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Publication date
2010

Document Version
Final published version

Published in
Silk Gold Crimson

What Colours Tell You: the Identification of Dyes in Historical Objects

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The study involved investigating the dyes present in a range of samples of fabric. Current analytical techniques make it possible to identify the approximate geographical origin of the dyes used. While the classification of a dye source is carried out primarily through chemical analysis of the major components, the minor ones and their relative amounts also play an important role. Together with technical and historical information,[1] dyestuff analysis can provide insight into the origin of the objects examined. Natural dyes are organic, being derived from plants and sometimes animals. Dyes can be extracted from a great many plants but the colour usually proves instable. As a result, only a limited number of sources yielding stable dyes were used with frequency. Three different procedures can be used with natural dyes, depending on their chemical nature, namely direct, mordant and vat dyeing. In the first case, the fabric can be dyed with no any additional pre-treatment. The dye can be dissolved in an aqueous solution and is fixed directly to the textile fibre. The wash fastness of these dyes is poor but can be improved through subsequent processing. The most important procedure is mordanting, in which the connection between dye and textile fibre is formed by a coordinating metal such as aluminium, iron or tin. Mordant dyes have a very good level of wash fastness. The third procedure is vat dyeing, so called because the dye becomes soluble in a vat, which is usually carried out with indigoids. These dyes are reduced through fermentation and soluble leuco-indigoids are formed and attached to the fibre. The dye sets when the indigoids are oxidized through contact with air into their insoluble counterparts. Many different colours can be obtained by varying the recipe. The final colour depends on the degree of concentration but also on the metal used in mordant dyeing. Different dyes can also be mixed to obtain a certain shade or colour.

Dyestuff analysis is often carried out nowadays by means of high-performance liquid chromatography combined with a photodiode array detector (HPLC-PDA). The dyestuffs are extracted from the sample with hydrochloric acid at boiling temperature prior to analysis and 0.5–2 mg of woollen fabric is usually required in order to obtain a good response. The extraction solvent is then evaporated to dryness and the dyes are dissolved in an organic solvent and subjected to HPLC analysis. The heart of the HPLC system is a column filled with chromatographic packing material (stationary phase). High-pressure pumps are used to pump solvents through this column and the dyes are separated on the basis of differences in their absorption behaviour, hydrophobic dyes being absorbed strongly in the stationary phase and retained whereas hydrophilic dyes are absorbed to a lesser degree and pass through the column more quickly. The dyes are then detected by means of PDA, which records the UV-VIS absorption spectra from the colourants. The spectra obtained already provide information about the class of dye present and final identification is carried out on the basis of known reference materials. Interestingly enough, it is not always necessary to know the exact chemical identity of a material as long as it can be linked to a known reference material. The elemental composition of the textile is determined by means of energy-dispersive X-ray spectroscopy combined with scanning electron microscopy.[2]

Mordant analysis

The overall signal was very low except for carbon and oxygen. Nearly all the samples showed a small but clear aluminium peak, which suggests that this element was probably used as a mordant. All the samples contained small amounts of sodium and chlorine, the source of which is salt, as well as potassium and calcium, possibly from the water used to wash or dye the fabric. Silk could be the source of the sulphur found. The occasional occurrence of a very small copper peak suggests the presence of particles containing this element or close contact with metal thread. Iron was found as a mordant in one case (ISAL 3).

Red Dyestuffs

Insect dyes were often used to create red fabrics. These dyes were very expensive as the dyestuff is obtained from small insects found in nature on different plants. These insects can only be harvested over a short period of time and yield a very small amount of dyestuff. Three important insect dyes were found on the fabrics examined, namely kermes, Polish cochineal and Armenian cochineal, which are all mordant dyes. The dye is extracted from dried insects in warm water. Insect dye has good levels of light fastness and wash fastness.

Kermes (*Kermes vermilio* Planchon) is a small insect that lives on the kermes oak (*Quercus coccifera* L.). Female insects are harvested just before they lay their eggs, when the dyestuff concentration is optimal. The insects are killed by means of steam or hot vinegar and dried. Polish cochineal or Saint John's blood (*Porphyrophora polonica* L.) is an insect that lives on the root of the perennial knawel (*Scleranthis perennis* L.), which is native to Middle and Eastern Europe. The cysts or insects are harvested in late June by uprooting the plant, removing the insects and replanting it. The insects are sprinkled with vinegar or cold water and then carefully dried in an oven or in the sun. The third important insect dye found is now known as Armenian cochineal or Ararat kermes (*Porphyrophora hameli* Brandt). The insects live on the roots of two grass species (*Auluropus littoralis* Paul and *Phragmites communis* Trin.). Armenian cochineal is usually collected early in the morning, when the insects come out to mate. The treatment procedure is similar to the one adopted for Polish cochineal.

