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The discovery of three lost ‘Salting’ carpets: Science as a tool for revealing their history

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The discovery of three lost 'Salting' carpets:

Science as a tool for revealing their history

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TABLE OF CONTENTS

1. INTRODUCTION **7**

2. THE 'SALTING' CARPETS **8**

2.1 Technique *8*

2.2 Style and Decoration *9*

2.3 The Guimarães Carpets *10*

3. DYES AND MORDANTS **13**

3.1 Colours and Dyes in Iran and Turkey *13*

3.2 Mordants *15*

4. LAC DYE LIBRARY **15**

4.1. Lac Insects *15*

4.2. Lac-dye *17*

5. EXPERIMENTAL **17**

6. RESULTS AND DISCUSSION **18**

6.1. Fibres *18*

6.2. Dyes and mordants *18*

6.3. Lac-dye and the HPLC-DAD Library *25*
6.3.1. Samples preparation 25
6.3.2. Lac-dye insect sources 25
6.3.3. Historical red-dyed textiles 26
6.3.4. *Paratachardina* and *Kerria* genera – reference insect sources 26
6.3.3. Lac-dye specimens from the collection of the Royal Botanical Garden at Kew – unidentified historical lac-dye species 27

6.4. Metal threads *28*

6.5. AMS Radiocarbon dating *29*

7. CONCLUSIONS **30**

8. REFERENCES **31**

APPENDICES **34**

APPENDIX I: Medallion Carpet inscriptions **35**

APPENDIX II: *Kerria* species found in literature **36**

APPENDIX III: Experimental Details **38**

APPENDIX IV: Experimental results from all dyes and correspondent colours identified **44**

APPENDIX V: Lac dye and resin markers database **56**

APPENDIX VI: Chromatographic profiles from lac-dye insect sources **58**

APPENDIX VII: PCA analyses: Insects sources origin VS Historical textile fibre **59**

APPENDIX VIII: Metal threads **60**

APPENDIX IX: Radiocarbon Analysis **62**

RESUMO

Em 2007 três tapetes “Salting” foram descobertos no Paço Ducal de Guimarães, a maior colecção fora do Palácio Topkapi (Istambul). No último século as opiniões de especialistas relativas à proveniência e datação dos “Saltings” têm sido divergentes.

A designação “Salting” provém do nome do famoso coleccionador George Salting (1835-1909) que, em 1910, doou um exemplar significativo ao Museu Victoria & Albert (V&A), Londres, cuja origem foi inicialmente atribuída ao Irão do século XVI. Porém, a vivacidade das suas cores e existência de exemplares semelhantes no Topkapi têm sido argumentos utilizados por diversos historiadores que defendem tratar-se de peças Turcas dos séculos XVIII e XIX, ou até mesmo falsificações dos clássicos tapetes Persas.

Neste âmbito e através de uma abordagem interdisciplinar, combinando História, História da Arte, Ciências da Conservação e Entomologia, este estudo pretende clarificar a proveniência e datação dos tapetes de Guimarães.

Identificou-se a presença de seda na teia e trama nos três tapetes. Os nós são constituídos por lã, sendo de destacar a extraordinária densidade de nós encontrada no tapete de Medalhão. Todas as cores foram analisadas, tendo sido os vermelhos objecto de um estudo mais aprofundado, de modo a obter possíveis informações relacionadas com a questão de proveniência. Verificou-se que os vermelhos foram obtidos com o corante Laca (*Kerria spp.*), à semelhança de outros tapetes Persas clássicos com um fundo vermelho.

Pela primeira vez foi criada uma base de dados de insectos de laca (géneros *Kerria* and *Paratachardina*) obtida com Cromatografia Líquida de Alta Resolução com Detector por Vector de Díodos (HPLC-DAD) e cujos resultados foram submetidos a uma Análise de Componentes Principais (PCA). Amostras históricas de insecto (87 amostras) oriundas do Royal Botanic Gardens, Kew (Londres), bem como de outras fontes entomológicas, foram analisadas e comparadas com amostras históricas de têxteis provenientes dos tapetes de Guimarães.

Identificou-se para os amarelos um corante à base de luteolina, possivelmente lírio-dos-tintureiros, o qual surge também nos verdes, associado ao índigo e, no caso dos laranjas, à garança. Os castanhos e beges foram obtidos com recurso a lã natural, com excepção dos castanhos presentes no tapete de Medalhão, nos quais se identificou a presença de ácido elágico. O tingimento foi obtido com o mordente alúmen em quase todas as cores, excepto os castanhos do tapete de Medalhão (Ferro), beges (lã natural) e índigo (corante de tina).

As análises de SEM-EDX revelaram um método característico de construção dos fios metálicos, o qual envolve o corte manual da lâmina de prata previamente revestida a ouro.

Verificou-se que o tapete de Medalhão foi possivelmente realizado entre o final do século XV e meados do século XVII, de acordo com os resultados de radiocarbono, os quais excluem uma data de concepção mais tardia ou mesmo falsificação.

Em suma, os resultados obtidos sugerem que os tapetes de Guimarães tenham sido concebidos possivelmente entre os séculos XVI e XVII no Irão, e que o tapete de Medalhão revelou ser uma descoberta excepcional. Estes resultados serão apresentados em diversas conferências (more details see page 30).

ABSTRACT

In 2007 three 'Salting' carpets were discovered in the Palace of the Dukes of Bragança, in Guimarães. Two are prayer rugs with central niches, while the third has a central medallion. Finely knotted in wool on a silk foundation, and embellished with metal threads, this is the largest collection of these carpets known outside the Topkapi Saray (Istanbul). For a century, their origin and chronology have been the source of considerable debate.

They take their name from the collector George Salting (1835-1909) who donated a significant example to the Victoria & Albert Museum (London), which was originally attributed to 16th-century Iran. However, the vivid colors of this and other carpets, and existence of similar examples in the Topkapi, led later historians to argue that they were Turkish rugs from the 18th or 19th centuries, and possibly even forgeries of classical Persians carpets.

