DHA 30

Dyes in History and Archaeology 30
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DHA 30

Dyes in History and Archaeology

Book of abstracts

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Programme:

Wednesday 12th October 2011
Reception 18.30 – 21.00
Conference Centre, 37 Bridge St, Derby, DE1 3LA

Thursday 13th October 2011
Presentations and Posters 09.30 – 17.25
Conference Banquet

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The Colours of Sweden
A short history of the use of organic dyes and lakes in Sweden

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According to tradition the Colours of Sweden – one of the oldest existing national flags of Europe -was dyed with woad and weld. Although there is evidence that dyeing has been known in Sweden since at least the Migration period, no comprehensive account or history has yet been written. A number of research projects have been conducted concerning painting materials, especially investigations into medieval and baroque painting-techniques [1]. The results of these studies give ample information on inorganic pigments and some binding media but due to analytical difficulties concerning their identification are rather vague on the use of organic substances. The combination of knowledge of dyes and lakes applied to textiles and painted surfaces comparing for example the medieval polychrome sculpture and ecclesiastical textiles could give new insights into the trade routes for colorants as well as other technical aspects. This paper will discuss and give an overview of possible case studies from the Migration Period up until today in order to present a short colour and dye history of Sweden.

Objects associated with this discussion, range from small archaeological finds of textile fragments to ecclesiastical antiquities, profane objects from the interiors of castles and farmhouses to such immense objects as the warship Wasa. For example the Migration Period burial (500 A.D.) of a chieftain in Högom in the north of Sweden included textiles dyed with madder and *Porphyrophora polonica*. The Viking Age textiles of Skog and Överhogdal show evidence of madder, woad and weld. St Bridget writes on the many aspects of 14th century life in the convent, the dye plants in the garden as well as the textile work of the sisters. The 18th century brought more written sources; Johan Linder´s *"Svenska Färge-konsten"* (1720) being the first Swedish book on dyeing. The 18th century was a period of activity aimed at strengthening the domestic industries and at the request of the government, Carl Linnaeus recorded the existence and use of dye plants during his travels through Sweden; from Lapland in the north to Skåne in the South. Sadly, there is little research done on dyes in the rich material of rural textiles remaining from this period. Specifically the use of local biological resources is not fully understood although there are many records of oral tradition on the use of local plants such as birch leaves and lichens. An ongoing project on the painted wall hangings of farmhouses from southwest Sweden could shed some light on this [2]. Archives and museums hold collections from the 18th and 19th centuries of textile samples or printing blocks, such as the Anders Berch Collection and the Lang Collection, to mention only a few. The collection of Nils Månsson Mandelgren, artist, art historian and conservator, contains 19th century material for painters and craftsmen. The Arts and Crafts movement brought a revival of vegetable dyeing which lasted well into the middle of the 20th century. In his research Gösta Sandberg [3] made existing collections of recipes available to generations of students of art and crafts, but in the 1970´s their interest turned to synthetic dyes, mainly fibre reactive dyes. Today we see a new interest in natural dyes. We also see a growing curiosity in organic painting material historically applied in interior decorations.

At the Swedish National Heritage Board we investigate the presence of organic colouring substances in both textiles and painted surfaces, relating mainly to the other Scandinavian countries. Since it will be essential to make use of recent technical developments concerning the analysis of organic material we hope to connect to other ongoing research with similar focus on dyes and lake pigments adding to the knowledge of the trade routes and use of colorants in Europe.

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3. Gösta Sandberg – Jan Sisefsky: *Växtfärgning,* Stockholm 1967

A colour boom: the di- and tri-aryl methane dyes

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The lecture will concentrate on the di- and tri-aryl methane dyes. These dyes produce brilliant hues, the range covered including yellows, reds, violets, blues and greens. During the second half of the 19th century they played an important role for dyeing textiles and other applications. The history of these dye classes is studied by the original historical sources, included the patent literature.

The tri-aryl methane dyes can be divided in two main groups, the Rosaniline and Malachite series. The start of the first group was the discovery of the red-violet dye Fuchsine, some months after Mauve, and turned out to be more useful. Some later it became clear that Fuchsine was not only a dye but also a key intermediate for other dyes of this series. In the beginning of the 1860s the number of this group was increasing, especially violet dyes, like Regina purple (1860), Methyl violet (1861) and Hofmann's violet (1863). In 1862 Nicholson found out that the basic dye Aniline blue (Lyon blue) (1861), when treated with concentrated sulfuric acid, was converted into the soluble acid dye Alkali blue (Nicholson blue). This discovery led to the preparation of a number of other sulfonated blue acid dyes, such as Methyl blue, Water blue, Cotton blue, Navy blue and Soluble blue.

Subsequently, at the end of the 1870s the Malachite series was discovered. The older members of this group are Malachite green (1877), Brilliant green (1879) and Victoria green 3B (1883). Sulphonation of this series resulted in the green dyes, like Helvetia green (1878), Light green (1879) and Guinea green B (1883). It was not until 1888 that sulfonated blue members, the Patent blues, were prepared.

A new episode started in 1883 when the Swiss company Bindschedler & Busch showed large samples of Crystal violet during the Swiss Federal Exhibition in Zurich. Kern employed phosgene for the synthesis of this violet dye. The process was complicated and not yet fully mastered, that's why the Swiss firm joined forces with BASF. This cooperation was so successful that in the same year violets, like Ethyl violet, and blues, such as Victoria blue and Night blue, were discovered. Some later by sulfonation several Acid violets and Alkali violets were invented between 1884 and 1891. The cooperation also led to the discovery of a new dye class: the di-aryl methane dyes, known as the Auramines.

The di- and tri-aryl methane dyes possess poor light-fastnesses. Lehne writes that: 'after five days of light exposure the colours are much paler and in eighteen days the colours have been very strongly or almost completely faded'.

The analysis of the di- and most of the tri-aryl methanes can be done by means of HPLC-PDA using a gradient of water, methanol and phosphoric acid, the same system used for the analysis of natural dyes.

The history, the chemical constitution and the production of the most important dyes of these chemical dye classes will be discussed. In addition, dyeing recipes and the identification of di- and tri-aryl methane dyes on different art-objects, such as robes, embroideries, furniture, umbrellas and parasols, will be presented.

At the close of the first synthetic dye epoch: synthetic and natural dyes and dyeing in review

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For about 125 years the synthetic dyestuff industry was firmly anchored in western Europe. It grew from a small kernel of aromatic organic chemical knowledge because of the serendipitous discovery and commercialization of “Mauveine”, by W. H. Perkin in 1856. It spread rapidly to become the huge synthetic organic chemical industry we know today, of which dye chemistry and dyeing technology are only a small fraction of the whole field of chemistry.

During the period until about 1980 many facets of chemistry grew at extraordinary rates, but only a few of these are of primary emphasis to the DHA. These facets include all the equipment and analytical techniques suitable for archaeologists to use for examining the surviving artifacts of cultural and historical interest.

The growth of polymer chemistry and the conversions of polymer products into fibres and fabrics, previously the sole domain of naturally occurring cellulosic and protein fibres, had been rapid and the growth of suitable synthetic dyes and colorants and their methods of application to the increasing gamut of polymer substrates - natural, man-made and synthetic - went hand in hand with the growth of polymer sciences.

However, now, at the end of this epoch, all the possible physical and chemical methods of attaching colour to polymeric substrates have been examined, and the rate of introduction of economical and commercially viable new polymeric substrates has diminished to a trickle. Thus, dye, colorant and polymer technologies are mature. All the associated manufacturing information is available to developing countries worldwide, and, the chemical industry in the west is looking for newer and more profitable fields to conquer.

This, then, is a good time to review where we stand with respect to current, and relatively static, polymer coloration technology. More particularly, how do the pre-1856 lessons, learned with such effort using natural dyes and fibres, tie into the overall picture of dyeing as understood today.

How surprising was the almost complete absence of indigo dyeing in the Pacific islands?

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In 1996, Virginia Bond (later Virginia Korda) submitted a Master's thesis to the Department of Advanced Studies in the Arts of Africa, Oceania and the Americas, at the University of East Anglia, Norwich[1]. This documented, with the help of Penelope Walton Rogers, George W, Taylor, Lauen Murdoch, Tamsin O'Connell and Christina Marsh, that the blue dye used in Santa Ysabel Island, in the Solomon Islands, in the late 1890s, was indigo. The plant source of the dye, identified at the Royal Botanic Gardens, Kew, was *Desmodium brachypodum,* a plant in the Leguminosae, in the same sub-family as *Indigofera*, and clearly an uncommon source, since it is not mentioned in a recent encyclopaedic work [2]. The technology for dye production involved chewing the leaves of the plant, and using spit, then coloured blue, to put the dye onto cloth. That technology was observed in the early 1900s, and presumably was that used earlier. The thesis described cultural practices involved in dyeing, as well as the absence of spread of the use of the plant as a dye source to any of the other Solomon Islands.

Roger Feldman, during a visit to New Zealand in 2000 to visit the Maori exhibits in the Auckland museum, and in discussions with the curator of textiles at the Museum, learned that there was no blue dye used in culturally important three strand twinned Maori mantles. A following literature review found Bond's Master's thesis, and a meeting with its author.

Further searching has suggested that indigo dyeing technology was not reported from islands of the Pacific when they were visited by European and other visitors to the islands, although such technology was present in the mainland and other islands of the Pacific Rim, including Japan, China, Burma, the Philippines, and Indonesia.

This presentation will consider whether the absence relates to:, (a) difficulty in transmitting information about dye technology [3]; (b) an effect of limited contact with other, but geographically separated neighbouring areas [4]; (c) botanical factors, (d) cultural factors, including the lack of common textile fibres [5].

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Mineral impurities as indicators of the origin of natural indigo samples

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Natural indigo can be obtained from processing the leaves of a variety of plant species grown in many regions of the world. The indigo, as a pure chemical, is identical whatever the plant source, and is chemically identical to synthetic indigo. There is currently no way of knowing where a sample of indigo came from, either in terms of the plant species or its geographic origin. However, the natural indigo product is never pure, generally containing more than 40% of its weight as impurities. It was proposed previously [1] that much of the contaminating material becomes trapped within the aggregates of newly formed indigo when these precipitate out during the extraction procedure. This encapsulation of the impurities by the indigo makes it difficult to purify natural indigo by simple washing procedures [2].

The impurities in natural indigo include mineral particles derived from the soil in which the crop was grown, and mineral materials added during the extraction process [1]. We now show that when indigo is made from alkali-hydrolysed indoxyl acetate, adding soil prior to the conversion of indoxyl to indigo causes the resulting indigo particles to be greater in size. This provides evidence additional to that provided previously [1,2] to support the proposal that soil particles can play a role in the formation of indigo particles.
Using natural indigo samples from a variety of sources, including a sample recovered from a Spanish galleon which sank in 1641 off the coast of Florida, we have used both micro-area elemental analysis via an environmental scanning electron microscope and X-ray powder diffractometry to show that washed samples from different sources show distinctive mineral profiles. This preliminary study reveals for the first time that the impurities firmly trapped in the natural indigo product can provide clues regarding its origin. The approach introduced here could be useful in identifying samples of indigo powder, or when the indigo has been used as a pigment.

We thank Mr Rex Cowan for the sample of indigo from the Nuestra Seňora de la Concepción, and Professor Luciana Angelini for other indigo samples and the soil sample.

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Dyes recovered from shipwrecks; special reference to indigo from a Spanish galleon

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Historic shipwreck explorer Rex Cowan will present the first half of this double paper. Cowan has spent almost four decades discovering and excavating shipwrecks of the seventeenth and eighteenth century and has been a member of HM Government's Advisory Committee on Historic Wrecks and awarded for his services to Dutch Underwater Maritime History. His teams have made many important discoveries and a special gallery in the Rijksmuseum, Amsterdam housed, among other material, a substantial collection of his recoveries from several Dutch East Indiamen. Cowan has also discovered other wrecks around the UK and collaborated with shipwreck divers in the Caribbean.

