Archaeol Anthropol Sci
DOI 10.1007/s12520-016-0334-z

ORIGINAL PAPER

Multi-technique investigation of historical Chinese dyestuffs used in Ningxia carpets

Eleonora De Luca[1] · **Gianluca Poldi**[2] · **Massimo Redaelli**[1] · **Chiara Zaffino**[1] · **Silvia Bruni**[1]

Received: 8 January 2016 / Accepted: 29 March 2016

Abstract In this article, an extensive work is presented concerning the characterization with both chromatographic (high-performance liquid chromatography) and spectroscopic (surface-enhanced Raman spectroscopy and visible reflectance spectroscopy) techniques of historical Chinese dyestuffs in several carpets, mostly coming from the Ningxia region in Northern China and dating to the seventeenth–nineteenth centuries. Notably, the color of the background of these fine artifacts has been an object of debate since, while being depicted as bright red in the ancient iconography, nowadays it appears as orange/yellow. Therefore, in addition to the identification of all the colorants used in the carpets, the present study investigated the reasons of this apparent inconsistency, pointing out an explanation based on the joined use of the yellow dye obtained from the pagoda tree and a "fugitive" dye obtained from brazilwood.

Keywords Chinese dyes · Carpet · SERS · HPLC · Vis-RS

Electronic supplementary material The online version of this article (doi:10.1007/s12520-016-0334-z) contains supplementary material, which is available to authorized users.

✉ Silvia Bruni
silvia.bruni@unimi.it

[1] Dipartimento di Chimica, Università degli Studi di Milano, Via C. Golgi 19, 20133 Milano, Italy

[2] Visual Art Centre (CAV), Università degli Studi di Bergamo, Via Pignolo 123, 24121 Bergamo, Italy

Introduction

A considerable group of classical Chinese carpets is attributed to the region of Ningxia, located in Northern China, from which it further stretches in the Mongolian outback. In 1691, during a voyage in this area, the Chinese emperor Kangxi (1662–1722) visited the laboratories in which carpets were produced and, as the French Jesuit François Gerbillon reported, expressed his admiration for their magnificence. Indeed, there is a documentation of Ningxia carpets consignment to Beijing and to other cities in a period following this event (König 2011).

The idea that those carpets could have been of a different color from that we can admire nowadays has always been widespread among scholars. Historical representations of such carpets in Chinese paintings usually show they had a bright red background, in contrast with the orange and yellow shades now observable (Tabibnia 2011). Therefore, the study of the dyes related to these artifacts resulted to be very interesting, as it queries possible degradation or fading processes of an unidentified red dye. To this aim, the identification of dyes used both for the background and for designs of 14 Ningxia textiles (seventeenth–nineteenth centuries), belonging to Moshe Tabibnia Gallery (Milan, Italy) was carried out with both chromatographic and spectroscopic techniques. At first, a non-invasive in situ examination by means of reflectance spectroscopy (vis-RS) was performed on Ningxia carpets, whereas subsequently samples were collected for micro-invasive high-performance liquid chromatography (HPLC) and surface-enhanced Raman spectroscopy (SERS) analyses. In addition, other ten carpets belonging to different regions of the Chinese empire, i.e., Khotan, Kashgar, Gansu and Yarkand, were examined only by non-invasive reflectance spectroscopy.

As far as we know, vis-RS can be a good tool in the first steps of diagnostics to identify some classes of dyes and complement chemical analyses (Gulmini et al. 2013; Pozzi et al. 2012). Indeed, this technique is effective in detecting rapidly some dyes or compounds, traditional and modern, typically blue like indigotin (from indigo and woad species, absorbing strongly at 650–670 nm), logwood (430, weak, and 570–590 nm absorption bands), and Saxon blue (610–620 nm absorption band). Vis-RS generally allows also to separate some classes of red dyes, i.e., reds coming from coccid insects (like cochineal, kermes, and lac dye, all with a double absorption band at 520–530 and 560–570 nm), madder (absorption around 510 and 550 nm), brazilwood (absorbing around 560 nm, as discussed below) and orcein (double absorption band at 550 and 585 nm). Carthamus or safflower red (from *Carthamus tinctorius* L.) can be identified by its strong single absorption band at 520 nm (sometimes indicated at 540 nm in literature) and a maximum at 450 nm. On the contrary, the possibility to identify yellow dyestuffs is very limited. Usually, the position of absorption bands for a given dye is not dependent on the particular textile fiber examined, but dark and very light hues, as well as fading, influence the correct reading of bands and of the spectral shape.

As far as micro-destructive techniques are concerned, HPLC analyses, especially when using a photodiode array (PDA) detector, allowed the identification of the largest number of colorants in works of art and ancient textiles (Karapanagiotis et al. 2007; van Bommel et al. 2007), while SERS became widely appreciated for its greatest potential for the analysis of minute amounts of colored samples in relatively recent times (Casadio et al. 2010). In comparison with UV-visible spectroscopy, SERS also exhibits the relevant specificity for molecular recognition typical of vibrational spectra. The main limitation of this non-separative technique is obviously encountered in the analysis of objects dyed with combined colorants to obtain a particular hue. In such cases, complex spectra are obtained or, alternatively, just one component gives a prevailing SERS response, while the others cannot be detected (Pozzi et al. 2012), requiring therefore the use of a chromatographic technique such as HPLC.

Table 1 summarizes the dyes of vegetal and animal origin mostly used in historical Chinese textiles. The use of mixture of dyes or of sequences of different dye baths to obtain a given hue is obviously also documented (Eiland 1979; Yu-kuan 1980), as is the case of madder with yellow dyes (Rostov et al. 1983), or of the latter ones with dyes extracted from redwoods (Allane 1993; Tiffany Studios 1969). Also purple tints could be obtained not only with gromwell but also by mixing blue and red dyes. Indigotin-based materials could be combined with pagoda tree yellow to yield green colors or even with brazilwood to develop a darker shade of blue (Cammann 1951).