Wool and silk were confirmed in the knotted pile and foundation, and the Medallion Carpet was found to have an extremely high knot count. All colours present were analysed, and a more detailed study was applied to the reds. Lac-dye (*Kerria spp*.) was identified and as this is the predominant dye of the red ground of classical Persian carpets, it appeared to offer a possible clue to their provenance. The first High Performance Liquid Chromatography-Diode Array (HPLC-DAD) data base was created for lac-dye insects (*Kerria* and *Paratachardina* genera) with the support of Principal Component Analyses (PCA), statistical analysis. Historical insect sources (87 samples) from the Royal Botanic Gardens, Kew (London), as well as other entomological sources, were analysed and compared with historical textile samples taken from the Guimarães carpets. The preliminary results revealed that probably the red dye is related with insect sources from Pakistan or a nearby region. However, narrowing the provenance further will require more rigorous taxonomic study of the wide variety of insect species known to produce lac dye (over 20), followed by chemical analysis and comparison with a wider range of carpets.

A luteolin-based dye, possibly weld was identified in the yellows, which also appears in the greens with indigo and in the oranges with alizarin, respectively. The browns as well as beige colours were obtained with natural wool, with the exception of the browns in the Medallion carpet in which ellagic acid was identified. All of the colours were applied to the textile fibres with alum, with exception of browns in the Medallion Carpet (iron), beiges (natural wool), and indigo (no mordant).

SEM-EDX revealed a distinctive method of manufacture of the metal threads, involving a hand-cut silver lamina of fine gauge covered with a gold coating.

The AMS Radiocarbon dating confirmed a date between the late 15th- and mid-17th century for the Medallion Carpet, excluding the possibility of either a late date or forgery.

Overall the data point to a 16th- or 17th-century date and Iran as the place of manufacture for the carpets. The Medallion Carpet is revealed to be an exceptional historical discovery.

1. INTRODUCTION

In 2007 three 'Salting' carpets were discovered in the Palace of the Dukes of Bragança (Guimarães). This is the largest collection of these carpets outside the Topkapi Saray (Istanbul). They derive their name from the famous Australian-born British art collector, George Salting (1835-1909), who gave a particularly significant example to the Victoria and Albert Museum (London) in 1909 [1]. Defining the "Saltings" as a group has proven a difficult task, but, in general, the presence of a silk foundation (warps and wefts), fine wool pile, high knot count, bright colours and embellishments in metal thread, along with arabesque designs, religious inscriptions and small dimensions, are regarded as the most significant characteristics [1]. The question of their provenance and chronology has also been the source of continuous debate.

At the end of the 19th century, they were originally ascribed by late 19th- and early 20th-century historians to 16th-century Tabriz (Iran) and were recognized to be part of a large group of well-preserved prayer rugs, with brilliant colours, in the Topkapi Saray[1]. As some of the religious inscriptions on the prayer rugs are almost exclusively Shi'ite in nature, it was originally proposed that they had survived in such good condition in Turkey as they were not suitable for use by the Sunni Ottomans. However, their presence in Istanbul encouraged subsequent authors, such as Tattersall (1931), Erdmann (1941), and Rogers (1987), among others, to claim they were 18th- or 19th-century Turkish rugs, and possibly even forgeries of classical Persian carpets. More recently, a new generation of carpet experts has returned to the subject and argued the 'Saltings' are 16th or 17th century, and that the Topkapi rugs were sent from Safavid Iran to the Ottoman court. Michael Franses proposed that the carpets could have been sent from Shah Tahmasp I (r. 1524-76) to Suleyman the Magnificent in 1556, as suggested by a letter mentioning a gift of "carpets spread on the floor of the mosque for the use of the congregation", or a decade later, to Sultan Selim II (r. 1566-1574) on the occasion of his accession in 1567 [1]. Jon Thompson has recently suggested, on the basis of an inscription on one of the carpets giving the date of 1590-91 (AH 999)[2], that they were a gift from Tahmasp's grandson, Shah Abbas I (r. 1587-1629), to the Ottoman Sultan Murad III (r. 1574-95), possibly on the occasion of the Treaty of Istanbul signed in 1590 [2].

Given this complex historiography, resolving the question of the origin and date of the 'Saltings' is obviously imperative, and the discovery of three carpets in Guimarães offers a unique opportunity to reflect upon these problems. The type of materials used to make a carpet and how they are prepared can reveal groups of carpets and help to establish their origin and/or date [3]. This type of data can also indicate whether these groups reflect a single, coherent production of short duration, or multiple workshops and a wide historical timeline. Only partial scientific information is currently available for the 'Saltings' [1], and hence, this study takes a multidisciplinary approach to the problems of their origin and date. Analyses are conducted on all of the materials used to make the three Guimarães carpets: namely, their fibres, dyes, mordants, and metal threads, and this data is then compared with published results for related examples documented in the literature to determine whether they are 1) products of

[1] "Salting Carpets" Oriental Carpets and Textile Studies, *The Salting Group: A History and a Clarification*,Danville, Califórnia, (1999), pg 2

[2] Islamic calendar

Persian or Turkish workshops, and 2) date from the classical period (16th to 17th centuries), or are later, from the 19th or even 20th centuries.

For tackling questions of provenance, yellow and red dyes are especially important, as the former are usually locally produced [4-7], while the latter in some cases have been shown to be culturally and temporally specific [3]. In previous work on Islamic carpets the red dye obtained from the lac insect, harvested in India and South Asia and widely traded throughout the region, has been shown to be the main colourant for the red ground of 16th- and 17th-century Persian wool carpets [8-10]. The previous detection of this dye in seven prayer carpets in the Topkapi collection would appear to support a Persian (as opposed to Turkish) provenance for the group [10-11]. Identification of the precise insect lac species would provide important evidence for associating the carpets with specific centers of production. For instance, several lac species are found in India (*Kerria lacca*), while others species are cultivated in China (*Kerria chinensis* or *Kerria mendingonsis*) [12] (Appendix I). However, no published study to date has used the HPLC-DAD (High Performance Liquid Chromatography-Diode Array) technique to differentiate the various species of lac insects in order to localize precise sources of production, as has occurred, for example, for cochineal or dragon's blood [13-14]. Owing to the high complexity of the Kerridae family and the lack of accurate entomological studies on lac species, it was not possible to obtain specimens of the 26 species referred to in literature [6,12,15]. Nevertheless, for the first time, several lac-dye samples from different geographical regions, as well as from different host plants, were analysed using HPLC-DAD and PCA (Principal Component Analyses). This foremost lac-dye comparative database can support and promote further research on lac-dye species, as well as reveal more detailed information about the source of the red dye and therefore assist with provenance and identification of historical textiles.