Cowan will summarize methods specific to underwater archaeology and give firsthand accounts of recovering dyes and dyed textiles from various important wrecks, using both illustrations and a display of actual objects and dyestuffs that had for centuries lain undiscovered on the sea bed. He will also show samples dyed with some of these recovered dyes, such as the formerly important red sandalwood, *Pterocarpus santalinus L..,* imported from India's Coromandel Coast.

Cowan will end his part of the presentation with an introduction to a renowned Spanish galleon, the *Nuestra Señora de la Concepción*, which sank in the Caribbean in 1641 with a priceless cargo that included much cochineal and indigo dyestuff. The story of the recovery of some of the indigo in the 1980s will form the second part of this paper.

Balfour-Paul will place the history of the wreck of the *Concepción* within the context of world trade in indigo, focussing on the West Indies trade of the seventeenth-eighteenth centuries, when huge quantities of indigo were being manufactured on European plantations to feed the appetite for the dye in Europe. The historical and archaeological sources on dry land are being backed by this more recent evidence of indigo and other dyestuffs found in the recovered shipwreck cargoes, notably since new scanning techniques became available in the 1980s.

The *Concepción* was the flagship of a notable plate fleet that sank off the Caribbean Turks Islands when returning to Spain from Mexico. Though the wreck and some of her cargo was discovered in 1687, the rest lay beneath a coral reef for almost three centuries, until it was rediscovered in 1980. Balfour-Paul will relate how, thanks to Cowan, some of the indigo cargo found its way to her UK house in 2007, and describe her experiences of dyeing with indigo that had been manufactured so long ago on a Mexican plantation using slave labour. She will display some of her samples and even a 'piece-of-eight' from *Concepción*, encrusted with indigo.

Balfour-Paul will conclude with a brief discussion on the reason for the revival of natural indigo in many parts of the world today, not least in Central America, India and Bangladesh, regions that supplied the lion's share of indigo to the Western markets until the early twentieth century.

Indigo dyeing among the Yorubas of South Western Nigeria: A historical perspective

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Dyeing with indigo has become a symbol of Nigerian textile craft. Although other natural and synthetic dyestuffs are available and used, cloths dyed with indigo, having intricate patterns, stand out vividly as a legacy of Nigerian contribution to textile arts of the world and will be discussed in this paper. The dye is widely used for two reasons, first, it is found naturally and readily across the entire length and breadth of the country and second, it is used on cotton which is the most convenient form of textile available in the country.

The Yorubas in the south-western region of the country are well known for their skills in dyeing using indigo. In most cases, the fermentation vat technique is the preferred method of dyeing. The essential features of extraction of the dye, raw materials preparation and the application process of the dye as is practiced in the ancient Yoruba art and the socio-cultural relevance of the cloth among the people will be highlighted in this paper.

Art, Trade and Chemistry in the Age of Enlightenment: The Colours of Cudbear and Galium and the Pioneering Work of Cuthbert and George Gordon of Leith and Glasgow

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At the Union between England and Scotland in 1707, English wool cloths were the staple of the economy and were measured by their quality at home and abroad but imported printed Calicos and dyed and embroidered silks dazzled by their colour and lightness. This would prove to be a conundrum for the Scots, who had a small fine wool manufacture and their own multi-coloured plaids but who had embarked upon a national policy to develop the linen trade.

The challenge of the 18thC was to produce fast and bright colours on linen and cotton and to secure a continuous supply of dye materials for the growing textile market. Dyers and drysalters began to experiment with native dye plants as substitutes for cochineal, indigo and madder which were costly and imported from distant and often hostile nations. The lichen based Cudbear, patented in 1758 by the Scottish Gordon brothers, proved to be a cheap and effective dye on wool and silk, especially in association with indigo, logwood and madder. A cousin of the imported Orchil, which came from the Cape Verde Islands, Cudbear could be manufactured for a fraction of the cost but was capable of yielding a variety of shades of violets, reds and pinks, though of variable light fastness. The Cudbear Works in Glasgow eventually covered a huge seventeen acre site in the later 18thC. Cuthbert Gordon, a trained chemist, continued to experiment with native dye plants to meet the demand for bright fast reds, blacks and drabs on cotton and linen, using lichens and the roots of the Galium plant which had grown plentifully in Scotland from the middle ages. He struggled in his career as a chemist and a practical dyer to overcome the secrecy and prejudices of the dyeing trade, where knowledge of recipes was often handed down from generation to generation, often travelling in person to the major textile producing towns in Britain to demonstrate his colours to merchants and manufacturers.

A study of natural dyes of Egyptian paper: preliminary findings and discussion

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Natural dyes are sources of colorants that have been used from early times. This research investigates the use of yellow natural dyes in Egyptian book manuscripts endpapers and their historic sources. The motivation for selecting yellow natural dyes is due to the prevalence noted, during extensive personal observation of collections, of yellow dyed endpapers in Egyptian medieval manuscript books. It is anticipated that these dyes will be amongst the most used sources (turmeric, weld and saffron), particularly as their application was widespread during most historical periods. In addition to examining original artefacts, and testing the anti-microbiological properties of traditional endpapers dyes, the study explores the historical context and trade interactions involved in the traditional uses of Islamic dyes.

To date, there has no conclusive evidence from primary texts, modern scientific publication or any other explanation as to whether yellow dyes were used for any specific purpose. This research aims to explore whether the traditionally used natural dyes in Arabic bookbinding endpapers were selected for their biocidal properties as well as their colour. The research aims also to investigate if bookbinders were knowledgeable about these properties, and to find out how effective they actually are as biocidal agents. This work seeks to address significant gaps in technical and historical knowledge about Islamic endpaper dyes and will contribute novel information from previously un-translated Islamic treatises. Further, findings will inform the conservation and preservation practices for book artefacts.

The period of interest of this research dates from the tenth to the seventeenth century. During that time local sourced and prepared dyes were used in Islamic book binding. However, after the seventeenth century local manufacture declined and an influx of European paper prevailed. Local production skills across the Islamic civilization were lost as a result. An interdisciplinary methodology is used in the research. This combines literature review and interpretative analysis, the interrogation of primary historic sources, the technical analysis of artefacts and empirical scientific study.

Preliminary results and findings from literature, including original manuscripts, suggest that turmeric, weld and saffron were the most commonly used sources of yellow colour during the medieval Islamic period in Egypt. The historical recipes, from original manuscripts, prove that dyeing paper was a direct method. Dyeing was done by dipping paper sheets directly into a dye bath and this was a job done by scribes not papermakers. It seems very likely that these three dyes have some useful biocidal properties. This is supported by evidence that they were historically used as medicinal drugs against some disease such as diarrhoea and skin complaints.

Natural dyes in Polish batik: a century of experiments

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At the beginning of the twentieth century Poland was one of several European countries to become fascinated by the technique of Javanese batik. During the years preceding the First World War, a group of artists associated with the organisation "Warsztaty Krakowskie" (Cracow Workshops), following systematic studies of Javanese design and technology of dyeing, introduced the batik technique into Polish textile decoration.

As the synthetic dyes available in Europe at that time yielded very poor results for low-temperature dyeing and the colours they produced were not light-fast, the artists decided to use only natural dyes. The recipes they developed were based on Central-Javanese methods of dyeing as well as the19th century dyeing formula used in Europe prior to the introduction of synthetic dyes. The dyes originated from India, Brazil and Mexico and were commonly used in the European textile industry before the development of synthetic dyes. The task of the Cracow Workshops team was to adjust these old recipes to low temperatures, necessitated by the use of wax resist. The most successful results were obtained with cochineal, sappan wood, Brazil wood, logwood and annatto. Occasionally, native Polish dyes were also used. The detailed formulae (in total: almost one hundred recipes) were published in the 1920s in three batik handbooks: by Okolowicz, Lorec and Wisz.

Batik on silk, natural dyes. National Museum, Cracow.

Almost a century later Dr Katarzyna Schmidt-Przewozna tested some of the formulae from the batik handbook by Norbert Okolowicz at the laboratory of the Institute of Natural Fibres and Medicinal Plants at Poznan. The results of these experiments will be presented at the conference.

Polish experiments with natural dyes adjusted to low temperatures are of interest to contemporary batik dyers in Indonesia who wish to expand the range of natural dyes used in Javanese batik textiles.

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Unusual dyeing recipes from 18th century Languedoc illustrated - Historical and technical comments

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At DHA 25, with several co-authors, I had presented an anonymous and mysterious manuscript, preserved in the south of France in a family's archives, containing "Memoirs on dyeing", with recipes illustrated by dyed samples of broadcloth. For DHA 30, I propose to present the results of the historical research I have pursued to better understand the context of this document, as an introduction. I shall then comment some of the recipes, showing how the choice of ingredients and the author's explanations of the processes contribute to situate the manuscript in its geographical and socio-economic environment and help date it fairly precisely.

Woad is more than blue

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The most predominant dye identified in the Hallstatt-Textiles is indigotin, interpreted as dyeing with woad (*Isatis tinctoria L.*) due to the historical and geographical context of the 3000 year old textiles [1]. The colours which the textiles show today could, however, not always be explained by the dyestuff analysis' results. Different woad processing and dyeing methods were carried out to reproduce the colours as they once may have been. During these experiments, several other colours than blue emerged. The aim of the presented research is to demonstrate how many variations in colour can be obtained by using different techniques with woad and how these colours can be explained by chemical analysis.

Woad was cultivated at the BOKU and harvested at two cutting times in summer 2010. Based on a literature review, dyeing experiments with wool were undertaken using fresh woad leaves, "green" woad balls and couched woad (both made of fresh and fermented leaf pulp). Woad pigment was produced and then used in urine vats and madder-bran-potash vats. The urine and potash vats were also carried out with natural indigo. The results of 33 dyeings with fresh leaves and 61 fermentation vats will be discussed. The colours obtained with woad comprise several shades of blue, violet, pink, green and beige. 22 dyed wool samples and 4 samples of the dyestuffs used (woad pigment, indigo and madder) were analysed with an HPLC quantitative analysis method.

An overview of the wide range of colours obtained by one single dye plant and the related analytical results will be presented. Most of the colour observations could be explained by the components found. A method to theoretically calculate hues of the dyed samples based on the relative absorption of woad components detected with HPLC will be discussed.

This research is part of the project "Dyeing techniques of the prehistoric Hallstatt-Textiles", funded by the Austrian Science Fund FWF, duration 08/2008-12/2011.

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Shellfish purple in pre-Roman Italy: new evidence from Strozzacapponi (Perugia/Corciano)

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While the earliest indication of the use of shellfish purple dye in Italy comes from the Early-Middle Bronze Age site of Coppa Nevigata in South Italy, where tens of thousands of mollusc *Hexaplex trunculus* shells have been excavated, until now none of the surviving pre-Roman textile fragments found in Italy have tested positive for this dye. The paper presents dye test results of mineralised textiles from the necropolis of Strozzacapponi near Perugia, Italy dated to the 2nd-1st centuries BCE. Textiles from several burials preserving traces of pink or purple colour represent the first and earliest direct evidence for the use of shellfish purple for dyeing textiles in Italy. The evidence for shellfish purple production in pre-Roman Italy will be reviewed in the context of this new discovery.

Identification of Tyrian Purple in Aegean Bronze Age pigments

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In the 23rd DHA meeting (Montpellier 2004), we reported the earliest direct chemical evidence for the use of the purple molluskan pigment [1]. Tyrian purple was identified in the form of pigment (17th c. BCE). The material was found after archaeological excavations in Akrotiri Settlement of Thera, an island located in the southern Aegean Sea. The univocal identification of the conchylian purple dyestuff was achieved using High Performance Liquid Chromatography with Diode Array Detection [1,2] and Mass Spectrometry [1,3] (HPLC-DAD-MS).