A calculation procedure developed by Wouters and Verhecken[3] makes it possible to distinguish between these and other insect dyes.[4] It should be noted that unknown side products were found in all samples treated with insect dyes. Kermes mainly contains kermesic and flavokermesic acid and no carminic acid. Carminic acid is the main component in Armenian cochineal (> 90%) and only a small amount of (flavo)-kermesic acid is present. Both carminic and (flavo)-kermesic acid can be expected in Polish cochineal in a ratio of 62–88% carminic acid to 12–38% flavokermesic + kermesic acid. As the ratios matched none of the individual species in some cases (ISAL 14, 31, 35, 36, 38), the insects must have been mixed. In other cases (ISAL 21, 23, 24), it proved hard to determine whether a mixture of dyes had been used. Interest attaches to the fact that that in every sample found to contain kermes or kermes together with another insect dye, an unknown red dye was also present.[5] This makes it possible to suggest that no kermes was added to the dye bath in the other samples, even though the number of analyses is too small to draw definite conclusions. A mixture of Polish and Armenian cochineal can also be expected in accordance with historical recipes.

The presence of alizarin and purpurin in three

Colouring Substances[1]

Cat. No.	Weave	ICN no.	Pile warp	Ground warp	Wefts	Binding warp	Additional	Selvedge
1	Figured velvet	2	Polish, tannins	Polish, tannins	Redwood			
2	Ironwork velvet	12	Polish, tannins	Polish, tannins	Redwood, weld			
3	Figured velvet	22	Polish, tannins		Redwood			
4	Figured velvet	23	Armenian, tannins	Armenian, tannins	Redwood			Undyed
5	Figured velvet	1	Polish, tannins	Redwood				
6	Figured velvet	24	Armenian, tannins	Redwood	Redwood, weld		2nd weft: weld, Young fustic	
7	Figured velvet	21	Armenian, tannins	Redwood, young fustic	Redwood, weld		2nd and 3th ground weft: weld, young fustic	
8	Figured velvet	40	Polish, tannins	Redwood, weld	Redwood, weld			
9	Figured velvet	25	Kermes, tannins		Madder, redwood			Weld
10	Figured velvet	14	Kermes, Armenian, tannins	Polish, weld	Weld, young fustic	Weld, young fustic	2nd pile warp: woad, weld, young fustic	
11	Figured velvet	5	Kermes, tannins	Redwood, young fustic	Pink: redwood, young fustic		Yellow Red: redwood, young fustic	
12	Figured velvet	7	Kermes	Redwood	Pink: Redwood			
13	Figured velvet	26	Kermes, tannins	Redwood	Yellow: redwood		Yellow Red: redwood, young fustic	
14	Figured velvet	39	Kermes, tannins	Redwood	Redwood, young fustic orchil		2nd ground weft: redwood, orchil	
15	Figured velvet	30	Woad, Weld	Weld	Woad, weld		2nd ground warp; young fustic, weld, woad	
16	Figured velvet	36	Kermes, tannins		Redwood			
17	Figured velvet	31	Polish, tannins	Polish, tannins	Redwood		Bouclé's silk core: young fustic	Weld
18	Figured velvet	35	Polish, tannins	Redwood	Redwood			
19	Damask	41		Kermes, other Insect dye	Kermes, other insect dye		Embroidery: yellow=weld; green=woad and unknown yellow	
20	Lampas	11		Redwood, tannins	Redwood, tannins			
21	Lampas	34		Sample not dyed		Weld, young fustic	Filé's silk core: weld, young fustic	
22	Lampas	18		Madder, redwood	Madder, redwood	Weld, young fustic	Filé's silk core: young fustic, weld	
23	Lampas	19		Redwood, weld	Redwood, weld	Young fustic		
24	Damask	28		Woad, Armenian, tannins	Woad, Armenian, tannins		2nd weft: weld, young fustic	
25	Ironwork velvet	27	Orchil, Woad	Orchil, woad	Orchil, woad			
26	Ironwork velvet	6	Woad	Woad	Insect dye, orchil			
27	Ironwork velvet	3	Woad (Indigo?), Weld, tannins	Woad (indigo?), weld, tannins	Woad (indigo?), weld, tannins			Woad (indigo?), weld, tannins
28	Ironwork velvet	10	Armenian, Weld, Tannins	Armenian, weld, tannins	Armenian, weld, tannins			
29	Damask		Sample not available	Sample not available	Sample not available	Sample not available		
30	Tapestry		Sample not available	Sample not available	Sample not available	Sample not available		
31	Tapestry		Sample not available	Sample not available	Sample not available	Sample not available		
32	Tapestry		Sample not available	Sample not available	Sample not available	Sample not available		
33	Ribbon	32		Insect dye, woad				
43	Satin	15		Armenian, tannins	Redwood		Low response	
43	Satin	16		Insect dye	Iron gallic, insect dye			
f.c. 01	Figured velvet	4	Armenian, tannins	Tannins				
f.c. 02	Figured velvet	38		Kermes, tannins	Weld, tannins	Weld		
f.c. 03	Figured velvet	13	Polish, tannins	Redwood, weld	Redwood, weld	Redwood, weld	Filé's red silk core: redwood, unknown orange components	
f.c. 04	Damask	29		Woad, unknown yellow	Woad, unknown yellow, unknown red			
f.c. 05	Ribbon	33		Woad, young fustic, tannins	Madder, woad, redwood, orchil	Woad		
f.c. 06	Ironwork velvet	37	Armenian, tannins	Armenian, tannins	Redwood			
f.c. 07	Ironwork velvet	17	Lac	Madder	Madder, tannins			Weld
f.c. 08	Ironwork velvet	9	Kermes, tannins	Kermes, tannins	Weld, redwood			
f.c. 09	Ironwork velvet XIX c.	8	Azo flavine R		Azo flavine R			
f.c. 10	Lampas	20		Kermes, redwood	Weld, young fustic	Weld, young fustic	2nd weft: weld, young fustic	