As for the question of the chronology of the 'Saltings', dye analysis is also useful, as the identification of synthetic dyes would provide good evidence for a late date, as demonstrated by Halpine for the Gobelins tapestry-upholstered furniture in the National Gallery of Art (Washington) [16], while AMS Radiocarbon Dating (C14-AMS) can confirm an earlier one. Previous C14-AMS analyses conducted on a small number of 'Salting' carpets [9] have indicated a 16th- to 17th-century date for them, but for unknown reasons a number of measurements gave "too high a carbon age" (circa 30% of the C14-AMS total analysis performed), and this question needs to be resolved [17]. The composition and morphology of the metal threads is also relevant for establishing a date, although work in this area is still in its infancy.

Finally, the Guimarães carpets reveal an intense *abrash* (dappled tones) which is usually attributed to subtle changes in dye recipes, and an indicator of the presence natural dyes. When present in moderation, *abrash* has been considered a sign of high artistic quality [18], but, in the case of the Guimarães rugs, it could also be a consequence of degradation effects, owing to their exhibition under excessive light conditions for many years [19]. Mordant analysis and quantification of the dye content is a first step for resolving this question.

2. THE 'SALTING' CARPETS

2.1 Technique

The structure of a carpet consists of warps, wefts and knots, and two processes are combined, weaving and knotting. The warps are the vertical threads that run the length of the loom and, when

cut, form the fringes at the ends; the wefts run horizontally across the warp. Patterns are created by the pile-knots which are wound around one or two warps. After each row of knots is complete, the wefts are inserted across the carpet, and beaten down tightly with a comb to form a strong, resistant fabric. As each coloured knot is applied in sequence, along successive rows, carpet patterns are constructed using a pointillist technique, and involve laborious pre-planning of the design [20].

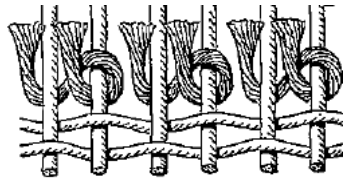


Figure 1: Detail of asymmetrical knots, open to the left [21].

The level of detail achieved in the pattern depends on the volume of the interlaced structure created by the warp, weft and knot, and hence, when the fibre diameter is low, designs with greater detail are possible. In the finest carpets, silk is used for all three threads, owing to its high strength in relation to its diameter.

While horizontal and vertical designs can be created easily using the grid of warp and weft, diagonal and curving lines require a relative high knot density (more than 3,500 knots/dm^2), and silk is often used for the warp (and weft) in wool carpets to enhance the knot count. This is the case for the 'Saltings', and an S-twisted silk thread is used for both the warp and weft to increase the knot count to render very detailed designs, including the tightly curving and scrolling vines which are typical of their designs. The knots are wrapped around two warps in an asymmetrical format, open to the left (figure 1), which also enhances the detail, as these knots are more compact and the pile is more evenly spaced.

In addition to knotting, carpet patterns can also be enhanced with decoration added in tapestry technique. Metallic threads are especially popular, and in the 'Saltings', decorative threads comprising a silk core wrapped with a metal strip are introduced in selected areas, such as the inscriptions.

2.2 Style and Decoration

Although the precise date of the 'Salting' carpets has been debated for over a century, their design characteristics reflect Safavid art, which was given a major impetus under Shah Tahmasp I (1514 - 1576), who was an important patron of the art of the book, but also commissioned magnificent carpets and other objects [2]. Under his patronage, artists from Herat migrated to Tabriz, resulting in a fusion of the two artistic styles prominent in Iran prior to the rise of the Safavids: the art of the Timurids and Turkmans. This new style features *tchi* clouds, angels, pheasants and multiple layers of winding scrolls as major decorative elements [2]. Figures and animals were also used increasingly, and integrated into compositions with geometric framing devices, such as elliptical and star-shaped medallions, cartouches, quatrefoils and poly-lobed forms, as seen in the borders of the 'Salting' carpets.

The splendour of this style stagnated after Shah Tahmasp became disinterested in the visual arts around 1555, and was only revived again with the rise of Shah Abbas I (1587-1629) [2]. At this time, the artists of the re-established court library began to generate a new decorative style of floral and foliate decoration, which, in accordance with the Shah's taste and political programme, was implemented across a wide range of arts, from illumination and bookbinding to textiles, carpets, and architectural tiles. In contrast to previous periods, the design elements are larger in scale, bolder in form and more homogeneous, and the same split-leaf arabesque can be found in bookbinding, a 'Salting' carpet, and building decoration (figures 2 to 4).

Figure 2: Book cover (Iran, 17th century), in leather, decorated with arabesques and filigree ornament. Detail of an arabesque scroll, with winding tendrils [Smithsonian Institution].

Figure 3: ´Salting' prayer carpet (Iran, 17th century), in wool, silk and metal-wrapped thread, decorated with arabesques inside the niche. Detail of an arabesque scroll, with winding tendrils [Private collection].

Figure 4: Ceramic tiles on the exterior of the Shrine of Shaykh Safi, Ardabil. Detail of an arabesque scroll, with winding tendrils [Shrine of Shaykh Safi, Ardabil].

A new colour palette was also introduced under Shah Abbas. In textiles, there was a preference for yellows, while the dark blues and reds typical of the 16th century gave way to a palette of softer shades of beige, pink, light green, and light blue [20]. An elaborate use of metal thread for decorative elements, as well as large areas of the background, to create a visual effect of splendor and luxury were also typical of the Shah Abbas period [22].