In the present investigation, we report the HPLC identification of Tyrian purple in four samples, which belong to the same archaeological period (Bronze Age) with the previously analyzed pigment [1]. The samples are as follows: (i) a microsample taken from a small quantity of purple pigment excavated recently, at a close area on the west of the Building Xesté 3, in which the previously studied paint sample was found [1]; (ii) and (iii) two samples taken from a wall painting belonging to a house excavated recently on the Site Raos, nearby Akrotiri; and (iv) a purple pigment, of the same archaeological period, from Trianda at Rhodes, an island located in the eastern Aegean Sea about 200km east of Thera.

The as received samples were treated with hot DMF or DMSO. The solutions were centrifuged and subjected to HPLC-DAD analysis. Separation was carried out using a C18 5μm column with dimensions 250mm×3.0mm. Gradient elution was performed using two solvents consisting of A: 0.1% (v/v) TFA in water and B: 0.1% (v/v) TFA, as described in detail elsewhere [4].

The following compounds were detected, in relatively high quantities, in the extracts of the historical samples: indigotin, 6 bromo indigotin, 6,6' di-bromo indigotin, the marker compound for the identification of Royal Purple, and 6,6' di-bromo indirubin. All four historical samples contained these four indigoid compounds. It is noteworthy that the same indigoids were identified in purple pigments from (i) Akrotiri (17th c. BCE) [1], (ii) a potsherd at Tel Kabri, Israel (7th c. BCE) [5] and (iii) a Darious I stone jar (5th c. BCE) [6]. Interestingly, the compositions of the archaeological samples analyzed in the present and previous [1,5,6] studies are similar according to the integrated HPLC peak areas, suggesting that the same raw material (Muricidae species) might have been used for the preparation of the purple pigments.

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What was The Royal Society doing with alum in the mid-17th century?

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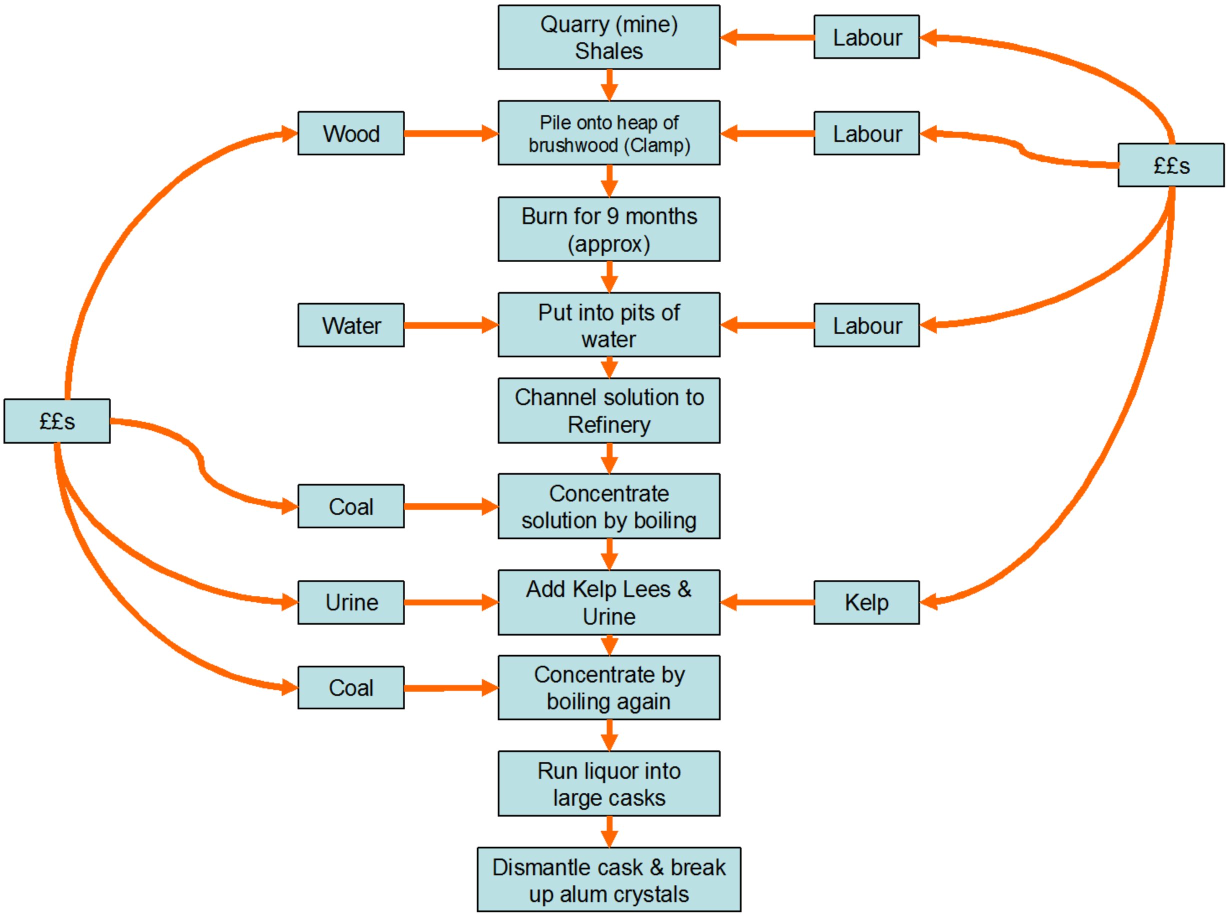
In the nascent years of The Royal Society, a group of interested people were pursuing a vigorous, Baconian inspired, 'History of Trades' programme, that included the Dyeing industry with apparently related investigations into the Alum and Copperas industries.

This presentation looks at the 17th century alum industry in Yorkshire in the context of the role of those early Fellows, together with other innovations in the development of a viable business that survived until the late 19th Century.

A possible rational explanation is also suggested for the development of the complex, convoluted, and in modern terms 'counter-intuitive', production process that involved roasting ore for nine months before leaching soluble salts from the ore to mix with urine and kelp to produce a marketable mordant.



The use of hand held XRF as an aid to the identification of dyes

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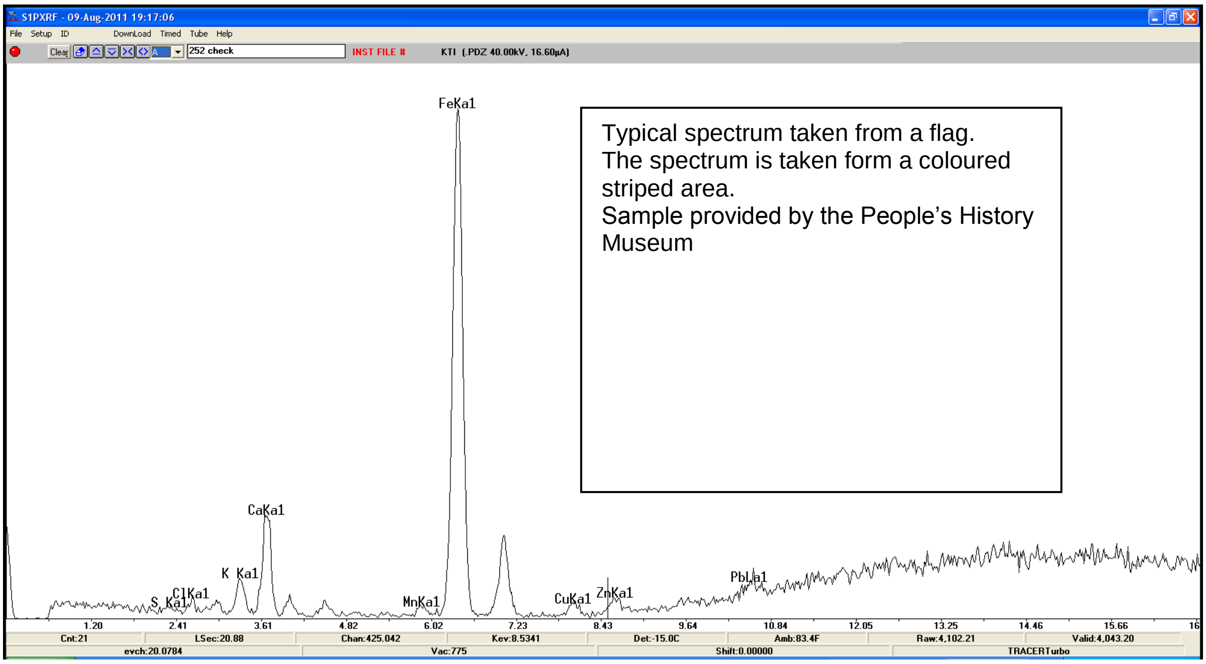
Hand held X Ray Fluorescence (XRF) offers a quick, portable and non destructive means of identifying a wide range of elements in virtually any material. With the advent of the latest detectors it is now possible to see even the lighter elements.

This presentation will start with a brief look at X-Ray Fluorescence (XRF) theory and some of the many variables within the technique including the all important depth of analysis. To get the best result the operator needs to have control of all the instrument variables, voltage and current and beam profile through the use of filters and secondary targets, which Bruker allow you to do. Often it is necessary to take 2 spectra under different conditions to find the full story. It is not always possible to produce meaningful numbers, quantification. As we look at the applications we will consider when quantification is possible and when not. Remember the answer is always in the spectrum!

We will then look at a few examples of spectra taken from a variety of fabrics followed by a live demonstration of the equipment.



A New Methodology for the Analysis of Cochineal Dyes in Historical Textiles

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The history of natural red dyes involves power and extravagance. Difficult to acquire, luxurious red-dyed textiles were extremely valuable and only worn by a wealthy elite. The most dazzling red-dyes were obtained from cochineal insects. Collected in Central Europe and Central Asia, different species of *Porphyrophora* were extensively traded in medieval Europe and Asia. With the Iberian Expansion in the 16th century, the Spanish began exporting American cochineal (*Dactylopius* species) from Mexico, which achieved great success in Europe and Asia. Richer in colorant than other insects, this dyestuff brought enormous financial profit to the Spanish Empire [1-3].

The main aim of this paper is to understand the extent to which American cochineal was assimilated by European and Islamic textile production centres, in contrast to other, locally-available, red dye sources, such as kermes or *Porphyrophora* species. A small group of European and Islamic textiles originating from Italy, Turkey, Iran and India, and made between the 15th and 17th centuries, were analysed by High Performance Liquid Chromatography with Diode Array Detector (HPLC-DAD) and multivariate data analysis. A new methodology based on a mild extraction method, combined with a new dye recovery treatment, was applied to obtain HPLC chromatograms with good resolution. Hence, Principal Components Analysis (PCA) and Mass Spectrometry (MS) were used to identify the cochineal species present in the textiles, by comparing the results with a powerful PCA reference database, which consisted of diverse species of cochineal, collected from different regions in Europe, the Americas and Asia [4]. The methodology developed has successfully shown that it is possible to obtain accurate and consistent information for the identification of cochineal sources, in order to trace the assimilation process of American cochineal in European and Islamic dyeing traditions, beginning in the 16th century.

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Are Transforms of Diffuse Reflectance Spectra Suitable for Use in Dye Identification?

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Portable UV-visible and x-ray fluorescence (XRF) spectrometers are often the only non-invasive analytical tools available for obtaining analytical data on the composition of objects in collections, especially in conservation laboratories with few technical staff and limited means. XRF spectroscopy collects elemental information. This data may suggest which mordants and dyeing aids are present, but the procedure is not capable of dye recognition.

A project to upgrade our capability to identify natural and early synthetic dyes in textiles has provided Conservation scientists at LACMA with an opportunity to reassess the information obtainable from diffuse reflectance spectra of dyed materials. UV-visible reflectance spectra of coloured objects frequently appear relatively featureless and somewhat indistinguishable, especially for red and yellow colours. The Kubelka-Munk transforms and derivatives of these data often reveal spectral features characteristic of particular dyes more clearly. This approach has been used to distinguish between yellow dyes and to track changes caused by ageing red dyes on wool, for example [1,2].