HPLC reference data are widely available in the literature both for dyes used not only in China but also in the Western world (Karapanagiotis and Chryssoulakis 2005; Mouri and Laursen 2012) as well as for those dyes that are characteristic of Chinese artifacts (Wouters 1994; Zhang et al. 2008). As far as SERS reference data for natural textile dyes are concerned, most systematic databases available in the literature as well as in the authors' laboratory (Bruni et al. 2011) include mainly spectra of dyes typical of Western textile artifacts. Nevertheless, in the literature, SERS spectra were also reported, with variable excitation wavelengths, for some molecules responsible for color in typical Chinese dyes, even if synthetic compounds were generally analyzed rather than real vegetable extracts. That was the case for example of shikonin (Leona et al. 2006), rutin (Leona et al. 2006; Zaffino et al. 2014), berberine (Strekal' et al. 2007; Leona and Lombardi 2007), and emodin (Bruni et al. 2011).

Experimental

Materials

Silver nitrate (purity, ≥99.5 %), sodium perchlorate monohydrate (assay, ≥99.0 %), trifluoroacetic acid (assay, ≥99.5 %), hydrofluoric acid (assay, 47–51 %), pyridine (assay, ≥99.8 %), and rutin trihydrate were obtained from Fluka. Methanol (assay, ≥99.9 %), trisodium citrate dihydrate (assay, 100.2 %), and acetonitrile (assay, ≥99.9 %) were purchased from Sigma-Aldrich. Hydrochloric acid min. 37 % was obtained from Riedel-de Haën. Reference indigo and brazilwood were obtained from Zecchi (Florence, Italy), while *Sophora japonica* flowers were purchased from a Chinese herbalist's shop in Milan (Italy) and extracted with methanol/water 8:2(v/v) at 70 °C. All the aqueous solutions were prepared by using ultrapure water (Millipore MilliQ).

Treatment of samples from carpets for micro-destructive analyses

As already reported by the authors (Pozzi et al. 2012), different procedures involving acids and/or organic solvents were used to extract dyes, depending on the color of each sample. In brief, red colorants were extracted from fibers by means of a well established HCl/methanol-based approach documented in the literature (Colombini et al. 2007). The extraction of yellow dyes was carried out using a milder approach, i.e., HF at room temperature (Sanyova 2008), to preserve the glycosides of flavonoids, while, for the blue sample, a method based on the use of pyridine and water, reported in the literature to be particularly useful for removing indigoid dyes (Walton Rogers 1999) was

Table 1 Principal dyes used in historical Chinese textiles [a]

Dye	Color	Dye molecules (dye class)
Madder (茜草) from *Rubia cordifolia*	Red	Purpurin and related species (anthraquinones)
Madder (茜草) from *Rubia tinctorum*	Red	Alizarin, purpurin (anthraquinones)
Carmine (大紅) from cochineal (*Dactylopius coccus*)	Red	Carminic acid (anthraquinones)
Kermes (大紅) from kermes (*Kermes vermilio*)	Red	Kermesic acid, flavokermesic acid, or laccaic acid D (anthraquinones)
Lac dye (虫胶 染色, *Laccifer lacca*)	Red	Laccaic acid A, laccaic acid B (anthraquinones)
Indian mulberry (海巴戟天, *Morinda citrifolia*)	Red-orange	Morindone, damnacanthal, soranjidiol, rubiadine (anthraquinones)
Brasilwood/Sappanwood (苏木, *Caesalpina echinata/sappan*)	Red	Brazilein (neoflavonoids)
Red sandalwood (檀香, *Pterocarpus santalinus*)	Red-orange	Santalin-A, santalin-B (biflavonoids)
Logwood (蘇木, *Haematoxylum campechianum*)	Red-brown	Hematein (neoflavonoids)
Gromwell (紫草, *Lithospermum erythryorizon*)	Purple	Shikonin (naftoquinones)
Dyer’s weed (木犀, *Reseda luteola*)	Yellow	Luteolin, apigenin (flavonoids)
Gardenia (栀子, *Gardenia jasminoides*)	Yellow	Crocin (carotenoids)
Pagoda tree (槐树, *Sophora japonica*)	Yellow	Rutin (flavonoids)
Amur cork tree (黄檗, *Phellodendron amurense*)	Yellow	Berberine (alkaloids)
Chinese mulberry (柘, *Cudrania tricuspidata*)	Yellow	Cudraxanthones (xanthones)
Turmeric (薑黃, *Curcuma longa*)	Yellow	Curcumin (curcuminoids)
Eurasian smoke tree (鲁木, *Cotinus coggygria*)	Yellow	Fisetin (flavonoids)
Saffron (番紅花, *Crocus sativus*)	Yellow	Crocetin (carotenoids)
Chinese rhubarb (大黄, *Rheum palmatum*)	Yellow	Emodin, chrysophanol, aloe-emodin, physcion (anthraquinones)
Tangerine (瓯柑, *Citrus reticulata* or *Citrus tangerina*)	Yellow	Hesperidine, naringine (flavonoids)
Safflower (紅花, *Carthamus tinctorius*)	Yellow	Carthamon yellow A, carthamon yellow B
	Red-purple	Carthamin (chalcons)
Chinese indigo (蓼蓝, *Polygonium tinctorium*) Indigo (木藍, *Indigofera tinctoria*)	Blue	Indigotin, indirubin (indigoids)
Woad (菘蓝, *Isatis tinctoria*)		
Chinese sumac (川棓, *Rhus chinensis*)	Black	Tannins
Buckthorn (鼠李, *Rhamnus*)	Green	Xanthorhamnin (flavanone)

[a] Data were obtained from Allane 1993; Cammann 1951; Grzywacz et al. 2010; Jing Han 2015; Rostov et al. 1983; Tiffany Studios 1969; Ye et al. 2000; and Yu-kuan 1980

here employed. In all cases, the analyses were carried out on extracts obtained from samples of dyed yarn measuring approximately 1–1.5 cm in length, which were removed from the knots on the *verso* of the carpets.

