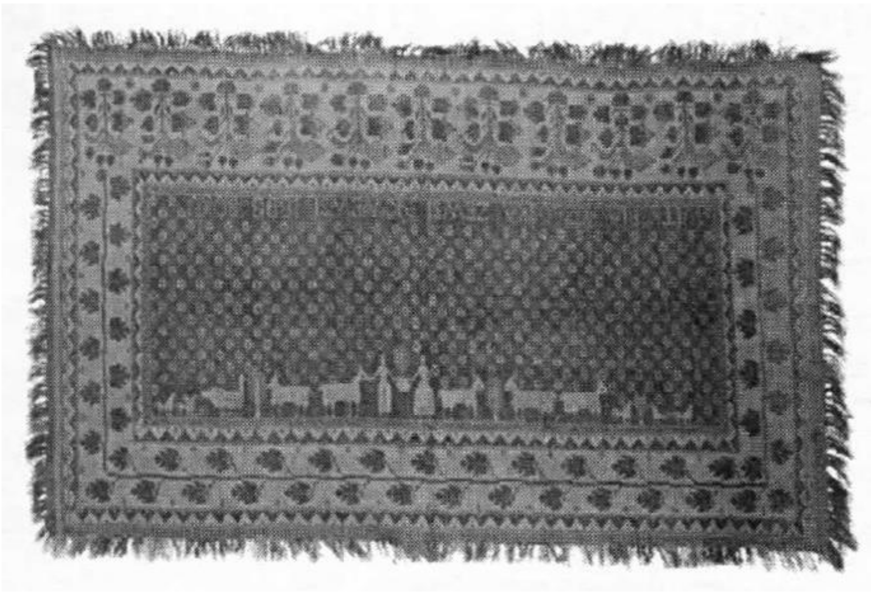

Figure 1. Double-warp tapestry, Wiktora Kozlowska, 1893

Creating Colours: The Making of Dyed Textiles and Organic Pigments

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Within the framework of the European project CHARISMA, an expert meeting was organized at the Netherlands Institute for Cultural Heritage in which textiles were dyed and organic pigments (lakes) were made. The expert meeting had two aims:
To disseminate general knowledge of textile dyeing and organic pigment preparation
To determine the most significant parameters in a recipe which affect the overall colour and the organic colorant composition on the created material
On the first day of the expert meeting, many different colorants were used to obtain a complete range of colours. Dye materials investigated were cochineal, redwood, logwood, iron gall dye, turmeric, saffron, indigo and a synthetic dye. All mordant dyes were dyed on alum, iron, tin and copper mordants to show the effect of the mordant on the different colouring matters.
Next, two days were spent on weld and madder only. Standard recipes were formulated to dye textiles and prepare organic pigments. Next, parameters such as temperature and duration of, firstly, extraction of the colorant from the botanical source and, secondly, dyeing, were varied in such a way that for each botanical source 10 different textile recipes were performed and 6 different pigments were created. The outcome of this experiment will be shown on the poster.
Within the framework of CHARISMA, two workshops will be organised in 2011, open to the professional public. One will be devoted to textile dyeing, the other to organic pigment preparation. These workshops will be announced in time; information can be obtained from the authors.

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