The 'Saltings' are enigmatic in sharing characteristics of both styles. On the one hand, they have poly-lobed medallions, cartouches, and a rich colour palette consistent with the Tahmasp style, and on the other, they have large-format arabesque scrolls and extensive use of metal thread usually associated with textiles produced under Shah Abbas. This mixture of styles is in part responsible, along with the bright colours of the Topkapi carpets, for associating the 'Saltings' with later Turkish production and for questioning their authenticity.

2.3 The Guimarães Carpets

Two of the three 'Salting' carpets found at the Palace of the Dukes of Bragança (Guimarães) are small prayer rugs, symmetrical along the longitudinal axis, with a niche occurring in the central field, a wide colour palette, religious inscriptions, and are profusely decorated with metal-wrapped thread. The first rug, previously in the collection of Vital Benguiat and known as the "Benguiat Prayer Rug" (figure 5), has vine scrolls decorating the red field, with the upper corners filled with irregularly-shaped areas of colour with short inscriptions, and a continuous inscription outlining the central niche. The main border has inscribed cartouches in red and green which alternate with lobed medallions on a beige ground. This carpet is related stylistically to six rugs preserved in the Topkapi Saray Museum (Istanbul), and five in private collections or of unknown provenance.[3] The carpet is in a poor state of conservation, and exhibits intense *abrash*, visible mainly in the blue, green and red areas of the upper corners.

[3] *The Salting Carpets* 1999, Group B.2c, pp. 86-93, cat. 21-27, 29-32.

Figure 5: *Benguiat* Prayer Rug (*PD77*)

Benguiat Prayer Rug

Materials: Wool pile, silk foundation, silver threads
Dimensions: 178 × 106 cm (máx.)
Knot density: 7.547 knots/dm^2
Inscriptions: (1) Main border: *Koran, II, 255, ending with "The Most Mighty, Beneficient God told the truth, and his Messager told the truth."*; **(2)** Inner border: Koran, VII, 204-5 (with one word omitted); IX, 129; I, 2.; **(3)** Band forming arch: *Koran, LIX, 22, and parts of 23 ending with invocations to God through His Attributes.";* **(4)** Cartuche in arch: *"Glory to my Most High Lord, and to His Praise";* **(5)** Field round arch: *Invocations to God through His Attributes.*
Provenance: Topkapi Saray, Istanbul (?); Vital Benguiat Collection, New York; George Robert Duff Collection; Perez & Co., Londres; Paço dos Duques de Bragança, Guimarães (IMC), *PD77*

The second carpet, known as the "Duff Prayer Rug" (figure 6), has a field of interlocking hexagons, with the upper corners filled with vine scrolls, while inscribed cartouches alternating with medallions in the upper half of the border. The inner border and niche also contain running inscriptions. Red predominates as the ground colour throughout. The hexagon field of this carpet is found in only one other example, in the Topkapi Saray (Istanbul)[4], but the format of the border with inscriptions located exclusively in the upper half can be seen in ten additional carpets, now in the Metropolitan Museum of Art (New York), Walters Art Gallery (Baltimore), Topkapi (Istanbul), and several private collections[5]. This carpet is also in a poor state of conservation and the *abrash* is located almost exclusively in the lower main border.

Figure 6: *Duff* Prayer Rug (*PD78*)

Duff Prayer Rug

Materials: Wool pile, silk warps and wefts, silver threads
Dimensions: 160 × 107 cm (máx.)
Knot density: 7.487 knots/dm^2
Inscriptions: (1) Outer border: Koran, II, 285, and half of 286; **(2)** Main border: Koran, II, 255. **(3)** Inner border: Koran, II, 256, and parts of 257. **(4)** Band forming arch: Koran, XIV, 40-1.; **(5)** Cartouche in arch: "*Glory to my Most High Lord, and to His Praise";* **(6)** top squares in main border*, in seal Kufic, in positive (left), and negative (right): Koran, XXI, parts of 87.* **(7)** Middle squares in main border, in seal Kufic, both positive:"Glory to God, and praise be to God, and there is no god, but The God, and God is Most Great".
Provenance: George Robert Duff Collection;
Paço dos Duques de Bragança, Guimarães (IMC), *PD78*

[4] *The Salting Carpets* 1999, Group B.2b, pp. 85-86, cat. 20.
[5] *The Salting Carpets* 1999, Group B.2a, pp. 81-85, cat. 9-18.

The third, and largest, carpet is an entirely new addition to the corpus of 'Salting' carpets and a very important discovery. It was previously in the collection of Messrs Perez (London) and published by Stanley Reed (1967), but not included in the study of Franses and Mills (1999), and only finally recognized in the study presented here.

It has a central medallion (as opposed to a niche) (figure 7), and an exceptionally high knot count (11.155 knots/dm^2), considering that the pile is wool and not silk. This knot density is more than twice that of the famous Ardabil carpet (V&A) and closer to rugs made exclusively of silk, such as the 'Kashans' [20]. The central field has a dark red ground covered with *tchi* clouds, a blue medallion in the centre, and green corner medallions. In the main border, lobed medallions alternate with the inscribed cartouches on a beige ground. The inscription appears to be a Persian poem, which describes it as "precious royal carpet… under the feet of such King Suleyman" (see appendix I). Reed has proposed that it was dedicated to the Persian Shah Suleiman (r.1667-1697) [22]. This poem is potential extremely important historical evidence and is currently being considered for greater clarity for this study by Professor Wheeler Thackston (Harvard University) (forthcoming information).

While the 'Salting' prayer or niche rugs are well defined as a group stylistically, the medallion group remains to be properly described, and few parallels can be found for the field design and inscription of the Guimarãs carpet, in contrast to the prayer rugs. In general terms, the quarter medallions decoration in the field and of the border can be related to four recorded examples in the Hermitage (St. Petersburg), Musée Historique des Tissus (Lyon), and Musée des Arts Décoratifs (Paris)[6]. It is also in a poor state of conservation, and *abrash* is visible throughout the carpet: in the central field and main border, as well as all the colours present.