However, many coloured textiles, especially from the eighteenth and nineteenth centuries, contain more than one dye and several dyeing aids. This situation can make dye identification based on reflectance spectral data a major challenge. By collecting data on mixtures of fibre samples from modern woollen yarns, dyed with known traditional dyes and dyeing aids, such as those in the Schweppe Collection at the Getty Conservation Institute, we are developing a library of absorption and derivative spectra of dye combinations to use as a reference for studying historic textiles. Comparison of the reference data to spectra of 19th century wool fibre samples, from yarns for which dyeing recipes are available, is aiding in the recognition, not only of unique combinations, but also of pitfalls in the procedure, such as different combinations of dyes and mordants that result in similar spectral features.

The qualitative data obtained from evaluation of reflectance spectra suggest the identity of dyes when sampling and extraction are not possible. The spectral information can also assist in the judicious use of microsampling for application of additional analytical procedures.

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Natural Organic Dyestuff Analysis: The Charged Aerosol Detector (CAD) compared to the Diode Array Detector (DAD)

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The identification of natural organic dyes and pigments mainly found on textiles, paintings and manuscripts is of great importance not only to get a general idea of the colouring materials applied in former times but also to restore dyed objects very similar to their original state.

A conventional High Performance Liquid Chromatograph (HPLC) connected with a Diode Array Detector (DAD) is the most commonly used equipment for those analyses purposes [1]. Nearly always the dyeing components are dissolved from their supporting materials by the “Standard HCl Extraction Process” [2,3] then following their separation by gradient elution on a reversed phase column (particle size 5 µm). Recently it was reported in literature on Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS), a method, which allows the direct determination of dyeing substances on different sorts of writing materials and fibres without prior extraction, thus having the advantage of being less time-consuming [1].

In this study we focused on the modern Ultra High Performance/Rapid Separation Liquid Chromatography (UHPLC/RSLC) technique which compared to conventional HPLC systems has important benefits like faster runs for a high sample throughput, better resolution of substances, a clearly reduced demand on organic solvents and therefore delivers much lower operating costs. This means for dyestuff analysis that the running time could be drastically reduced from 35 min to well below 10 min, because the pumps are constructed for pressures up to 800 bar thus allowing the use of columns with a particle size lower than 3 µm.

This binary gradient RSLC system is ideal to couple it either with a modern high-resolution DAD or a Charged Aerosol Detector (CAD) singly or in series and this was done for analysis of dyeing materials. While UV/VIS detection is limited to compounds that possess a chromophore, the CAD is well-known for its consistent response independent of analyte chemical structure and helps to measure analytes that cannot be seen by UV/VIS and may not be readily detected by mass spectrometry. The CAD works with a high-voltage corona to charge nitrogen molecules which collide with analyte particles resulting in the formation of charged particles. The aggregate charge is measured using a conductive filter and a sensitive electrometer (sensitivity in high-pg).

The following dyes were selected to find out the pros and cons of DAD and CAD: purple from *Murex trunculus*, indigo from *Isatis tinctoria* and *Indigofera tinctoria*, madder from *Rubia tinctorum*, cochineal from *Opuntia decumana* and weld from *Reseda luteola*.

Moreover the RSLC-method in combination with DAD and CAD was applied to a Turkish carpet with brown, yellow and red colour elements.

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Determination of Yellow Dyes based on Quantitative Analysis of Protoberberine Alkaloids

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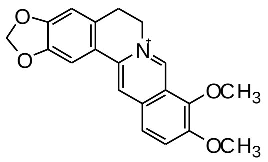
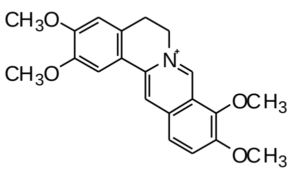
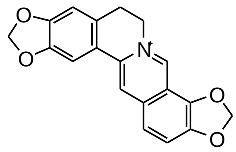
Ingredients and their ratio in natural dyes frequently reflect their habitat and plant species. Dye plants including Protoberberine alkaloids have been used as medicinal herbs since ancient times. Particularly, the Amur cork tree which was widely distributed and has been used as a traditional natural dye in East Asia, is easy to detect non-destructively based on its characteristic spectroscopic properties of the major ingredient, Berberine. In this research, we focused on determination of dye plants including Protoberberine alkaloids by quantitative analysis. HPLC analysis of the dye extracts showed the difference of chemical species in the quantity [1]. Then, determination of habitat of the tree on the ratios of minor ingredients, Palmatine and Jatrorrhizine, to the major one, Berberine strongly reflected the difference of the species between *Phellodendron amurense* in Japan and *Phellodendron chinense* in China. Analyses conducted on Japanese and Chinese cultural textiles stored at Kyoto Institute of Technology also showed similar distributions of the ratios of ingredients in the Amur cork tree (Fig. 1), and summarized relations of Palmatine to Berberine vs. Jatrorrhizine to Berberine in Fig. 2. Thus, this quantitative analysis will provide a methodology of determination of a production area for the cultural textiles on the basis of the habitat of the Amur cork tree.



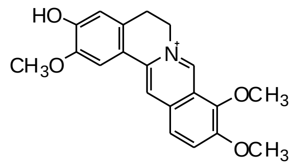
Berberine (B)



Palmatine (P)



Coptisine (C)



Jatrorrhizine (J)

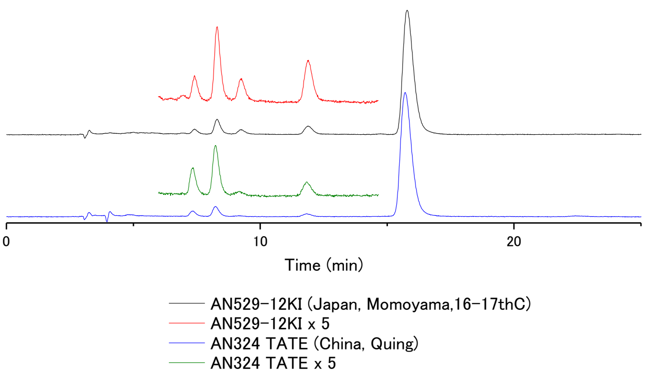


Fig. 1 HPLC chromatogram of extract from traditional textiles from KIT Collection
AN.529-12KI and AN.324TATE

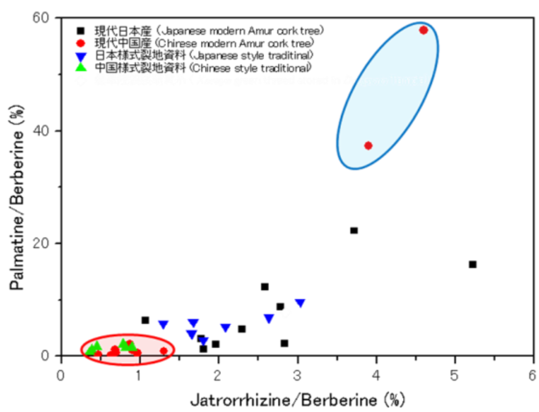


Fig. 2 Plot of relative amount of Palmatine to Berberine vs. Jatrorrhizine to Berberine based on HPLC analysis in extracts from silk clothes dyed by modern Japanese (■)and Chinese (●)Amur cork tree, and Japanese (▼)and Chinese (▲)style traditional textiles stored in KIT Museum

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Identification of Dyes in Rare Fatimid Textiles in the Museum of Faculty of Archaeology, Cairo University, Egypt

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This study aims at investigating dyes on some Fatimid textile objects in the Islamic Textile Collection in Museum of Faculty of Archaeology, Cairo University Egypt. Investigation of dyes is a necessary step in the documentation of textile objects, it helps the conservators to develop and establish methods for conservation, treatment of these objects and to choose suitable and safe materials for conservation treatment. It helps the historians and archaeologists to solve, interpret and reply to many questions. These objects also contain different colours such as red, blue, green and yellow. The textile objects contain many decorations such as plants, words, animal and geometric decorations. Modern textile samples were dyed with natural dyes to be used as known dyed textile samples (reference samples). Representative dyed textile samples collected from the studied museum were identified with A High Performance Liquid Chromatographic method coupled to a Diode-Array-Detector (HPLC-DAD).

Keywords: Dyes, Islamic textiles, HPLC-DAD, Identification, Archaeological textile

Analysis of organic colorants at the British Museum and preliminary results from study of the Andean textile collection

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The British Museum (BM) Research Laboratory, established in 1919, has a long history of scientific investigation of its collections. Records show an increasing interest in organic colorant analysis from the 1950s, and particularly from the mid-1980s onwards, primarily relying on TLC, spectroscopic methods and microchemical tests. Emphasis on molecular-level chemical investigation of organic materials has increased since 2000 following strategic expansion in this area, to complement the already well-established study of inorganic and biological materials. In 2008 the BM acquired an HPLC with a photodiode array detector.

The BM's collection of over 7 million items, spanning 1.8 million years of human history includes examples of organic dyes and pigments from all over the world and the BM continues to actively collect contemporary artworks. This wide geographical and temporal range is the main challenge when undertaking colorant analysis on the collections. However, it is important to be able to characterise specific colorant sources and explore dye and pigment production processes to address major archaeological, anthropological, art historical, cultural or technical questions and thus improve understanding and interpretation of the associated objects. Characterisation of organic colorants is also important to inform and improve conservation and display strategies, and to understand changes in condition or appearance.

Over the last three years, research on organic colorants has focussed on developing chromatographic, spectroscopic and imaging techniques for their characterisation with a particular focus on non-Western colorants and to addressing the conservation challenges presented by such materials. This work is benefitting from the BM's involvement in the CHARISMA project [1] and from research being conducted as part of the *Andean textiles: organic colourants, biological sources and dyeing technologies* [2] and *Interventive conservation of black-dyed organic materials* [3] projects.
In this paper, the HPLC analytical procedure developed and optimised for the characterisation of both organic dyes and pigments at the BM will be presented. Initial work on the optimisation of methods for extraction of organic colorants from a range of substrates and matrices (e.g. dyed, painted or stained samples) will also be discussed, outlining the approach that is being adopted. Particular emphasis has therefore been placed on developing extraction methods that, while not always fully quantitative: (i) maximise the information that can be obtained from a sample; (ii) are suitable for the widest range of colorant classes and preserve highly sensitive dyes which may be present in mixtures; (iii) preserve the glycoside content and other chemically labile components which can be highly informative of the biological source and/or dyeing or pigment-making technologies and (iv) are suitable for the analysis on non-Western colorants and the BM's ethnographic and archaeological collections.

To illustrate this analytical development, preliminary analytical results from the *Andean textiles: organic colourants, biological sources and dyeing technologies* project will be presented, focusing on material from Peruvian weavers' workbaskets from the Late Intermediate period in the BM collections.

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Renaissance pigments from textiles: silks from the Victoria & Albert Museum and sources of dye for pigments in paintings from the National Gallery Collection

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Analyses of red lake pigments in paintings dating from the 15th to the 17th centuries in the National Gallery Collection indicate that for madder, kermes and Old or New World cochineal lakes, the dyes were often extracted from textile shearings. The dyeing process is therefore the first stage, and the resulting textiles the 'raw material', for pigment production. A recent project cataloguing some of the rich collection of 14th- to 17th-century silk velvets in the collection of the Victoria and Albert Museum, London, provided an ideal opportunity to consider this first stage in the production of lake pigments derived from dyed silk.

Until the first decades of the 16th century, kermes and lac (a dye not normally extracted from shearings for pigment use) have been found to be the predominant dye sources for lake pigments. Carminic acid-containing dyes are infrequently found at this time, although they become very common in the later 16th century. However, in the velvet textiles dating from the 15th century on stylistic grounds, the use of Old World cochineals (Armenian and Polish) was most prevalent. The dating of these textiles was useful as the analytical distinction between Armenian and New World cochineal dyes on silk is difficult. In addition, textiles thought to be Ottoman on stylistic grounds were found to have a very different dye profile from the Italian textiles. Purple lichen dyes, which to date have not been identified in lake pigments, were also found on one or two of the velvets.