In detail, red and orange samples were treated with 3 mL of methanol and 100 μL of 37 % HCl at 70 °C for 1 h, filtering the obtained solution through a 0.45μm GHP Acrodisc membrane filter and drying it under a N_2 gentle stream (Colombini et al. 2007). The residual matter was then dissolved in 120 μL of methanol: 50 μL of the solution were used for the HPLC analysis and the remaining for the SERS one.

Yellow samples were suspended in 450 μL of 4 M HF and placed in a polyethylene test tube which was kept at room temperature under magnetic stirring for at least 30 min. The resulting extracts were thus loaded onto a Discovery Supelco C18 SPE cartridge previously preconditioned by 5 mL of a 1:1 methanol/acetonitrile solution and 5 mL of MilliQ water. Fluorides were washed away from the cartridge with 5 mL of MilliQ water with 0.01 % trifluoroacetic acid, and the dyestuffs were then eluted using 3 mL of 1:1 methanol/acetonitrile solution acidified with 0.01 % trifluoroacetic acid. The obtained solutions were finally evaporated under a N_2 gentle stream (Sanyova 2008). The residual matter was then dissolved in 120 μL of methanol. Fifty microliters of the solution were used for the HPLC analysis and the remaining for the SERS one.

Finally, blue samples were treated with a 1:1 pyridine/water solution at 90 °C for 15 min, filtering the obtained suspension through a 0.45μm GHP Acrodisc membrane filter and drying it under a N_2 gentle stream (Walton Rogers 1999). The residual matter was then dissolved in 120 μL of methanol.

Again, 50 μL of the solution were used for the HPLC analysis and the remaining for the SERS one.

Synthesis of silver nanoparticles for SERS analyses

Silver colloids were prepared by reduction of silver nitrate with trisodium citrate dihydrate (Lee and Meisel 1982). All glassware was washed with diluted HNO_3, deionized and ultrapure MilliQ water in an ultrasonic bath and accurately dried. Of the silver nitrate, 18 mg were suspended in 100 mL of deionized water previously degassed under an N_2 gentle stream and heated to boiling. Dropped under vigorous magnetic stirring was 2 mL of a 1 % solution of trisodium citrate. The solution was held at boiling point for 60 min with continuous stirring.

Instrumentation

HPLC

HPLC analyses were performed with a HPLC PU-1580 Jasco pump equipped with an LG-1580-02 Jasco gradient valve and a GASTORR GT-103 solvent degasser, by using a MD 1510 Jasco diode-array detector in order to obtain spectral information between 200 and 600 nm. A 25-μL injection volume of a methanolic solution of the sample was used for the analysis, which was executed on a Supelco Discovery C18 column (25 cm × 4.66 mm, particle diameter 5 μm), with (A) ultrapure water and (B) acetonitrile both with 0.1 % of trifluoroacetic acid as solvents, setting the flow rate at 1 mL/min. The solvent gradient was as follows: 95–70 % A in 0–25 min, 70–40 % A in 25–30 min, 40–5 % A in 30–38 min, and 5–95 % A in 38–65 min.

SERS

SERS spectra were collected using a micro-Raman portable instrument, equipped with a 1800-lines/mm grating, a notch filter, an Olympus 50× microscope objective and a Peltier-cooled charge-coupled device (CCD) detector, by using a back-scattering geometry. A Nd-YAG (neodymium-doped yttrium aluminum garnet) laser provided the exciting radiation at 532 nm, with a power at the sample of about 1.5 mW. All SERS spectra were recorded between 2000 and 200 cm^{-1} as the average of 30 scans with an exposure time of 4 s. A resolution around 8 cm^{-1} is estimated in the examined spectral range. Samples for SERS analysis were prepared by adding in a test tube 300 μL of a methanolic solution of the unknown dye extracted from the textile to 3 mL of silver colloid, with subsequent addition of 125 μL of 1.8 M $NaClO_4$ under magnetic stirring, in order to induce aggregation of the nanoparticles. SERS measurements were performed upon deposition of a drop of the dye–colloid system on the surface of a glass slide and focusing the laser beam directly on the drop.

The fluorescence background observed in the SERS spectra of the extracts from historical samples was subtracted from the same spectra by means of the software Grams (Thermo Scientific).

Vis-RS

Diffuse reflectance spectroscopy measurements, mainly in the visible range (vis-RS), were obtained using a handheld spectrophotometer Minolta CM-2600d spectrometer: 360–740 nm range, 10 nm acquisition step, integrating sphere included, UV source included, d/8 geometry, 3 mm diameter spot, acquisition time 1 s, specular component included and excluded. Three measurements were performed on each sample. A broad personal reference database was used to interpret results, together with literature data.

Vis-RS was generally performed before sampling, on both sides of the carpets, as the first step of the analytical protocol.

Analytical results

HPLC and SERS analyses

In many Chinese classic carpets, particularly those belonging to the Ningxia type, a hue declined into many variants, from yellow and orange to pinkish brown, recurs in the background as well as in some designs. Textile samples of these shades were therefore collected and investigated with the aim to research possible connections, in terms of chemical origin, between the different tints. Moreover, the yellow color appearing in several designs was sampled from different pieces and analyzed with the aim to identify and compare the employed dyes.

Among the dyes in question, the principal ones here identified are the colorants derived from brazilwood (including under this name also the indigenous dye of analogous composition sappanwood) and pagoda tree (Table 2). These could be used individually or jointly in order to obtain different tints: evidence gathered from the analyses revealed that brownish red, orange, and pink hues of the backgrounds of eight carpets were obtained with brazilwood (inv. entries 10102, 11317, 11504, 14105, 3162, 5910, 6563, 12406), while the yellow shades recurring in the designs of ten carpets were obtained with the pagoda tree dye.