Medallion Carpet

Materials: Wool pile, silk warp and weft, silver threads.
Dimensions: 244 × 170 cm (máx.)
Knot density: 11.155 knots/dm^2
Inscriptions: Currently under study (see Appendix I);
Provenance: Paço dos Duques de Bragança, Guimarães; (IMC) *PD76*

Figure 7: Medallion carpet (*PD76*)

[6] *The Salting Carpets* 1999, p. 6-16, fig.4, 7, 14.

3. DYES AND MORDANTS

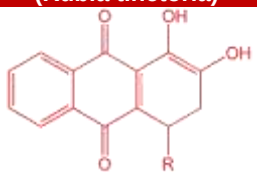
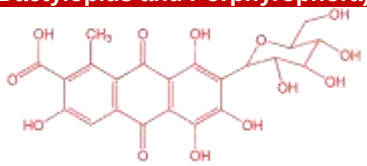
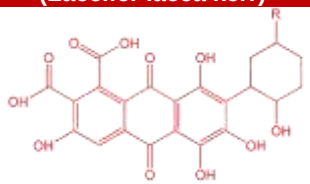
3.1 Colours and Dyes in Iran and Turkey

The colours used in 16th- and 17th-century Persian and Turkish carpets, referred to here as "classical", were obtained from natural sources, namely plants or insects. It was only in the 19th century, with the discovery of mauve dye by Perkin (1856) and several coal-tar-based dyes, that synthetic dyes were adopted in Iran and Turkey to produce bright and vivid colours [10]. Regional taste also played a factor in colour choices and in the composition of the colour palette. The combination of contrasting primary colours is a general feature of Turkish carpets, while in many classical Persian carpets red dominates the central field and blue or green are used for the border, and in the decoration, secondary colours are juxtaposed beside primary ones, such as orange with blue or green with yellow [20]. Published analyses of the dyes used in Islamic carpets also reveal a number of interesting trends in the choice of dyestuffs in these two regions, which are useful for studying the 'Salting' carpets [10-11]. The number of analyses is too small to make firm conclusions, but some general observations can be made.

For the **reds,** the most common dye found in 16th- and 17th-century Turkish carpets was extracted from the roots of the madder plant (Rubiciaea family).

It occurs more rarely in classical Persian carpets, there it is exclusively used for the oranges [8-9]. The main chromophores of madder are alizarin and purpurin, both compounds based on 1,2 dihydroxy anthraquinone chromophore, table 1. In addition, dyes prepared from coccid insects were popular [23]; *Porphyrophora* genera have been found in Persian silk carpets, such as the "small silk Kashans" [8,23]. Other red dye sources of animal origin were used in Iran and India, such as lac-dye (*Kerria* genera) [3], not found in Turkish carpets, along with cochineal [11]. Lac dye and cochineal are easily distinguished by the presence of laccaic acids and carminic acid chromophores, respectively (table 1). Lac-dye has been identified in a large number of classical Persian carpets [8-9] usually in the red ground; its presence in the 'Saltings' is potentially an important indicator for determining their provenance and for this reason is discussed extensively below [1].

Table 1: Red dye sources and main chromophores molecular structures.

Madder (Rubia tinctoria)	Coccid insects (Dactylopius and Porphyrophora)	Lac insect dye (Laccifer lacca kerr)
 Alizarin R= H Purpurin R= OH	 Carminic acid	 Laccaic acid A R= $CH_2CH_2NHCOCH_3$ Laccaic acid B R= CH_2CH_2OH Laccaic acid C R= $CH_2CH(NH)_2COOH$ Laccaic acid D R= $CH_2CH_2NH_2$

The **blues** in historical carpets from both Iran and Turkey use exclusively indigo dye extracted mainly from the indigo shrub *(Indigofera tinctoria L.)* or from dyer's woad (*Isatis tinctoria* L.*)* [12,18]. The main chromophore of indigo is indigotin (figure 8) and its identification in historical rugs is an important indicator of authenticity, as indigo was the most successful and prolific natural blue prior to the invention of synthetic dyes in the 19th century.

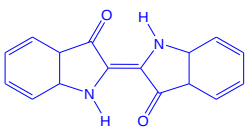


Figure 8: Indigotin molecule from indigo dye source *(Example: Indigofera tinctoria* L.*)*

The **yellows** in classical Persian carpets were generally obtained from local plants, such as asbarg (*Delphinium semibarbatum*) which is composed primarily by quercitin, kaempferol and isorhamnetin chromophores. Weld *(R. Luteola),* rich in luteolin-7-*O*-glycoside was also found in Persian carpets (figure 9).

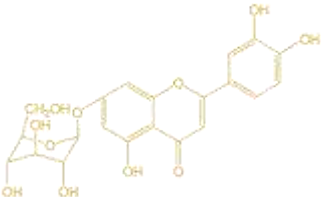


Figure 9: Luteolin-7-O-Gl molecule from weld dye source *(Reseda luteola* L.*)*

The use of related plants with luteolin glycoside derivatives [3,11] have been identified in both Persian and Turkish rugs. The luteolin-based compounds are very well documented and considered characteristic of an ideal dye[7], and thus commonly identified in high quality textile products [4]. By contrast, the yellows found in historical Turkish rugs do not reflect the use of asbarg, as it does not occur in Turkey; according to the literature, it is unlikely that this plant was ever imported into Turkey, as more than enough indigenous yellow dye plants are available for use [11,18].

Curiously, the **oranges** in Persian carpets do not include lac-dye, but, instead, madder mixed with a yellow dye. As for Turkish rugs, the results obtained do not offer a precise conclusion; although it is generally agreed that some Turkish plants such as chrysanthemus (*Chrysanthemus coronarium* L.) or dyer's sumac (*Cotinus coggygria* SCOP.) are used to obtain this colour [18].

Greens in both Turkish and Persian rugs are obtained by using a mixture of indigo with a yellow dye [11].

In both Iran and Turkey, the **browns** and **blacks** are obtained using tannins from local sources, for example, knobby or gallnut oak *(Quercus spp.)*.

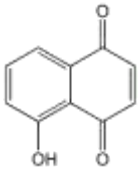


Figure 10: juglon molecule from walnut dye source (Juglan regia)

Beige colours were often obtained with natural wool in both Persian [8-9] and Turkish Carpets [18]. However, in some Persian carpets, analyses of beige areas have shown the presence of the juglone chromophore probably obtained from the walnut tree *(Juglans regia* L.*)* (figure 10). This dyestuff does not appear to have been identified in Turkish carpets [11].