This study has highlighted some of the differences in the analytical results from textiles and lake pigments and the comparison between the two has proved to be extremely helpful. Most importantly it has shown that the few, somewhat tentative identifications of Old World cochineal dyestuffs in lake pigments are probably not anomalous. Possible reasons for their apparently infrequent occurrence in lake pigments will be suggested and the results from the Victoria & Albert Museum textiles discussed.

The preparation of madder-based pigments in antiquity

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Madder dyes and pigments were widely used in antiquity but no clear descriptions of the preparation of madder-based pigments from these times have been found. Previous analyses of pigments from Greek, Roman, Parthian and Egyptian contexts have been reviewed, focusing both on the organic components and the inorganic substrate or support. Chalk-, gypsum- and alumina-based substrates are reported, but what is most striking is the strong UV-induced luminescence typically shown by the samples and the high proportion of purpurin/pseudopurpurin frequently reported.

To start to investigate whether the high proportion of (pseudo)purpurin indicates the use of *Rubia peregrina* as the predominant colorant source in these contexts (rather than *Rubia tinctorum*) or reflects the method of pigment production, a series of pigments have been prepared using the methods hinted at in the literature. to investigate how these influence the final composition of the pigment. These experiments have also allowed the practicality of making pigments by these various methods to be evaluated.

Pigments have been prepared directly from the plant material and via dyed wool, and include examples where the dye components have been co-precipitated with the substrate and where the dye components have been adsorbed onto a solid substrate added to the dye solution. The experiments suggest that a high degree of fractionation of the different madder glycosides and aglycones is possible. The resulting pigments and various intermediate products have been analysed using a combination of high performance liquid chromatography with photodiode array detection (HPLC-PDA) and Fourier transform infrared and X-ray fluorescence spectroscopy. For the HPLC-PDA analysis, soft extraction techniques have been used to preserve information about the fate of both the aglycone and glycosidic components. The analytical results together with the physical and chemical properties of the dye/pigment precursors have thrown new light on the methods and technology of pigment production.

The Gösta Sandberg collection of dyed textile samples, dying equipment and archival material at the Museum of World Culture in Gothenburg

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Gösta Sandberg, the Swedish author of “The Red Dyes: Cochineal, Madder and Murex Purple: A World Tour of Textile Dyeing” (1994), has bequeathed/donated his vast collection of dye related specimens, and archival material from around the world to The Museum of World Culture in Gothenburg (Världskulturmuseum, VKM).

Professor Gösta Sandberg was one of Sweden’s most renowned textile connoisseurs, with a particular interest in natural dyes and dyeing processes from the whole world. He has written several books about textile dyeing, among which the one on Indigo, “Indigo Textiles: Technique and History”, first published in 1986, is probably the most well known.

After his death in 1995, the Collection was brought from his house in Nora to the Museum in Gothenburg and the more than 1500 objects were arranged, catalogued and digitised to enable them to function as a cohesive Study Collection, available to researchers and textile experts, according to the will of the donator.

The Collection contains objects/samples from the whole world, medieval tol contemporary, and explain the different dyeing techniques there are; the genesis series showing step by step procedures. The collection includes textile tools such as wooden blocks for printing, weaving frames for ikat, cantings for applying wax to batik, etc.
Apart from the textile samples and technical equipment there is also an impressive archive containing books and texts from the 16th century and onwards.

This presentation wants to give a closer look at the Collection and show its great value and usefulness to textile researchers, in particular to those interested in the history of dyeing techniques and dye analyses.

Dyes as Ink, Ink as Medicine - Drinking the Word of God in Northern Nigeria

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Historically what is today Northern Nigeria encompassed the thousand year old polity of Bornu-Kanem adjacent to Lake Chad, Hausaland with its vibrant trans-Saharan trading centres of Katsina and Kano, and the Sultanate of Sokoto. These were major Islamic intellectual centres that created substantial collections of manuscripts in Arabic script of ink on paper. Recent research and chemical analysis of the inks used in these manuscripts revealed a reliance on dyes made from native plants. Sixty-three species or genera were identified, each of which produced dyes, tannins or additives of use in ink making. Many of these plants also produce the dyes used in textiles, leather and straw dyeing. 90% of these plants also have medicinal properties.

Arabic is the language of the Qur'an and as such is regarded as the veritable word of God. Its use in writing charms confers an aura of sanctity on anything written in its script. There is a wide spread tradition of charm writing in West Africa. The words are rinsed off the surface of the charm and the results drunk – drinking the word of God. There is evidence that some of the writers of these charms also used the medicinal properties in these inks to deliver medicine. This paper explores how charm writers in Northern Nigeria used their knowledge of plants, and the local dyers' craft, to deliver effective medicines to treat a wide variety of the multitudinous ills affecting the local population, with the ink they used in charm writing.

POSTERS
(listed alphabetically by presenting author surname)

Application of Laser Induced Fluorescence as a Non-destructive Technique in Identification of Dyes on Museum Textiles in Egypt

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This study aims to evaluate the use of laser induced fluorescence (LIF) as a non-destructive technique for identification of dyes on museum textiles in Egypt. Various dyed textile samples were collected from different museums across Egypt. The dyes in these textile samples were identified with high performance liquid chromatography (HPLC). These textile samples were also investigated with SEM-EDAX to identify the mordant on them. A new batch of samples were dyed with the identified natural dyes, such as cochineal, cutch, henna, indigo, lac, madder, safflower, saffron, sumac and turmeric. These new samples will be used as a standard guide to identify future unknown archaeological dyes. Both the new samples and the originals were investigated directly without any treatment with laser induced fluorescence for identification of each dye. Most of investigated dyes in the samples were identified with LIF. This study confirms that laser induced fluorescence may be used as a rapid and as a non-destructive technique for identification of natural dyes on archaeological textile objects.

Keywords: Tapestry Textile Samples, Laser Induced Florescence, High Performance Liquid Chromatography (HPLC), Museum of Faculty of Archaeology

Effect of After Treatment Process on Woollen Dyed Properties by Madder

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Nowadays, the application and production of natural dyes is becoming more popular owing to the growing awareness of environmental problems coupled with the toxicity associated with synthetic dyes. As a result, deep understanding of natural dyeing process and effective parameters is very important. In this study, the pre-mordanting and dyeing were carried out on the woollen yarn with Ardakan madder, that is, the best known madder in Iran. It is known that water is very important in the textile wet process. If the natural dyeing is carried out in the traditional workshop then hardness will be more important and considerable. After the dyeing process of wool yarns by madder, we used 6 different conditions. Samples were treated in different conditions of traditional washing simulation.

Effect of the after treatment process on the dyeing properties has been studied by a number of techniques. Spectrophotometer (Gretag Macbeth Colour-Eye 3100A) is used to measure the range of colour obtained on textile materials by using L*, a*, b*, h*, C* and dye absorption concentration on the surface of Textile materials by using K/S values. They are examined under D65/10 light respectively. Fastness testing of samples also has been done. The results show that kind of hardness and its degree is very important in the dyeing properties.

Keywords: Colorants, mordant, natural dyes, plants

Optimization of variables in the dyeing of woollen yarn by madder in order to dye matching

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A literature review showed it was possible to replace synthetic dyes with eco-friendly natural dyes. The aim of the study is optimisation of the natural dyeing process in order to find a reputable method for dye matching. Effects of varying time, temperature, pH, material to liquor ratio, concentration of mordant, concentration of dye have been studied for optimisation of the conditions of dyeing. Fastness tests on dyed samples for light and washing are carried out. The range of colours developed on dyed materials are evaluated in terms of (L*, a*, b*) CIE LAB coordinates and the dye absorption concentration on the woollen yarn dyed by madder is studied by using K/S values.

Keywords: Madder, natural dyeing, dye match, wool

Dyestuff analyses and decoration methods of the Chalcolithic painted and dyed pottery of Azerbaijan

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In studying of the Chalcolithic painted and dyed pottery of Azerbaijan there was held dyestuff analyzes of this pottery by the AAS-300 instrument from Perkin Elmer. Introduced samples picked out from the Mugan, Garabakh, Ganja-Gazakh and Nakhchivan Chalcolothic settlements in Azerbaijan. In the issue of the results of the analysis it became clear that the dyes obtained were by the synthesis of the natural pigments and organic matter. Basically, iron oxide was used together with hematite, pyrite, limonite and ochre. According to the results of the researchers hematite was used in getting dye for the first time.

In the ornamentation of the pottery different kind of paintbrushes were used. The different kinds of lines and stripes drawn over the pots prove this.

A table of dyestuff analyses and methods of ornamentation are also included in this paper.

Determining stability constants of kermesic acid and flavokermesic acid complexes with tin(II) by potentiometric method

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The insects 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 the 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 °C were found. The formation constants of tin(II) 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-tin(II) complex logK’ = 7.44 and for flavokermesic acid-tin(II) complex logK’ = 7.84 at the 25 °C. Conditional formation constants of complexes, under the assumption that only the existence 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 constants reach a maximum was determined.

Raman spectroscopy of nineteenth century synthetic textile dyes

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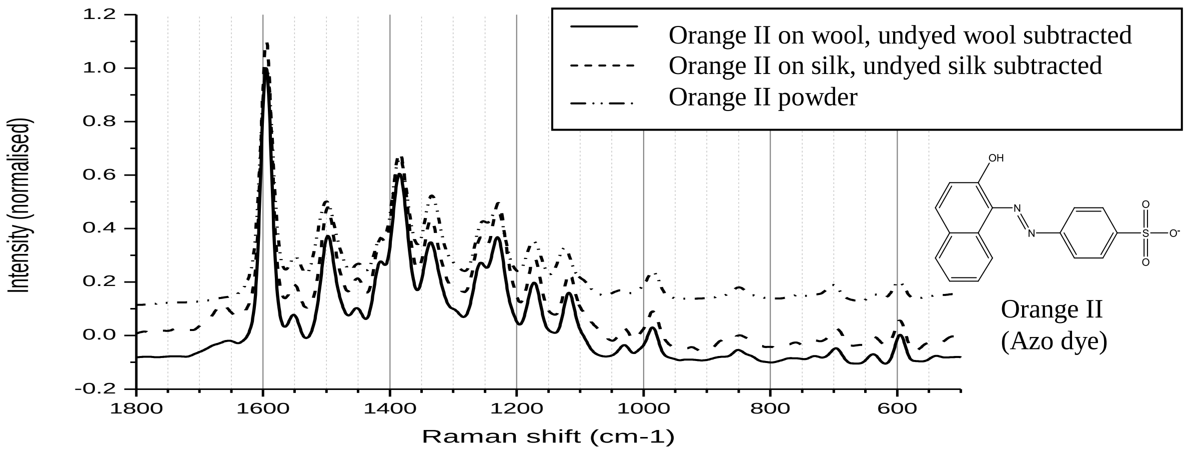
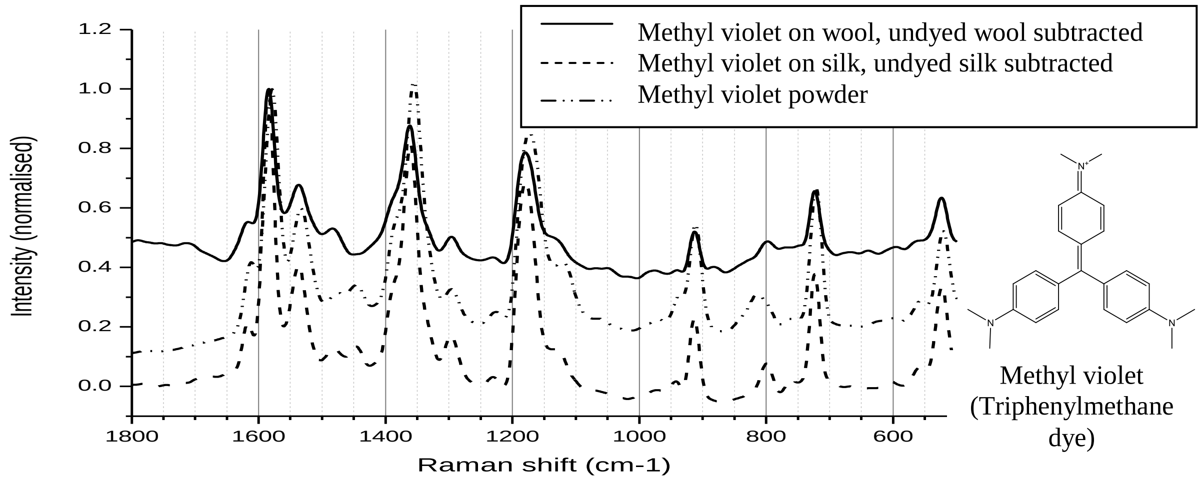
Spectroscopy is a technique for analysing the chemical composition of materials. In Raman spectroscopy the sample is illuminated with laser light of a single wavelength which may interact with the chemical structure of the molecule and re-emerge with a different wavelength. The intensity of this scattered light is plotted against the change in wavelength producing a spectrum which is specifically related to the composition of the material. Fourier transform Raman (FT-Raman) is a refinement of this technique which produces a higher resolution spectrum and is preferred for weak spectra.