Notably, the identification of brazilwood by means of HPLC analysis does not stem from the recognition of brazilein, its characteristic constituent dye molecule (Table 1), but rather from the detection of the so-called “type C compound” (see for example the analyses of carpet 10102 in Fig. 1a–c), which other scholars have also found in textiles of

Table 2 Dyes identified by HPLC, SERS, and vis-RS analyses in Ningxia carpets

Carpet	Color	Dye
10102	Pink	Brazilwood + pagoda tree
	Yellow	Pagoda tree
	Yellow (background)	Pagoda tree + brazilwood
11317	Pinkish brown (background)	Brazilwood
	Light yellow	Gallotannin-based dye[a]
11504	Reddish brown	Brazilwood
	Mustard yellow	Pagoda tree + brazilwood
	Light yellow	Pagoda tree
12260	Yellow (border)	Gallotannin-based dye[a]
	Yellow (background)	Gallotannin-based dye[a]
12716	Gold Yellow (background)	Pagoda tree + brazilwood
14105	Orange (background)	Brazilwood
	Light yellow	Pagoda tree
	Yellow	Pagoda tree
3162	Orange (background)	Brazilwood
	Yellow	Pagoda tree
4618	Yellow	Pagoda tree
5851	Orange (background)	Madder
	Yellow	Pagoda tree
5910	Reddish	Brazilwood
	Yellow	Pagoda tree
6563	Orange (background)	Brazilwood
	Yellow	Pagoda tree
9363	Light yellow	Pagoda tree
	Dark yellow (background)	Brazilwood + gallotannin-based dye[a]
12406	Yellow	Pagoda tree
	Brown	Brazilwood
13901	Red (background)	Lac dye[b]
	Purple	Lac dye + indigo
	Blue	Indigo

[a] Gallotannins are present in the different parts of many vegetal species, and therefore it has not been possible to identify the dye more precisely

[b] In addition to these two molecules characterizing lac dye, the results of the analysis indicate the presence of an unidentified compound, to which color fading in some areas of the pile surface may be associated

different origin and imputed to brazilwood (Karapanagiotis et al. 2008; Karapanagiotis et al. 2009; Karapanagiotis et al. 2011; Nowik 2001). Of note, although this compound is univocally identifiable by the corresponding UV-visible absorption spectrum (showing maxima at 258, 305, and 332 nm), its chemical structure and formation mechanism starting from the molecules originally present in the dye are still unknown. The authors of the publications quoted above surmise that this substance may develop upon the acid extraction of the dye itself from the yarn. This hypothesis, however, is challenged by some preliminary tests carried out in our laboratory.

More recently, it has been suggested that the "type C compound" may derive from the ageing of the dye due to exposure to light (Manhita et al. 2011): indeed, differently from what happens to other dyes, the ageing of brazilwood does not only involve color fading but also hue variation. In fact, as some authors pointed out (Kenjo 1987; Padfield and Landi 1966), brazilwood red strongly fades particularly when exposed to UV and visible light; also, the yellow-red bands of light can produce some amount of discoloration. Another cause of discoloration, but more related to today's polluted urban air, is atmospheric ozone (Ye et al. 2000). Fading produces in the crimson red or red-pink color of red brazilwood/sappanwood tints (aluminum or tin mordant) light pinkish or whitish tones, a phenomenon well known to European dyers of eighteenth century, as the edition of 1797 of the Encyclopaedia Britannica indicates (Vol. 6, 1797, p. 189).

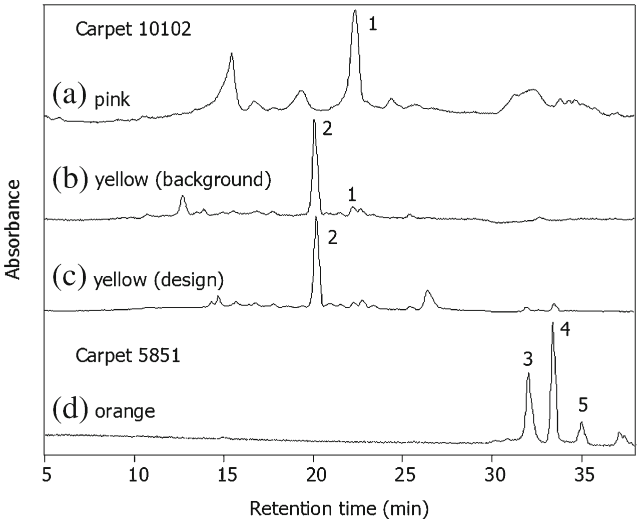


Fig. 1 HPLC chromatograms of the dyes extracted from the specimens of carpet 10102: (*a*) pink ($\lambda = 330$ nm), (*b*) yellow (from the background) ($\lambda = 350$ nm), (*c*) yellow (from the design) ($\lambda = 360$ nm), and carpet 5851: (*d*) orange ($\lambda = 430$ nm). Legend: *peak 1* = type C compound of brazilwood, *peak 2* = rutin, *peak 3* = lucidin, *peak 4* = alizarin, *peak 5* = purpurin

Concerning the analytical method used for the identification of the dye in question, it is worth mentioning that the SERS technique allows a more immediate recognition because ancient specimens and fresh colorant essentially have analogue spectra (Fig. 2), even when in the HPLC analyses only the "type C compound" was found and not brazilein. The good correspondence with the SERS spectrum of the unaltered colorant could possibly suggest that the molecular moiety responsible for the interaction with the silver particles is maintained in the degraded dye molecules (Zaffino et al. 2014). In comparison to the spectrum of unaltered brazilwood, however, two additional peaks are observed at ~600 and 682 cm^{-1}. Such peaks can be related to the degradation of the dye or, possibly, to the fact that the colorant used for the carpets was obtained from a different vegetable source in comparison to the one we used as reference. Differences in normal Raman spectra of brazilwood deriving from various plant species were indeed reported in the literature (Edwards et al. 2003).