It should be mentioned that some of the dye analyses reported in the literature were performed with extraction methods based on strong acids (usually with HCl) [7,24] and, even with Thin Layer Chromatography (TLC) [11]. TLC was used before HPLC-DAD, but does not provide complete results, as it is not possible to identify the precise chromophores and hence the correct dye-source [4].

The HCl method is an aggressive extraction method which can promote the degradation of chromophores in some dyes. In yellow dyes, it can cause decomposition of the glycosidic dye compounds to their parent aglycons, with consequent loss of information about the original dye source. For example there are numerous plants with different luteolin glycoside derivatives such as weld (*Reseda luteola* L.), dyer's greenwood (*Genista tinctoria* L.), true chamomile (*Matricaria chamomilla* L.) or three-leafed sage (*Salvia Triloba* L.) [18]. When these plants are submitted to a HCl extraction, the various luteolin glycosides present are destroyed during the process and usually only luteolin is detected in the final dye extract. Frequently, the identification of luteolin in dyed yellow fibres is attributed to the presence of weld, one of the most stable yellow dyes. Nevertheless, when the HCl extraction method is used, it is not possible to exclude the utilization of other related plants such as the ones mentioned previously. Therefore, mild extraction procedures such as those used in this work,

[7] "it is not altered by washing the fabric or exposure to light or air." in Ferreira, E., et al. "The natural constituents of historical textile dyes." The Royal Society of Chemistry, 33, 2004: 329-336.

and sucessfully reported in literature, are necessary to obtain greater information about the dye source [4,7].

3.2 Mordants

In order to attach these natural dyes to the textile fibre to ensure they are fixed permanently and will not bleed, a metallic ion (mordant) was usually applied in both Persian and Turkish carpets (figure 11). The mordant acts as an intermediary between the fibre and the dyestuff, and is usually obtained from a mineral source (salts in the form of crystals, efflorescence or crusts, mud, metal oxides). The choice of mordant can determine both the wash-resistance of a colour and its intensity [12,18].

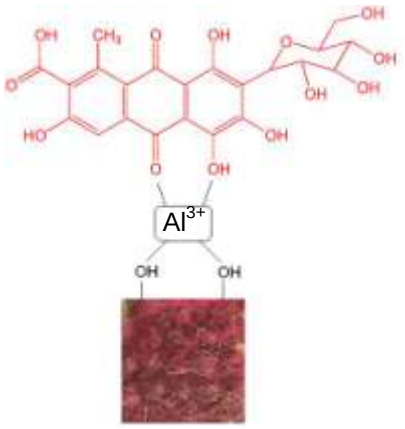


Figure 11: Mordent scheme were in metal ion Al^{3+} binds to natural wool fibre.

The presence of aluminium, iron and copper as mordents has been observed in both classical Persian and Turkish carpets for different colours [9,18]. For the yellows and reds usually an alum mordant was used, while in the dark browns the presence of an iron mordant has been detected [9,18]. For some beige colours, no mordant was detected at all. Also in blue fibres dyed with indigo, no mordant is applied, as indigo is a vat dye which precipitates in the fibres through an oxidation-reduction reaction [4,8].

4. LAC DYE LIBRARY

The Indian and South Asian origin of lac-dye would appear to support a Persian (as opposed to Turkish) provenance for the 'Salting' carpets. However, no study to date has used HPLC-DAD to differentiate lac-insect species to identify locations of dye production. Indeed, of the lac species of Asian origin belonging to the *Kerria* genera (ca. 26 species) [15,25], only *Kerria lacca Kerr* has been characterized using HPLC-DAD [6,12,26]. In this study, for the first time, 82 lac-insect historical samples of unknown species *Kerria* genera and 2 samples from *Paratachardina* genera, with diverse provenance, as well as from different host plants, were analyzed using HPLC-DAD. This data base methodology is applied here for the first time to lac-dye represents a first step towards developing necessary research on lac-dye species, to reveal greater information about the precise source of the red dye and therefore assist with provenance identification of historical textiles.

4.1. Lac Insects

Lac-dye was highly appreciated in Asia and is documented in India as a textile dye, from at least the 4th century BC [12]. Lac-dye was also known and used by the Romans for dyeing purposes since the 2nd century AD, which suggests that lac was probably one of the first insect dyes to be used in West Asia [26]. The dyestuff is obtained from female scale insects of the Kerridae family (figure 12) which contains nine genera and approximately 100 described species. Lac-dye can be obtained only from *Kerria* and *Paratachardina* genera [15].

The *Kerria* genera comprises 26 species [15], which can be found mainly in India, China, Taiwan, Sri Lanka, Australia, and Pakistan, and the *Kerria lacca Kerr* species is the most important (Appendix II). There are several publications about the *Kerria* species [5,15,28]; however, none of them have used molecular taxonomic studies for confirmative species identification. According to Penny Gullan[9] it is essential that fresh specimens are collected from Asia and molecular taxonomic studies are performed to correctly identify the lac insect species as has occurred, for example, for the *Paratachardina* species [29-30].

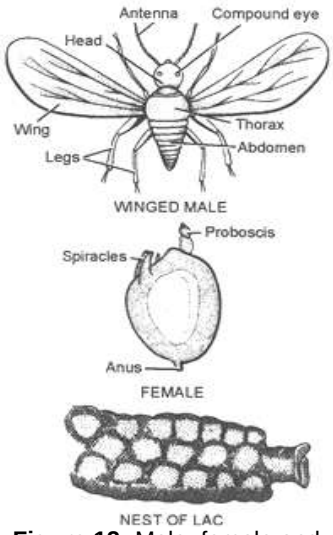


Figure 12: Male, female and lac-insect nest[8].