[1] Complete analyses in www.setainlombardia.org.

textiles (ISAL 18, 25, 33) indicates the use of madder (*Rubia tinctorum* L.), a well-known red-dye plant with a vast area of distribution. Among the many species containing alizarin and purpurin, *Rubia tinctorum* L. is native to Europe, North Africa and the Near East. It is a perennial herb growing to a height of about 60–80 cm, and only the root can be used for dyeing. The concentration of dyestuff increases with age to reach an optimal peak after three years. The bark is scraped off after harvesting to leave only the core of the root, which is then ground into small pieces. The dye can be extracted in warm water and fabrics can be dyed using a mordant. It has a good level of light fastness, albeit inferior to the insect dyes. While madder can be used to dye both wool and silk, as a cheaper and less stable dye it was mostly used for wool.

Redwood was identified in many samples (see chart, p. 168) through the presence of brasilein or an unknown component labelled Type C by Nowik,[6] which absorbs exclusively in the UV range and is therefore not responsible for the colour. This component is, however, a typical marker for redwood dyes. Redwoods are not native to Europe and this dye was most probably extracted from *Caesalpinia sappan* L., which grows in Asia. Large blocks of the wood are ground into small fragments, sprinkled with water and left to ferment. The colourless brasilin is extracted from the wood during fermentation and oxidises to form brasilein. The orange liquid is then poured off and fabrics can be dyed using a mordant. While the use of redwood, which has a poor level of light fastness, was forbidden in many major dyeing centres, it was added to other red dyes in order to enhance their colour or used to treat parts of fabric not exposed to view. In the samples examined here, redwood was mainly found in the ground weft and warp, often in a severely faded state.

Yellow dyes

Many of the yellow samples were found to contain luteolin and apigenin, two dyestuffs that indicate the use of weld (*Reseda luteola* L.). Glycosides of luteolin and apigenin, components abundantly present in the weld plant, were also found. Weld is a dye plant native to Europe, North Africa, the eastern Mediterranean and South-West Asia. The plant can grow to a height of 130 cm and is harvested after most of the flowers have turned into capsules. The stem, leaves and flowers are used for dyeing. The dyestuff can be extracted in warm water, to which potash and/or stale urine is often added. Weld is a mordant dye and was used for both wool and silk. It has a good degree of light fastness.