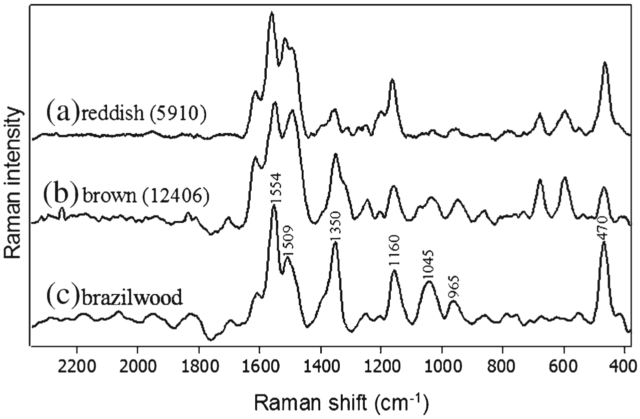


Fig. 2 SERS spectra ($\lambda_{\mathrm{exc}} = 532$ nm), obtained on Lee-Meisel silver colloid, of (*a*) the reddish dye extracted from a yarn specimen of the carpet 5910, (*b*) the brown dye extracted from the yarn specimen of the carpet 12406, and (*c*) brazilwood

The identification of the yellow dye obtained from the buds of pagoda tree has been possible by HPLC analysis, through which the flavonoid diglycoside rutin was detected (Fig. 1), and also by SERS analysis, which brings to the fore a fair correspondence between the spectrum of the yellow dye sampled from historical carpets, the spectrum of the flower extract of *S. japonica*, and the spectrum of rutin (Fig. 3).

For four carpets this yellow dye could be recognized also in the background, that generally exhibits a darker tone with respect to the yellow color used in the decorative motif (as it can be seen in Online Resource 1 for carpets 10102 and 12716). In three of such cases, the "type C compound" characterizing brazilwood was also detected, even if in small quantity, along with the rutin molecule of the pagoda tree dye. The joint use of the two colorants gave a chromatic effect that originally was most probably quite different from the present one because brazilwood, due to its poor light fastness, has faded away. Thus, the analytical results offer an explanation to the historical and iconographical issues arising from the incongruence between the ancient representations of Ningxia carpets, depicted as bright red, and the appearance of almost all the surviving exemplars of this type (to which a significant number of the pieces examined herein belong), showing yellow or reddish-yellow shades instead.

Although the two dyes discussed above prevail in our findings, some exceptions to their use were found in the carpets examined (see Table 2). As far as yellow is concerned, an exception is represented by the use of a dye presumably containing gallotannins, which has been detected by HPLC (the corresponding peak exhibits UV absorption maxima at 225 and 270 nm) in the light yellow design of carpet 11317, the yellow shades of carpet 12260, and, mixed with brazilwood, in the yellow background of carpet 9363. It is worth

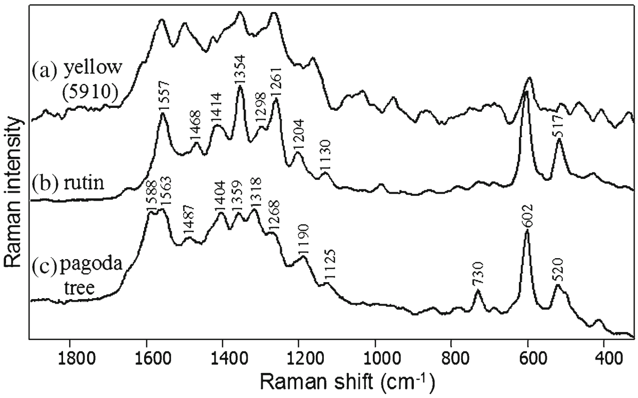


Fig. 3 SERS spectra ($\lambda_{\mathrm{exc}} = 532$ nm), obtained on Lee-Meisel silver colloid, of (*a*) the yellow dye extracted from the yarn specimen of carpet 5910, (*b*) rutin, and (*c*) the dye extracted from pagoda tree

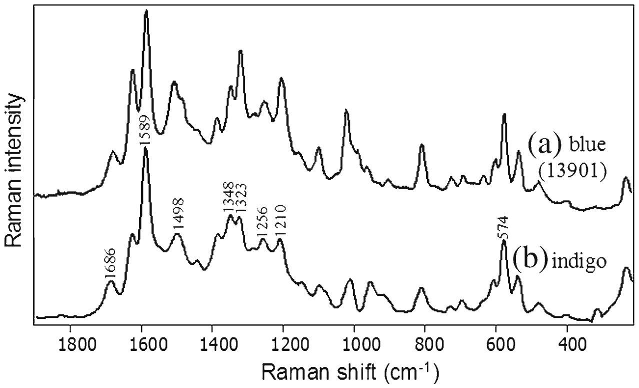


Fig. 4 SERS spectra (λ_{exc} = 532 nm), obtained on Lee-Meisel silver colloid, of (*a*) the dye extracted the from the blue sample of the carpet 13901 and (*b*) indigo

remembering that gallotannins are present in the different parts (leaves, fruits, roots, bark) of many vegetal species, and therefore, it has not been possible to identify the dye more precisely. With regard to reddish and orange hues, it is worth highlighting the case of the orange background of carpet 5851 where the color was not obtained with brazilwood, but rather using madder (Fig. 1d).