The *Paratachardina* genera comprises a total of nine species, which have been recently revised, mainly from China, India, Sri Lanka, Philippines and Papua New Guinea [29]. However, species belonging to *Paratachardina* genera do not produce lac-dye of commercial importance and mainly *Kerria spp.* are exploited [15]. Nevertheless, as the *Paratachardina* genera is the only one for which accurate taxonomic studies have been published, it was included in this study and specimens were analysed.

Several entomologists supplied five *Kerria spp* and two *Paratachardina spp* correctly-identified insect-specimens for HPLC-DAD analysis. As the taxonomy of the *Kerria* genera is not well established (Appendix II), it was not possible to obtain reliable insect-specimens for all of the 26 *Kerria* species described in the literature. Hence, in this study, as a first approach to studying the *Kerria* insects, 76 unknown historical lac-dye insect sources from different geographical regions (India, Australia, Taiwan, Vietnam, Laos, Singapore, Pakistan, Bangladesh Sri-Lanka and others), as well as from different host plants (*Ficus spp.*, *Schleichera spp.*, *Butea spp.*, *Zizyphus spp. and Shorea sp.*) (figure 13), were characterized by HPLC-DAD and submitted to PCA analysis. These 76 historical sources of lac-dye, dating from the 19th century and belonging to the Royal Botanic Garden at Kew, provide a good starting point for establishing similarities between the sources and for identifying insect groups according to their provenance and host plants. In future research, these insect samples should be submitted to molecular taxonomic studies and compared with the 26 *Kerria* species correctly-identified by entomologists.

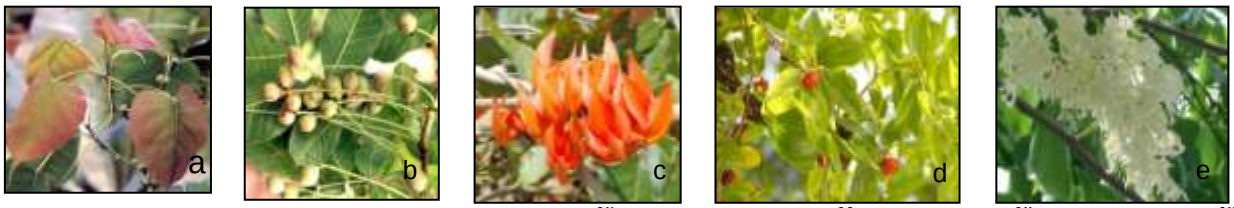


Figure 13: Insects specimens host plants **a)** Ficus spp.[10], **b)** Schleichera spp.[11], **c)** Butea spp.[12], **d)** Zizyphus spp[13] and **e)** Shorea sp[14].

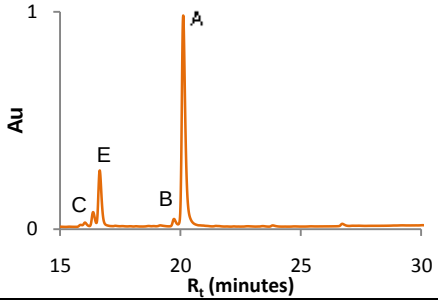
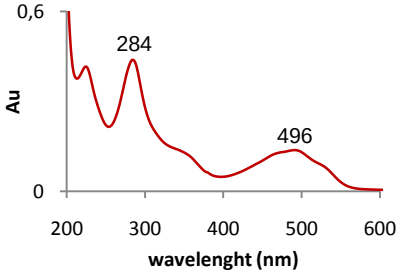
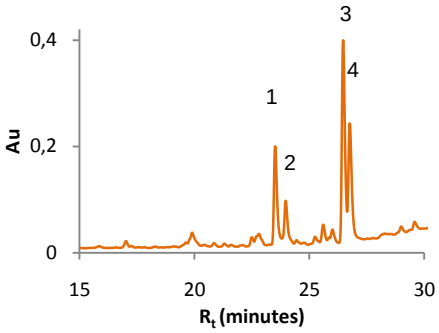
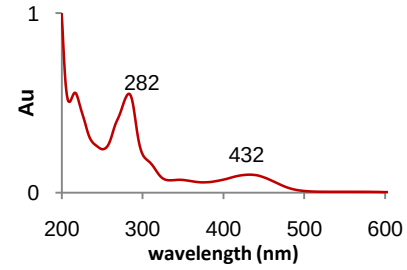
[8] Source: http://www.2classnotes.com/images/12/science/Zoology/Lac_Insect.gif
[9] The only entomologists specialized in the Kerriidae family: Penny J. Gullan and Takumasa Kondo, which will be available during next years to participate in a join research.
[10] Source: http://image.gardening.eu/piante/Immdata/ficus_religiosa.jpg
[11] Source: http://www.azerbaijanrugs.com/images/Schleichera%20oleosa.jpg
[12] Source: http://www.steevedubois.com/images/Flora/Butea%20superba%2000001.jpg
[13] Source: http://upload.wikimedia.org/wikipedia/commons/d/d9/Ziziphus_zizyphus_foliage.jpg
[14] Source:http://herb.ohojunk.com/wp-content/uploads/2009/09/9_006.jpg

4.2. Lac-dye

The process of production of lac dye involves thousands of lac insects attach themselves to twigs and the fleshy young leaves of suitable host plants (figure 13), from Moraceae, Sapindaceae or Dipterocarpaceae families, usually in November [31-32]. By March, each insect covers itself with a predator protection layer, exhibiting the appearance of a red oval-shaped, smoothly polished lifeless sack entirely filled with a beautiful red liquid [33]. The coated branches of the host plants are cut and harvested as sticklac, which contains both resinous matter and the red organic dye composed of laccaic acids. In order to obtain the pure deep red colouring matter suitable for dyeing purposes, known as lac-dye, it is necessary to perform a simple water extraction process. In extractions with 100% water, the principal chromophores of lac-dye, namely laccaic acid A, B, C and E, are obtained in the final water extract (table 2). On the other hand, ethanolic extractions of the sticklac product will remove only the resinous matter which is composed mainly of yellow compounds (table 2).

Lac comes onto the market as a raw product, occurring in many forms; among the most common are the already mentioned *sticklac*, *grain/seed lac* (material removed from the twigs), and a subsequent variety which is fused and cast into moulds, *caked lac* or *lac dye* (table 2) [33]. The pale perforated kind, in which no insect exists, constitutes the material for *shellac* employed for varnish-making.