This technique has been applied to a range of nineteenth century synthetic textile dyes applied to modern samples of wool and silk. Examples of azo and triphenylmethane dyes were used. The spectra produced show some similarities between chemical classes of dyes as well as differences between individual dyes. The spectrum of the dye on the fabrics could be extracted by subtraction of the spectra of the undyed fabric as shown in the two examples below.





This paper will present the results for a range of dyes and discuss the application of the method to the identification of dyes in situ on fabric.

Portable and micro-XRF: a non-destructive way to screen textiles and identify mordants

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Traditionally, the analysis and identification of mordants and inorganic components in fabric has required the irrevocable removal of a sample and its destructive treatment by ashing and elemental analysis, either by semi-quantitative energy dispersive spectroscopy (EDS) with a scanning electron microscope (SEM), or by X-ray fluorescence (XRF) [1-3]. Recent work at the Smithsonian Museum Conservation Institute has shown that modern, portable X-ray fluorescence (PXRF) instrumentation is well suited for in-situ identification of mordants and other inorganic components in textiles. PXRF spectrometers have been used to identify iron, copper and chromium mordants in some late 19th century Alaskan Chilkat textiles as well as tin in weighted silks and a range of metal mordants (iron, copper, nickel and chromium) in textile samples from a collection of textile technology books from the early 20th century. Such instrumentation also has been used to screen large numbers of objects (including textiles) in the Smithsonian Museums' collections for the presence of heavy metal pesticides, such as arsenic and mercury compounds [4-6].

Despite the benefits of handheld XRF instrumentation for analysis of textiles, there are some drawbacks which include the large area of analysis (usually 4-10 mm^2 or larger) which limits spatial resolution and an inability to detect some light elements fundamental to textile history, dyeing, and pesticide use. Some of these issues can be overcome with micro-XRF instrumentation, such as the Bruker ARTAX 800 spectrometer which, with helium purging, is capable of detecting elements in the range from Na(11) to U(92) and, with a spatial resolution of ca. 80µm, permits the non-destructive analysis of individual textile threads and other fine detail.

Micro-XRF has been used successfully to identify mordants in small cotton printed textile designs and those in sheer wool challis. Textiles also have been screened for the inorganic elements of pesticides, finishing agents and, after dyeing treatments, for surfactant residues, pollutants and soil characteristics; even for the identification of bromine in Tyrian purple. This poster highlights recent work involving portable- and micro-XRF characterization of textiles.

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Characterisation of organic pigments by HPLC-ESI-Q-ToF: preliminary investigations

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The wide use of synthetic products in art and in restoration makes mandatory the assessment of their stability and degradation pathways, and the development and evaluation of adequate analytical methods for their characterisation in artworks. This knowledge is extremely relevant for the selection of preventive conservation conditions so as to reduce the frequency and invasiveness of restoration work. In the context of the PAR-FAS Regione Toscana COPAC Project - *Preventive Conservation of Contemporary Art* (2011-2013) we are studying the ageing processes undergone by synthetic organic pigments in alkyd paint systems.

Reference mock ups have been prepared with Winsor & Newton alkyd paints containing Phthalo green (PG7), Winsor Lemon (PY3), Winsor red (PR170 plus PR188) and Phthalo Blue (PB15) as pigments. The reference paint layers will be characterised by means of colorimetric techniques (FORS) and several chromatographic and mass spectrometric methods (GC/MS, Py-GC/MS, DE-MS, HPLC-DAD, HPLC-ESI-MS) during natural and artificial ageing.

Preliminary results obtained by HPLC-DAD and HPLC-ESI-Q-ToF analysis of the reference mock ups are presented. The preliminary results allow us to evaluate the suitability of High Resolution Q-ToF mass spectrometry for the characterisation of synthetic organic pigments in alkyd paint system.

The extremely high number of possible synthetic organic pigments that can be encountered in samples from contemporary art requires the adoption of a highly sensitive and selective recognition technique such as tandem mass spectrometry. Moreover, the use of high resolution mass spectrometry enables us to determine the exact molecular formula of unknown components, allowing us to approach the characterisation of paint samples containing complex mixtures of both known and unexpected organic components.

A case study relative to the application of the HPLC-ESI-Q-ToF method to samples from artworks by Fernando Melani (Pistoia, 1907 - 1985) conserved at the Museum-Studio Melani in Pistoia (Italy) is also presented. Residual original paint materials found in the studio have been analysed and the relevant results will also be presented.

Examination on RP-HPLC-DAD, colour and fastness properties of dyed silk fabrics with madder (*Rubia tinctorium* L.) and Walloon oak (*Quercus ithaburensis* Decaisne)

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Natural dyes used in dyeing fibers are made from natural living sources such as plants and animals [1]. The most important red dye source, madder (*Rubia tinctorium* L.) plant contains alizarin, pseudopurpurin, munjistin and as many as 15 other anthraquinones as effective dyes [2]. The roots of madder are the source of a natural dye and have been used for dyeing of the textile fibres such as wool or silk in many parts of the world since ancient times [3]. Their active components are essential anthraquinones — alizarin and purpurin [4]. Madder is a member of the Rubiaceae family that has historically been used since ancient times (~2000 BC) as a source of lake pigments for textile dyeing (cotton, wool and silk) and for painting [5]. The several anthraquinone derivatives used in dyeing fibres were exhibited various biological activities, such as anti-oxidant, anti-microbial, anti-fungal, cytotoxic, larvicidal, anti-viral and unfortunately also genotoxic activities [6]. Walloon oak (*Quercus ithaburensis* Decaisne) is a tree growing to 15-20 m in open forests in Turkey and Greece. Their acorn caps contain 25-35 % tannin. The complicated chemistry of tannins has been explained by Schweppe. The hydrolysable tannin *i.e.*, ellagic acid is found in the bark of oak [7].

The aim of the study, 100 % silk fabric samples were dyed according to eight different dyeing processes with madder (*Rubia tinctorium* L.) and Walloon oak (*Quercus ithaburensis* Decaisne) extracts. A reversed phase high performance liquid chromatography (RP-HPLC) with diode-array detection (DAD) method was utilized for the identification of dyes present in the dyed fabrics and the plant extracts. Using of two natural dye sources together in the same dye bath in general appears to improve wash fastness. The light and wet/dry rub fastness test results are quite good. In contrast, perspiration fastness values were in most cases slightly decreased. Dyeing protein fibres with natural dye (alizarin, munjistin, purpurin, gallic acid, ellagic acid, *etc.*) can be an important advantage for the environmental processes.

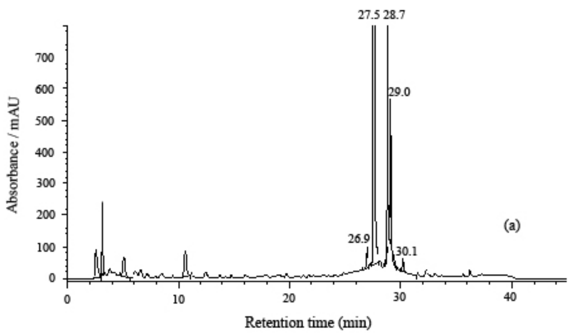

Figure 1. HPLC chromatogram of the acid hydrolysed madder.
(26.9; munjistin, 27.5; alizarin, 28.7; purpurin, 29.0; rubiadin, 30.1; xanthopurpurin).

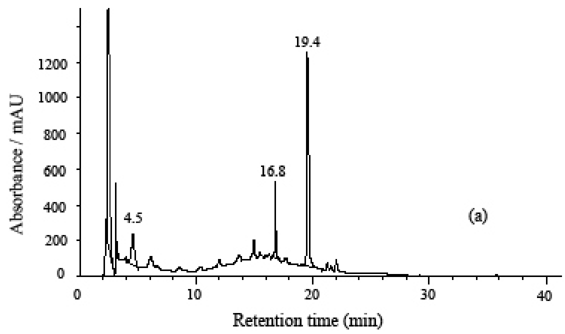

Figure 2. HPLC chromatogram of the acid hydrolysed Walloon oak.
(4.5; gallic acid, 16.8; ellagic acid derivative, 19.4; ellagic acid).

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Investigation of dyeing properties of silk fibres dyed by weld (*Reseda luteola* L.) and Walloon oak *(Quercus ithaburensis* Decaisne*)*

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Weld (*Reseda luteola* L.) is an annual or biennial herb. The whole of the plant was used for the dyeing of wool and silk. The yellow dyes as the colouring matter is concentrated mainly in the leaves, inflorescences and fruit [1]. Luteolin and apigenin flavonoids are the effective dyes present in the weld plant [2]. Luteolin from these dyes is known to posses antibacterial and anti-inflammatory properties [3]. The weld-dyed textiles have very good light fastness [4]. Walloon oak (*Quercus ithaburensis* Decaisne) is a tree growing to 15-20 m in open forests in Turkey and Greece [5]. Their acorn caps contain 25 - 35% tannin [1,4]. The hydrolysable tannin; ellagic acid is found in the bark of oak [6,7]. Interest relating to ellagic acid has increased lately due to antimutagenic, antiviral and anticarcinogenic effects. [8].

In the study reported here, for the analysis and the dyeing of silk fabrics an analytical method was developed. According to the results of HPLC analysis of the dye plants, it was determined that luteolin and apigenin in the acid hydrolysed weld extract (Figure 1) and gallic acid and ellagic acid in the acid hydrolysed Walloon oak extract. The effect of different percentages of dye plants on the colouring scale of the dyed silk fabrics was investigated. 100% silk fabric could be dyed with the natural dyes (gallic acid, ellagic acid, apigenin and luteolin) using various dyeing processes. However, the light fastness properties of dyed fabrics were not extremely high, the rub fastness properties were quite good.The colouristic properties, the rub and light colour fastness of the exhaust dyed 100 % silk fabrics by the natural dyes. These were evaluated and compared with each other.

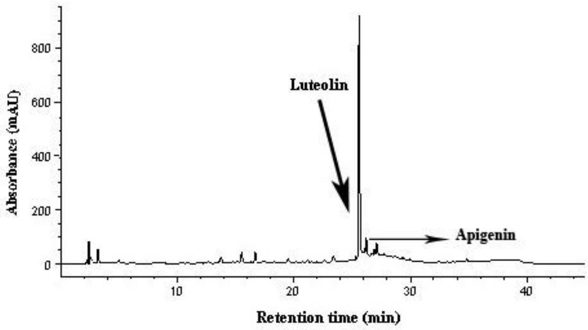

Figure HPLC chromatogram of the acid hydrolysed weld.

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Can colour protect? The role of yellow dyed endpapers in protection against biological attack

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This poster presents research in progress investigating the use of natural dyes in Egyptian book endpapers. Included is a review of the sources, use and preparation of a selection of significant Arabic dyes for endpaper dyeing in Egypt. The intercultural influences affecting the introduction and spread of the use of these dyes are also discussed.