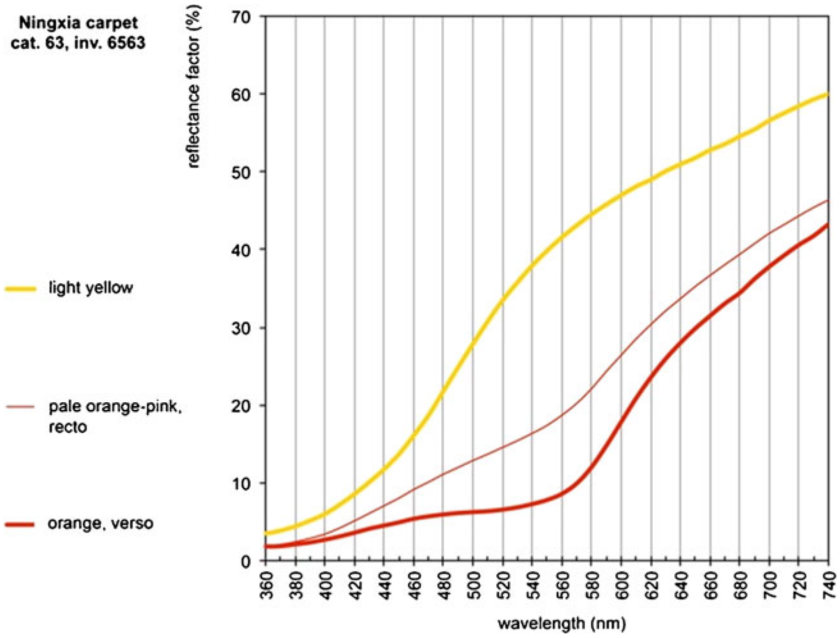
Deserving special attention is the wool chair cover 13901, whose red color was obtained using lac dye, as already reported by the authors on the basis of SERS analysis (Zaffino et al. 2014) and as indicated by the HPLC detection of laccaic acid A and of a compound with unknown structure called sII (Wouters and Verhecken 1989), both characterizing the dye derived from the resinous secretion of *Kerria lacca*. Color fading from red to yellow can be seen observing the pile yarns from the top to the base and, interestingly, there is a relationship between the findings of visual examination and laboratory analysis: the HPLC results, in fact, indicate the presence of an unidentified compound whose color could be pale yellow (based on the UV-visible spectrum, characterized by a maximum at ~240 nm and two broad absorptions at ~290 and 340 nm) and whose quantity is higher in that part of the yarn where the presence of the red shade is lesser visible to the naked eye. This compound seems to be more probably a degradation product of the original dye and not a yellow substance mixed with it upon dyeing, at least on the basis of vis-RS analysis. In fact, vis-RS measurements proved the existence of a coccid-based red dye (see below), whose color appears to be better preserved in the *verso* of the carpet and in the internal part of the knots, where spectra exhibit a higher reflectance in the red region (580–700 nm). No higher absorption in the blue region of the spectrum commonly due to yellow dyes can be seen.

Finally, it may be noted that lac dye was used mixed with an indigotin-containing dye to obtain a purple hue, as demonstrated by the predictable results of the HPLC and SERS analyses, also providing evidence that the same indigotin-based colorant was also used for the dark blue color of this carpet's decorative motif (Fig. 4).

Vis-RS analysis

Non-destructive vis-RS examination was carried out on 24 wool and silk carpets during the exhibition held in Moshe Tabibnia Gallery, providing a large database (hundreds of spectra) about ancient Chinese dyes of textiles belonging to

Fig. 5 Vis-RS spectra of a carpet with fading of the red threads. The *yellow line* refers to a dye extracted by pagoda tree flower (*Sophora japonica*) and *red lines* to brazilwood (*Caesalpina sappan* spp.), more (*thin line*) and less (*thick line*) faded



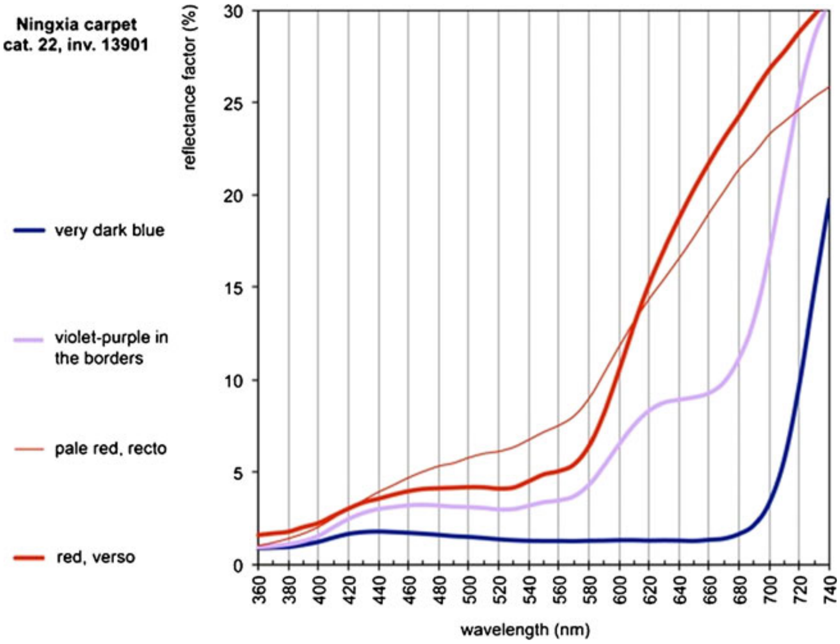


Fig. 6 Vis-RS spectra of a carpet with partial fading of the red threads. The *red lines* refer to a red dye extracted by coccid insects (identified as lac dye by chemical analyses), faded (*thin line*) and not (*thick line*): the different intensity of absorption bands is evident. The same dye is mixed with and indigotin-containing blue dye in the pale violet line, while the spectrum of indigotin is marked in the blue spectrum, with very small amounts of red

different regions of Chinese empire: Ningxia, Khotan, Kashgar, Gansu, Yarkand.