In addition to weld, young fustic was found in numerous samples. Identified by the presence of fisetin and sulfuretin, this yellow dye is extracted from both wild and cultivated species of the smoke tree (*Cotinus coggygria* Scop.), a shrub native to eastern and southern Europe. While the heartwood yields yellow or orange dye, the leaves and twigs can be used to dye fabrics black or brown. The dye is extracted in warm water from heartwood chopped into small pieces. Though not as lightfast as weld, young fustic was quite popular due to its more orangey shade of yellow and the fact that large amounts of dyestuff could be extracted.

Blue and purple dyestuffs

The blue and purple samples were found to contain indigotin and indirubin, which indicates the use of indigo (*Indigofera tinctoria* L.) or woad (*Isatis tinctoria* L.) as a blue vat dye. Isatin was also found as well as a degradation product of indigotin. While indigo and woad cannot be distinguished on the basis of chemical analysis, the dating of the samples makes it more probable that the blue dye was extracted from woad, as this is native to the whole of Europe (except Scandinavia) and large parts of Asia.

The presence of small amounts of hydroxy orcein and equivalents in some of the samples indicates the use of orchil (*Roccella*), the species most commonly used being *Roccella tinctoria* DC. This lichen is a symbiosis of a fungus and a (blue-) green alga, which is responsible for photosynthesis. While the algae produce alcoholic sugars that are consumed by the fungus, the fungus holds rainwater that can be used by the algae and protect them from sunlight. It is the fungus that contains the colourant, which can be extracted with water and ammonia to convert the precursors present in the fungus into the final colourants, a complex mixture of orceins. It has a low degree of light fastness and is therefore often subject to degradation.

Tannins

One black fabric (ISAL 3) was found to contain ellagic acid, a marker for the use of tannins. Tannins are extracted from gallnuts and form a bluish-black colour with iron. Gallnuts develop when gall wasps (*Cypnips tinctoria* Oliv.) puncture the gall oak (*Quercus infectoria* Oliv.) to deposit their eggs, (other species are known as well.) The gallnuts are preferably harvested before the insects hatch as adults in order to obtain the maximum quantity of tannins available. The tannins can be extracted in hot water after grinding the nuts. Tannins were also used for other purposes over the centuries, one being to make silk heavier. As silk was a very expensive material sold by weight, this simple procedure was often used.

Unknown dyes

While most of the dyes were identified, some of the samples also proved to contain unknown components, usually related to the primary dyestuff found. In the case of the unknown red or orange dye found at a significant concentration together with a redwood dye in sample ISAL 38, however, the orange component does not seem to be related to the redwood nor to any of the other dyes found in this study. As it proved possible to rule out alkanna, henna, safflower, carotenoids and barberry root, the identity of this dye remains unclear.

Conclusion

It proved possible to identify nearly all the dyes in the samples examined. Expensive insect dyes were used for pile warp and cheaper redwood for ground weft and warp. The only yellow dyes identified were weld and young fustic. Woad was used for blue dye with purple orchil also detected in a few cases. With the exception of redwood, all the dyes are of European origin. Some of the insect dyes were imported from the Black Sea area.

[1] The information on dyestuffs is drawn primarily from H. Hofenk de Graaf, *The Colourful Past*, London 2004, and D. Cardon, *Natural Dyes*, London 2007.

[2] I. Joosten and M.R. van Bommel, 'Critical evaluation of micro-chemical analysis of archaeological materials, experiences from the Netherlands Institute for Cultural Heritage', *Microchim Acta* 162, 2008, pp. 433–66. For complete details of the analytical procedures used, see www.setainlombardia.org/materie/…

[3] J. Wouters and A. Verhecken, 'The Coccid Insect Dyes: HPLC and computerized diode-array analysis of dyed yarns', in *Studies in Conservation*, no. 34, 1989, pp. 189–200.

[4] For the results of these calculations, see www.setainlombardia.org/materie/…

[5] For the spectra, see www.setainlombardia.org/…

[6] W. Nowik, 'The Possibility of Differentiation and Identification of Red and Blue "Soluble" Dyewoods', in *Dyes in History and Archaeology*, 16-17, 1997, pp. 129–44.