The research is investigating whether natural dyes used in traditional Islamic book binding methods, - such as saffron, turmeric and weld - were selected for their biocidal properties as well as their colour. It is uncertain how knowledgeable bookbinders were of these properties or how effective these dyes actually are as biocidal agents. This work in progress summarises interim evidence from previous research and historical information about how these dyes were used. Future work will include a technical study of the selected dyes, to establish some empirical evidence for their biocidal properties.

Methods for the research:

- Primary literature review, interpretation and translation: Review the historical background of traditional paper dyeing techniques; identify protective traditional methods of paper from the biological attack.
- Field study: Collect archaeological samples (endpaper samples) from Egyptian museums and libraries undertake applying relevant analytical techniques such as High Performance Liquid Chromatography and Scanning Electron Microscope examination.
- Empirical testing: Explore practically the selected natural dyes materials by making up some dyed samples from original recipes. Testing the antibacterial properties of three selected natural dyes (saffron, turmeric and weld) against some common species of bacteria frequently found in museums and libraries by using the Poisoned Food Technique bacteriological testing.

Findings from literature, including original manuscripts, suggest that turmeric, weld and saffron were the most commonly used sources of yellow colour during the medieval Islamic period in Egypt. The historical recipes, from original manuscripts, prove that dyeing paper was a direct method. Dyeing was done by dipping paper sheets directly into a dye bath and this was a job done by scribes not papermakers. It seems very likely that these three dyes have some useful biocidal properties. This is supported by evidence that they were historically used as medicinal drugs against some disease.

Decaying markers of some wall painting artificial aging pigments by the air pollutants agents and the biologic attack

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Restoration processes mainly involve the most appropriate interventions for cleaning and consolidation of the painting layers on the support and even the support itself [1-3]. The available procedures have to be related to the types of chemical compounds in the decayed layers [3], [4]. Usually the decayed products are mixtures of different compounds in small amounts which are hardly detected in situ by non-invasive methods. For this reason we need to know the fingerprints of the decayed products in different non-invasive techniques. This paper deals with the systematic study of the markers of the artificial ageing products of the synthetic and natural malachite painting pigment, under step by step action of the most common air pollutants SO_2, CO_2, NO_2 in saturated moisture atmosphere as well as by the biological attacks by means of vibration spectroscopic methods FT-IR, FT-Raman.

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The development phases of the dyed and painted pottery in Azerbaijan

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Many samples of painted and dyed pottery were found during archaeological excavations of graves and settlements. The painted and dyed ceramics vary in form, artistic arrangement and technique depending on their period and territory.

The first samples of painted pottery belong to the Neolithic period. Starting from the Chalcolithic period, manufacture of the dyed and painted pottery was developed. Chalcolithic period pottery has been found at more than 43 sites. In the Early Bronze Age painted pottery typical of the South Caucasus and Azerbaijan Kura-Araks archaeological culture could be found. Afterwards, in the Middle Bronze Age there were four development stages to the “dyed pottery culture” There are typical forms and decorations related to the Bronze Age. The early Antique period was the new stage for producing painted and dyed pottery.

This paper presents the analysis of the development phases of the dyed and painted pottery belonged to the periods above. It includes the artistic arrangement and applying techniques of the paint.

Dyeing techniques of the Hallstatt-Textiles: analysis, experiments and inspiration for contemporary application

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In the prehistoric salt mine of Hallstatt in Upper Austria, coloured textile fragments have survived for more than 3500 years due to the impregnation by salt, the constant climate of the mine and the protection from light. These circumstances offer unique conditions for research in prehistoric dyeing techniques.

Knowledge about the prehistoric dyeing processes is gained by identifying the dyestuffs, the dyeing materials, the origin of the chemical elements aluminium, iron and copper detected in the textile fibres, and their influence on colours and fibre degradation. About 68 samples of prehistoric textile fragments, especially of the multi-coloured ribbons, are analysed by optical microscopy, scanning electron microscopy with energy-dispersive X-ray analysis (SEM-EDX) and high performance liquid chromatography with photo diode array detection (HPLC-PDA).

Results of this analytical research are applied in reproductions of three prehistoric ribbons to show how they once may have looked. Methods of experimental archaeology are applied in experiments using authentic materials (wool, natural dyes) and traditional spinning, dyeing and weaving techniques. The experiments also contribute to knowledge about the prehistoric production processes.

The project creates links between the unique cultural heritage of the Hallstatt-Textiles and inspiration for textile art as well as today's commercial products. A scientific concept for textile products is developed and examples of textile objects made of natural materials and natural dyes are designed by students of the University of Applied Arts, Vienna.

The multidisciplinary project “Dyeing techniques of the prehistoric Hallstatt-Textiles” is funded by the Austrian Science Fund FWF (duration 08/2008-12/2011).

This poster is the updated version of a poster presented at the *International Symposium & Exhibition on Natural Dyes* ISEND 2011 in La Rochelle, France.

Extraction methods for the HPLC characterisation of organic colorants in cultural heritage objects: creations of an online searchable bibliographic reference database

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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). 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.

At the 29th *Dyes in History and Archaeology* conference in Lisbon, work undertaken within the European CHARISMA project [1] to review the literature relating to the extraction of organic colorants in cultural heritage objects was presented [2]. The review resulted in a database containing standardised descriptions of the extraction protocols. On the basis of this review, work is on-going within the CHARISMA project to explore the advantages, limitations and applicability of the different extraction methods with the aim of developing a ‘universal’ extraction procedure (or sequence of steps) optimised for samples from the cultural heritage field or to provide a number of optimised methods suitable for a range of sample types [1].

To permit other researchers undertaking HPLC analysis of samples from cultural heritage objects to benefit from the review when selecting the most appropriate extraction procedure, work has been undertaken to convert the database of extraction methods into an online searchable bibliographic reference database. The resulting online database has significant advantages over the previous static database in that it will possible to add additional articles keeping the database up to date, and retrieval of information is easy via a user-friendly interface. The database has been created using open source software (MySQL/PHPmyAdmin database) and has been designed to allow expansion or addition of further data ‘layers’ as required in the future.

The online bibliography reference database currently contains near 150 articles and is hosted by the Cultural Heritage Agency of the Netherlands on the www.organic-colorants.org website. The database will continue to be expanded and improved as a resource that will remain available and relevant beyond the period of the CHARISMA project.

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James Watt and Turkey Red

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In March 2011 the Science Museum in London opened a new exhibition about the eighteenth century steam pioneer James Watt. One primary driver was to place on display the Garret Workshop that James Watt had installed in his retirement home Heathfield, near Birmingham; this contained material from nearly every aspect of the great man's life and times, including a collection of white ceramic pots containing a large number of chemicals.

Using the chemicals as a starting point, it is possible to see the extent to which problems in practical chemistry intrigued Watt, and, later, his two sons. Links will be made between items in the workshop and the interest that the Watt family had in the entrepreneurial opportunities presented by a burgeoning chemical industry.

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In Vitro Testing for Genotoxicity of Indigoid Dyes by Comet Assay

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Indigo and indigoid dyes are natural dyes and have been known since pre-Roman times in the Mediterranean region. Nowadays, indigoid dyes are widely used in the industry of textile, cosmetic, food and medicine [1]. The aim of the this study was to perform indigotin analysis using High Performance Liquid Chromatography with a diode-array-detector (HPLC-DAD) in historical textile samples and in addition to, DNA damage of indigotin, 6-bromo indigotin, indirubin and 6-bromo indirubin was to estimate by in vitro alkaline single-cell gel electrophoresis (SCGE-Comet) in the peripheral lymphocytes.

The historical objects were provided from the collection of the Topkapi Palace Museum in Istanbul-Turkey [2]. Indigotin was found in some examined samples. The identification of natural dyestuffs is a necessary stage in the conservation of art objects.

Comet assay is a fast and cost effective test method used to reveal the occupational and environmental exposures to genotoxins. The alkaline comet assay was performed using an adaptation of the method of Singh *et al.* [3].Technical steps of comet assay consist of preparing slides with agarose gels, lysing cells to liberate DNA, exposing the liberated DNA to alkali to produce single stranded DNA, to express alkali-labile sites as single-strand breaks, electrophoresing the DNA using pH>13 alkaline conditions, alkali neutralization, DNA staining with ethidium bromide, comet visualization and data collection.

The cytotoxic effects of indigo and indigoid dyes were assessed by trypan blue exclusion. The cells were incubated with 10, 25, 50 μg/mL of the test substances for 30 min at 37 °C. Our results revealed that indigotin and 6-bromo indigotin increased the DNA migration in a dose-dependent manner. DNA damage was higher in cells that had been incubated with 50 μg/mL indigotin and 6-bromo indigotin ($p<0.05$).

Our results indicate that indigo and indigoid dyes would be genotoxic at higher concentrations. It is probable that a genotoxic effect might occur due to the fact that the individuals who have worked with these dyestuffs, both in the past and today, used highly concentrated dyes.

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A rapid and reliable quantification protocol for the study of the artificially ageing of indigo pigment

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We can say about indigo that is the oldest painting pigment used in human history in Egypt, Israel, China, India and the Roman Empire [1-4]. Restoring-preserving processes of the indigo painting needs extensive knowledge of the decaying products of indigo and its support. It was reported in literature mass spectrometric analysis of faded indigo paint samples that identified the weII known ageing products of indigo and several other aging products present are the subject of some current research. A correlation was found between the visual changes and the changes in chemical composition [5]. The aim of this study was to identify the accelerate in artificially aged products of indigo by UV-VIS and GC-MS. The ageing tests included exposure to common pollutants NO_2, CO_2 and SO_2. The experimental swatches were subjected to ageing tests, and subsequently studied for colour changes by means of colorimetric measurements. The greater colour difference is caused by the formation of degradation compounds of indigo in the aging conditions. The formation of these compounds was confirmed by GC-MS spectra in different conditions. We designed the possible decaying mechanisms and we assigned the structure of the decaying products.

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Describing the "elusive": Availability, Preparation and Use of Anthocyanin Colorants in the North of Europe from the 14th to the 16th century

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Due to their trade value, a huge range of artistic materials are documented and recorded in historical written sources. However, certain substances are not registered in these archives because they did not have a market value. This is especially the case for vegetal species which artists easily found in nature and used for their colouring principles, like anthocyanin colorants. As they are characterized by a great sensitivity to the slightest changes in pH and as they are highly unstable in ordinary daylight, these colorants were not frequently used in the dyeing of quality materials or in painting. Up until now, they have been mainly considered as being used in a domestic context, for the dyeing of everyday clothes. Moreover, after ageing, the plant species are difficult to identify with currently-used analytical methods.

This project research proposes to bring to light these «elusive» substances through the close examination of original and primordial source: artistic recipe books. Previous research has highlighted that these books not only describe these organic colorants, but that they also indicate their use in illumination. More precisely, we can learn that these colorants were not only used for modelling and shading but also for the realization of flesh tints, draperies and landscapes. According to these instructions, they were also applied as glazes on layers of gold or silver in gilding. They also served for making inks which were used to underline rubrics or some elements of decoration in illuminated manuscripts.

From the 14th to the 16th century, hundreds of recipe books containing information relating to these colorants were produced. They describe their preparation, their diverse applications and the required conditions for their conservation. These recipe books also inform us about the different hues obtained from these colorants.

This study will involve analysing the significance of these organic substances as well as a (re)definition of their use with a view to increasing our knowledge of historical artistic practices and materials. Furthermore, it could also help to identify specific artistic productions or workshops. Finally, it would be possible to learn more about the status of artists, their working conditions and their training.

It will be based on a corpus of more than 300 manuscripts from the North of Europe. These texts have been selected because they contain a great number of prescriptions specifically dedicated to anthocyanin colorants. These manuscripts and their content have previously been recorded in a specific database containing records of and information on every recipe in these books. This tool will facilitate their consultation and allow them to be analysed according to different search criteria. The database has been cross-checked for integrity and consistency using random query techniques. Thanks to subject classifications, queries can been done by keywords for specific recipes, methods or materials. The global frequency and recurrence for each ingredient can be derived from the corpus of texts. Moreover, it is possible to observe, through factors such as frequency in the corpus, basic structure, and evolution, the way in which recipes were modified over time or by other external phenomenon.