The spectra of deep yellow or orange areas containing brazilwood (as confirmed by HPLC and SERS) are characterized by an absorption edge at 560 nm (Fig. 5, red lines). The weak absorption band can be explained because the color is not red, currently. We can suppose that the original color had a more intense orange or red hue because the *verso* of the carpet sometimes keeps a deeper color, and the related vis-RS spectrum shows the above mentioned band of brazilwood more evidently. Differences between *recto* and *verso* spectra are evident (Fig. 5).

About yellow-dyed threads, the dye that chemical analyses recognized as derived from the flowers of the pagoda tree (*S. japonica*) shows a stronger absorption below 450 nm, with an inflection point around 480 nm (Fig. 5, yellow line). Such characteristics are not sufficient to identify it univocally by vis-RS.

Brazilwood red was identified in all the Ningxia carpets (dating from seventeenth to nineteenth century) except for two artifacts: one containing madder (inv. entry 5851; nineteenth century, second half) and the other a coccid-based red (inv. entry 13901; dating around 1700 AD). The previous exhibits the typical 510 and 550 nm bands of purpurin, while

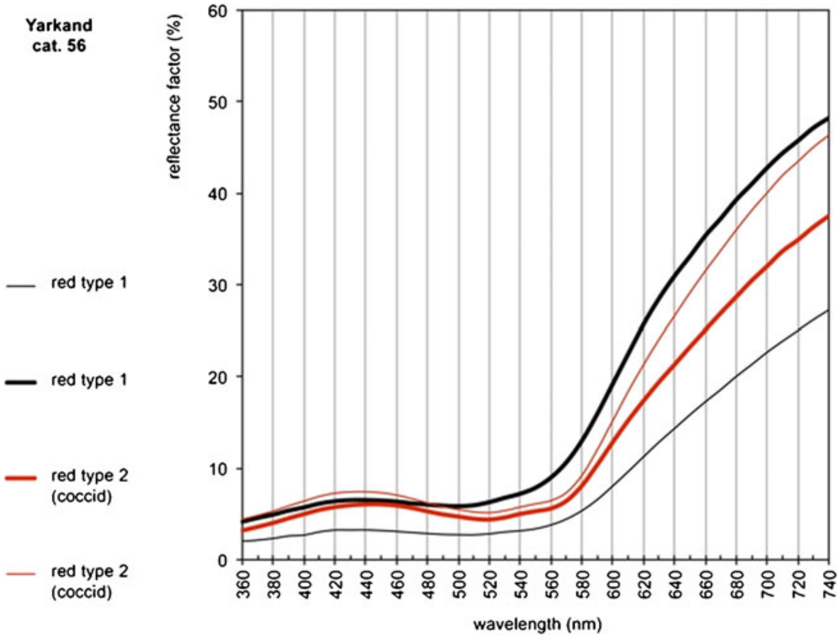


Fig. 7 Vis-RS spectra of a Yarkand carpet, without evident fading processes. The *red lines* refer to a red dye extracted by coccid insects and *black lines* to a madder dye

the second, showing 520–530 and 570 nm bands, was better identified as lac dye by chemical analyses as reported above (Fig. 6). It is mixed with an indigotin-containing dye to obtain purple colors (Fig. 6, violet line).

Vis-RS provided also significant information regarding carpets of peripheral regions of China: in the two Gansu pieces (about 1800 AD), only madder was found; in four Yarkand (eighteenth–nineteenth century), madder or a red dye coming from coccids is used, sometimes in diverse areas of the same piece to obtain different red tones (Fig. 7); in three Kashgar of eighteenth century, we could observe both these two dyes, also on silk; and in one Kothan of the same period, only madder was found.

Conclusions

Results from both non-destructive (vis-RS) and micro-destructive analyses (HPLC, SERS) on 14 Ningxia carpets allowed to identify brazilwood as the most used dye for those carpets' background, often combined with the yellow dye obtained from the flowers of pagoda tree. The unstable nature of brazilein, the main dyeing component of brazilwood, explains the color change from red in ancient times to the orange and yellow tints observable nowadays of Ningxia carpets. Among the carpets here analyzed, brazilwood resulted to be the prevailing red dye for the artifacts coming from the imperial area of China over a period of some centuries, while for those manufactured in the Western regions, madder or insect dyes were preferred. Indigotin was found in all the blue and purple hues, while in carpets from the Ningxia region, madder, lac dye, and gallotannins were used only occasionally.

Acknowledgments The authors wish to thank Mr. Moshe Tabibnia for giving the authors the opportunity to access his own collection of textiles and Dr. Tiziana Marchesi (Galleria Moshe Tabibnia, Milano) for providing the samples and for her constant support throughout the entire investigation. Moreover, Dr. Federica Pozzi is thanked by the authors for preliminary analyses of samples from two of the examined carpets. A special thanks to André Verhecken for providing some test samples that we analyzed by means of vis-RS.

References

Allane L (1993) Chinese rugs, a dyer's guide. Thames and Hudson Ltd, London

Bruni S, Guglielmi V, Pozzi F (2011) Historical organic dyes: a surface-enhanced Raman scattering (SERS) spectral database on Ag Lee-Meisel colloids aggregated by $NaClO_4$. J Raman Spectrosc 42:1267–1281

Cammann S (1951) The making of dragon robes T'oung Pao. Second Series 40:297–321

Casadio F, Leona M, Lombardi JR, Van Duyne R (2010) Identification of organic colorants in fibers, paints, and glazes by surface enhanced Raman spectroscopy. Acc Chem Res 43:782–791

Colombini MP, Andreotti A, Baraldi C, Degano I, Lucejko JJ (2007) Colour fading in textiles: a model study on the decomposition of natural dyes. Microchem J 85:174–182

Edwards HGM, de Oliveira LFC, Nesbitt M (2003) Fourier-transform Raman characterization of brazilwood trees and substitutes. Analyst 128:82–87

Eiland ML (1979) Chinese and exotig rugs. A. Zwemmer Ltd., London

Grzywacz CM, Wouters J, Bomin S, Yuquan F (2010) Asian organic colorants: a collaborative research project. In: Agnew N (ed) Conservation of ancient sites on the Silk Road. The Getty Conservation Institute, Los Angeles, pp. 450–456

Gulmini M, Idone A, Diana E, Gastaldi D, Vaudan D, Aceto M (2013) Identification of dyestuffs in historical textiles: strong and weak points of a non-invasive approach. Dyes Pigments 98:136–145

Han J (2015) Botanical provenance of historical Chinese dye plants. Econ Bot 69:230–239

Karapanagiotis I, Chryssoulakis Y (2005) Investigation of the red natural dyes used in historical objects by HPLC-DAD-MS. Annali di Chimica (Rome, Italy) 95:75–84

Karapanagiotis L, Valianou L, Daniilia S, Chryssoulakis Y (2007) Organic dyes in Byzantine and post-Byzantine icons from Chalkidiki (Greece). J Cult Herit 8:294–298

Karapanagiotis I, Lakka A, Valianou L, Chryssoulakis Y (2008) High-performance liquid chromatographic determination of colouring matters in historical garments from the Holy Mountain of Athos. Microchim Acta 160:477–483

Karapanagiotis I, Minopoulou E, Valianou L, Daniilia S, Chryssoulakis Y (2009) Investigation of the colourants used in icons of the Cretan School of iconography. Anal Chim Acta 647:231–242

Karapanagiotis I, Theologou J, Lakka A, Ozoline A, Panayiotou C (2011) Investigation of the colouring materials of Fustat carpet fragments. Archaeometry 53:587–599

Kenjo T (1987) Discoloration of red colors irradiated with some monochromatic lights. Art and Archaeology Technical Abstracts 25

König H (2011) Intrecci cinesi. Antica Arte Tessile (XV - XIX secolo). Galleria Moshe Tabibnia, Milano

Lee PC, Meisel D (1982) Adsorption and surface-Enhanced Raman of dyes on silver and gold sols. J Phys Chem 86:3391–3395

Leona M, Lombardi JR (2007) Identification of berberine in ancient and historical textiles by surface-enhanced Raman scattering. J Raman Spectrosc 38:853–858

Leona M, Stenger J, Ferloni E (2006) Application of surface-enhanced Raman scattering techniques to the ultrasensitive identification of natural dyes in works of art. J Raman Spectrosc 37:981–992

Manhita A, Ferreira T, Candeias A, Dias CB (2011) Extracting natural dyes from wool—an evaluation of extraction methods. Anal Bioanal Chem 400:1501–1514

Mouri C, Laursen R (2012) Identification of anthraquinone markers for distinguishing Rubia species in madder-dyed textiles by HPLC. Microchim Acta 179:105–113. doi:10.1007/s00604-012-0868-4

Nowik W (2001) The possibility of differentiation and identification of red and blue "soluble" redwoods. Dyes in History and Archaeology 16/17:129–144

Padfield T, Landi S (1966) The light-fastness of the natural dyes. Stud Conserv 11:181–196

Pozzi F, Poldi G, Bruni S, De Luca E, Guglielmi V (2012) Multi-technique characterization of dyes in ancient Kaitag textiles from Caucasus. Archaeol Anthropol Sci 4:185–197

Rostov CI, Guanyan J, Linpan L, Zhang HZ (1983) Chinese carpets. Abrams, New York

Sanyova J (2008) Mild extraction of dyes by hydrofluoric acid in routine analysis of historical paint micro-samples. Microchim Acta 162: 361–370

Strekal' ND, Motevich I, Nowicky JW, Maskevich SA (2007) IR absorption and surface-enhanced raman spectra of the isoquinoline alkaloid berberine. J Appl Spectrosc 74:31–37

Tabibnia M (2011) Intrecci cinesi. Antica Arte Tessile (XV - XIX secolo). Galleria Moshe Tabibnia, Milano

Tiffany Studios (1969) Antique Chinese rugs. Charles E. Tuttle Company, Rutland, Vermont and Tokyo

van Bommel MR, Vanden Berghe I, Wallert AM, Boitelle R, Wouters J (2007) High-performance liquid chromatography and non-destructive three-dimensional fluorescence analysis of early synthetic dyes. J Chromatogr A 1157:260–272

Walton Rogers P (1999) Dyes in the Hochdorf textiles. In: Hochdorf IV, Die Textilfunde aus dem späthallstattzeitlichen Fürstengrab von Eberdingen-Hochdorf (Kreis Ludwigsburg) und weitere Grabtextilien aus hallstatt- und laténezeitlichen Kulturgruppen Forschungen und Berichte zur Vor- und Frühgeschichte Baden-Württembergs 70., Stuttgart, Theiß pp 240–245

Wouters J (1994) Dye analysis of Chinese and Indian textiles—with special emphasis on the recognition of Miscanthus tinctorius and *Sophora japonica* and the composition of green and blue colours. Dyes in Hist Archaeol 12:12–22

Wouters J, Verhecken A (1989) The scale insect dyes (Homoptera, Coccoidea)—species recognition by HPLC and diode-array analysis of the dyestuffs. Annales De La Societe Entomologique De France 25:393–410

Ye Y, Salmon LG, Cass GR (2000) The ozone fading of traditional Chinese plant dyes. J Am Inst Conserv 39:245–257

Yu-kuan L (1980) Art rugs from Silk Route and Great Wall areas. Oriental House Ltd., Tokyo

Zaffino C, Bruni S, Guglielmi V, De Luca E (2014) Fourier-transform surface-enhanced Raman spectroscopy (FT-SERS) applied to the identification of natural dyes in textile fibers: an extractionless approach to the analysis. J Raman Spectrosc 45:211–218

Zhang X, Good I, Laursen R (2008) Characterization of dyestuffs in ancient textiles from Xinjiang. J Archaeol Sci 35(1095–1103)