The database will function on three different levels. First, it will help us not only to observe the recurrence of the recipes dedicated to anthocyanin colorants but also to deduce the availability of these colorant in a chronologically and geographically defined area. It implies the identification of the specific processes and species through the recipe texts. Secondly, it will be possible to establish and to compare the different ways in which these colorants were prepared and how they were used in illuminating techniques. Several series of dummy samples will be prepared from the juice of *Papaver Rhoeas* L. and some *Sambucus* species. They will be characterized by colour spectrophotometry and HPLC, before and after ageing process. The final step will consist of the comparison with historical witnesses in works of art.

Black dyed wool: Production techniques, degradation and their effect on conservation

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Research into historic recipes (ca. 1650 - 1850) shows that the black colours were composed of multiple ingredients, applied in successive colour baths. Dyers used a variety of methods to produce a black colour, which made black dyeing a complex and laborious process [1]. As a consequence black was an expensive colour to work with, and dyers regularly played fast and loose with the regulations (imposed by the guilds). Expensive ingredients were replaced by cheaper ones and banned products were used to speed up the dyeing process [2].

A significant obstacle in investigating micro-innovations like dyeing is the fragmentary nature of the different sources that document the life of the craftsmen and the techniques they used in the workshops [3].

This study focuses on the interrelationship between archival and bibliographic research in addition to object related study and chemical analysis.

1. Technological approach:
To gain a better knowledge of the use of the different ingredients and techniques and their effect on the wool product itself three different categories of historical recipes have been reconstructed in the laboratory: I: Indigotin + alizarin, II: Tannins + Iron salts ($FeSO_4.7H_2O$ and $CuSO_4.5H_2O$) and III: Blue background (indigotin or haematoxylin) + Tannins + Iron salts ($FeSO_4.7H_2O$ and $CuSO_4.5H_2O$). Each different kind of recipe gives different kinds of shades of black colours. After artificially ageing of all samples - at 60°C in a solarbox 1500 E, optical filter indoor, soda-lime glass UV filter (simulates indoor-exposure), 550W/m^2, at 4 different times – the influence of the dyeing process on the actual condition of the wool was investigated by Scanning Electron Microscopy (SEM), portable X-ray fluorescence (PXRF) analysis and Tensile strength measurements. A comparison between SEM and PXRF results was investigated to determine the efficiency of the non-destructive PXRF technique for in-situ analysis of the metals (Fe and Cu) that are present in the organic matrix.

2. Historical sources:
In order obtain a better knowledge about the relationship between historic recipes and prescriptions on one hand and the actual practice in the workplace on the other: different Belgian archives have been studied resulting in the finding of 42 black woollen samples from well-defined and precisely dated archive collections. Dyes and mordants of all historical wool samples were analysed with respectively High Performance Liquid Chromatography (HPLC) [4] and Scanning Electron Microscopy (SEM) analysis in an attempt to shed light on the range of practically applied dye recipes in specific periods.
Both technological and historical approaches of the research will contribute to extend the knowledge of the different kinds of dyeing methods that were historically applied to dye wool black and of their effect on the current day condition of the textile.

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Effects of sizing agents on the mechanical and dyeing properties of native cotton fabric dyed using dyestuff from *Morinda lucida* (Brimstone tree)

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Native cotton fabric was treated with starch sizes from different natural sources – cassava (*Manihot esculenta),* potato (*Solanum tuberosum)* and corn (*Zea mays)* and the amount of each resin retained in each fabric sample at 30^{o}C was evaluated in mg/g of fabric. The fabric samples were dyed at 50^{o}C using natural dyestuff obtained from the plant *Morinda lucida* (Brimstone tree). The effects of the pre-treatment with sizes were assessed against the crease recovery angle, tensile (mechanical) and dyeing properties of the fabric. Treatment with cassava resin (*M.esculenta)* led to the highest value in resin retention followed by potato (*S. tuberosum)* and corn (*Z.mays*) in that order. Correspondingly higher values were obtained for crease recovery angles for cassava with values of 24-38 ^{o} compared to 18-31 ^{o} for corn and 23-33 ^{o} for potato from the control value of 15 ^{o}. Values of Modulus (Mpa), energy at break (J) and extension at break (mm), decrease with the level of resins retained in the fabric. There is, however, a substantial increase in these values when compared with the untreated control with cassava producing the highest effect followed by potato and corn in that order. The result of the study also shows that dye uptake in mg/g of fabric decreases with increase in the level of resin retained in the fabric for each resin type with corn (*Z.mays*) producing the least inhibitory effect on the dyeing of the fabric.

Let Glasgow Flourish: dyes research in the new Centre for Textile Conservation and Technical Art History

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In September 2010, the University of Glasgow opened the Centre for Textile Conservation and Technical Art History, the first conservation training centre in Scotland. Based within the UK universities' number one-rated History of Art department, the Centre brings together expertise in textile conservation, conservation science, textile history and technical art history to offer multidisciplinary object-based teaching and research.

The Centre runs three postgraduate programmes that are attracting students from around the world: a 2-year taught Masters programme in Textile Conservation; a 1-year taught Masters programme in Technical Art History (*Making and Meaning*); and a 1-year taught Masters in the History of Dress and Textiles. The textile conservation, and dress and textile history programmes build upon the excellent pedigree of the internationally-acclaimed Textile Conservation Centre which was sadly forced to close in 2009 amid much outcry after 10 years at the Winchester School of Art and, prior to that, 20 years at Hampton Court Palace, London.

Within a short space of time, a strong synergy has already formed between the four current research staff in the Centre, and is set to flourish within the high academic standing of the university through new and continued collaborations with cultural organisations, academic institutions and research partners worldwide. This brings exciting prospects for research in dyes in historical textile and paintings, with chemical analysis and scientific investigations for conservation being major specialisms for the Centre.

Thanks to generous funding from the Getty Foundation, the Centre has initiated a network to get its research off to a fantastic start. Five themed meetings are being held during 2011 and 2012 to bring together researchers to initiate new interdisciplinary projects and to apply for research funding. The five themes and meeting dates are:

1. Modern Materials (held in 10 June 2011)

2. The Real Thing? The value of authenticity and replication (held in 7 October 2011)

3. Technical Studies: exploring concept, practices and results. 5 December 2011

4. Enhancing the Value of Collections: investigation and preservation. 30 March 2012

5. Connected Histories: making, meaning, interpretation. 14 May 2012

The network culminates with a two-day international conference based on The Real Thing? on 6-7 December 2012 at the University of Glasgow.

This poster outlines the range of projects being developed and proposed for the history, identification and conservation of dyes in textiles and paintings within these themes. We welcome interest from all dyes researchers in the potential development of collaborations with the Centre.

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

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Rouge Cotton (*Enji-wata*) was the colour of material of *Yuzen*-dyeing or Japanese style painting in Edo period, 10000 sheets were imported per year from China in Ming and Qing dynasty. The origin of Rouge Cotton (*Enji-wata*) was in India, but a major source was south China, Suzhou. The production was stopped at the end of 19C and the manufacturing method was not handed down. Identification for red dyes used for Rouge Cotton (*Enji-wata*) is really important [1].

As a result of having examined ancient documents [2], there was a possibility that safflower (*Carthamus tinctorius*),Japanese (or Chinese) madder (*Rubia akane*), sappanwood (*Caesalpinia sappan L.*), lac and /or cochineal were used.

Several Rouge Cotton (*Enji-wata*) were analysed for their dye, using fluorescence spectra, visible reflection and HPLC [3], and ESI-MS. Some samples were dyed by lac and/or cochineal, but no samples were dyed by safflower, Japanese madder or sappanwood.

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Development of an RP-HPLC Method for the Analysis of Flavonoids in *Achillea biebersteinii* and Investigation of Wool Dyeing

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There are about 115 species of the genus Achillea L. (Asteraceae) centered in SE Europe and SW Asia and are widely spread over Eurasia to North America [1]. Achillea is a perennial plant with beautiful white to white yellow or white-purple flowers and grows up to 80 cm tall. The plant also has a long history as a powerful "healing herb" used topically for wounds, cuts and abrasions [2]. *Achillea biebersteinii* contains flavonoids (Figure 1) which can be used for natural dyeing. In this study, *Achillea biebersteinii* was extracted with different rates of methanol with Accelerated Solvent Extractor (ASE). The dried *Achillea biebersteinii* was used for dyeing wool yarns. The wool yarns were mordanted using Fe, Sn, Al salts and then dyed with different amounts of the dried plant's flower, leaf and stem. Also, Al-*Achillea biebersteinii* and Sn-*Achillea biebersteinii* pigments were obtained with different pHs. The extracts, pigments and dyed wools were analysed qualitatively by reverse phase high performance liquid chromatography (RP-HPLC).

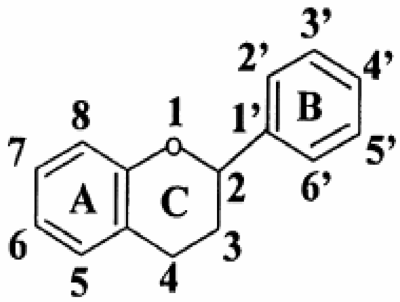

Figure *Quercetin* (3'=OH 4'=OH 3=OH 5=OH 7=OH) 2*. Apigenin* (4'=OH 5=OH 7=OH) 3*. Patulitrin* (4'=OH 5'=OH 3=OH 5=OH 6=OCH_3 7=OGlc) 4*. Axillarin* (3'=OH 4'=OH 3=OCH_3 5=OH 6=OCH_3 7=OH) 5*. Kampherol-3-O-galactoside* (4'=OH 5=OH 7=OH 3=OGalactocide) 6*. Luteolin-7-O-galactoside* (3'=OH 4'=OH 5=OH 7=OGalactocide) 7. 4'6-dihydroxy-3'-methoxy-flavon-7-O-glycoside (3'=OCH_3 4'=OH 6=OH 7=OGlc)

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Dyes from ship wreck Vrouw Maria

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Dutch sailing ship Vrouw Maria sank in a storm in the Sea of Archipelago at Gulf of Finland in the year 1771. According to the customs declarations made earlier in Øresund of Denmark she carried a remarkable dye cargo: thousands of kilos of Dutch madder, indigo, wine stone and brazilwood. She also carried dyed textiles, luxury items and valuable paintings to Catherine the Great, Emperor of Russia.

An unknown portion of the dyes were salvaged after the shipwreck and soon auctioned. The paintings were never found.

During the underwater excavations in the summer of 2011 at the Sea of Archipelago some of the dye cargo of Vrouw Maria was found. After centuries under the water it is still blue to bare eyes – it even dyed the wet suits of the marine archaeologists blue!

The dye finds and other organic finds will be later analysed to obtain more details.

Investigation of Metal Wired Coloured Historical Textile Using Scanning Electron Microscopy (SEM) and HPLC-DAD

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Scanning Electron Microscopy -Energy Dispersive Spectrometry (SEM-EDS) and HPLC-DAD were used to examine metal-wrapped coloured textiles. The sample was provided from Azerbaijan History Museum. Material included silk and thin wire.

SEM micrographs showed that the metal strip had 250 μm width and 6 μm thickness. SEM-EDS results indicated elemental composition of the wrapping: the presence of gold and silver as the components of the gilt metals. Furthermore, sulphur and chlorine were determined as contaminants. EDS analysis also revealed that both sides were gilded.

In the same sample were identified colouring compounds by HPLC-DAD. The major colouring compound found in the red fibre sample in large quantity was carminic acid and fuchsin components. The presence of fuchsin, which is a synthetic dye, dates the sample to between the end of 19th and beginning of 20th century. In the yellow fibre, fisetin was detected, which is a natural dye.

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