Table 2: HPLC-DAD analysis of **i)** lac-dye extracted with 100% of water, where it is possible to identify the acid laccaic A, B, C and E and **ii)** shellac (resinous matter) extracted with 100% of ethanol, where it is possible to identify four unknown compounds. For more details see section 6.3.

Type	Sample	HPLC-DAD chromatogram	UV-Spectra
i) Lac-dye			Laccaic acid A UV spectrum 
ii) Seed lac			Peak 3 UV spectrum 

5. EXPERIMENTAL

A detailed characterization of the materials present in the three Guimarães carpets was performed using different methods. The fibres were identified by optical microscopy in longitudinal section; the colours were characterized using colorimetric measurements; all dyes were identified by High-Performance Liquid Chromatography with Diode Array Detector (HPLC-DAD) and when necessary with Mass Spectrometry (LC-MS); all mordants were analysed by Inductively Coupled Plasma with

Atomic Emission Spectrometry (ICP-AES); and the metal threads were characterized by Energy Dispersive X-ray Fluorescence (μED-XRF) and Scanning Electron Microscopy (SEM-EDX). C14-AMS analysis was performed in one sample from the medallion carpet.

Prior to HPLC-DAD identification of the red dyes, several historical lac-dye sources were analyzed by HPLC-DAD and submitted to a PCA analysis. Also several parameters in the samples preparation were tested in order to obtain HPLC chromatograms with good resolution. For more details about experimental proceedings see Appendix III.

6. RESULTS AND DISCUSSION

The two Guimarães prayer carpets, *Benguiat* (PD77) and *Duff* (PD78), share features commonly identified in the 'Salting' group, namely the presence of a bright colour palette, silk foundation, wool pile, metal-wrapped silk threads, arabesques designs, religious inscriptions and small dimensions. The Medallion carpet, by contrast, is distinguished by the absence of religious features, in both its composition which lacks a prayer niche and inscriptions which are not excerpts from the Koran but probably a secular poem. Analyses undertaken thus far on the 'Salting' group have focused mainly on the prayer type, and hence, the study undertaken here of the Medallion carpet offers new and important data for appreciating this under-studied type. With the aim of tacking the questions posed at the start of this study, concerning the date and provenance of the carpets, the results of the diverse analytical techniques utilized here (described above) are integrated and presented below, according to the standard method of preparing the materials for constructing a carpet: beginning with the fibres, followed by the colours and dyes (with special emphasis given here to lac-dye), and ending with the metallic threads, which were usually purchased from an external source outside the sphere of the carpet-making workshop. As C14 offers exclusively evidence for dating, it is dealt with at the end.

6.1. Fibres

Silk and wool fibres were identified in Guimarães rugs with optical microscopy, respectively in foundation and knot pile, which are known to been used for the 'Salting' carpets.

6.2. Dyes and mordants

A total of eight principal colours were identified using macro and microscopic observation of the Guimarães carpets: red, pink, blue, yellow, green, orange, brown, and beige. These were then confirmed by colorimetric analysis (for more details, see Appendix IV), and then the dyes were analysed by HPLC-DAD, and the results, as described below. In order to understand if the intense *abrash* (dappled tones) observed in the three carpets occurred as result of subtle changes in dye recipes or as a consequence of degradation effects, the mordants were also quantified.

6.2.1. Reds and pinks

Red is one of the principal colours in the 'Salting' carpets, and usually represents more than 50% of the total area in all the carpets analyzed. It is mainly visible in the central field, but in the *Duff* rug (PD78), it is also found in the main and inner borders.

In all of the rugs, a total of three red hues were identified in different areas of the ground, each of which have distinct *lightness* coordinate values (L) according to the CIELab colorimetric system: *light red* which presents the highest L coordinate value (**L* =** 33.88±1.31); *medium red*, where the **L* =** 26.77±0.01; and *dark red* with the lowest L coordinate value (**L* =** 17.59±0.98). The *light red* from

Benguiat Rug (PD77) is more yellowish (**a* =** 9.37±0.65, **b* =** 10.78±0.47) than the other hues, while the *dark red* from *Duff* Rug (PD78) is the most reddish hue (**a*** 17.08±0.07, **b*** = 6.07±0.09) identified in all the three carpets. There is also a "*pink"* hue observed only in the *Benguiat* Rug, and which, in contrast to the red tones, is present in two irregularly-shaped areas that fill the upper corners of the niche. This *pink* colour is similar to the *light red* hue; however, it has a lower value of the red component (Δa*= - 3.04) and is more yellowish than the *light red* hue (Δb*= +1.60).

As the *Benguiat* Carpet (PD77) exhibits the widest range of colours and hues, at least 2-3 samples of all the red hues were analyzed with HPLC-DAD and ICP-AES, and the results compared with a smaller number of samples taken from the other two carpets. All of the red shades (total 13 samples) were shown to have been obtained with lac-dye and alum mordant.

HPLC-DAD and LC-MS analyses revealed the presence of laccaic acids, the main chromophores of lac-dye and documented previously in other Persian carpets from the 16th and 17th centuries [8,9,11]. Besides laccaic acid A (R_t= 20.10 min., λ_{max}= 284, 496 nm, $[M-H]^-$= 536), usually the major compound, laccaic acids B (R_t= 19.72 min., λ_{max}=288, 490nm, $[M-H]^-$=495), C (R_t= 16.37 min, λ_{max}= 284, 494 nm, $[M-H]^-$=538) and E (R_t= 16.64 min, λ_{max}= 284, 494 nm, $[M-H]^-$= 494) were also recognized, as reported in literature (33)(25). Two minor unidentified compounds (<6%) were found, namely, C1: R_t= 25.80min, λ_{max}= 432nm and C2: R_t= 26.30min, λ_{max}= 462nm) (figure 14) (Appendix IV, table IV.1), which are probably from the resinous lac matter (Appendix V). These compounds were also detected in some historical resinous lac-dye sources from Kew Garden (for more details, see section 6.3).

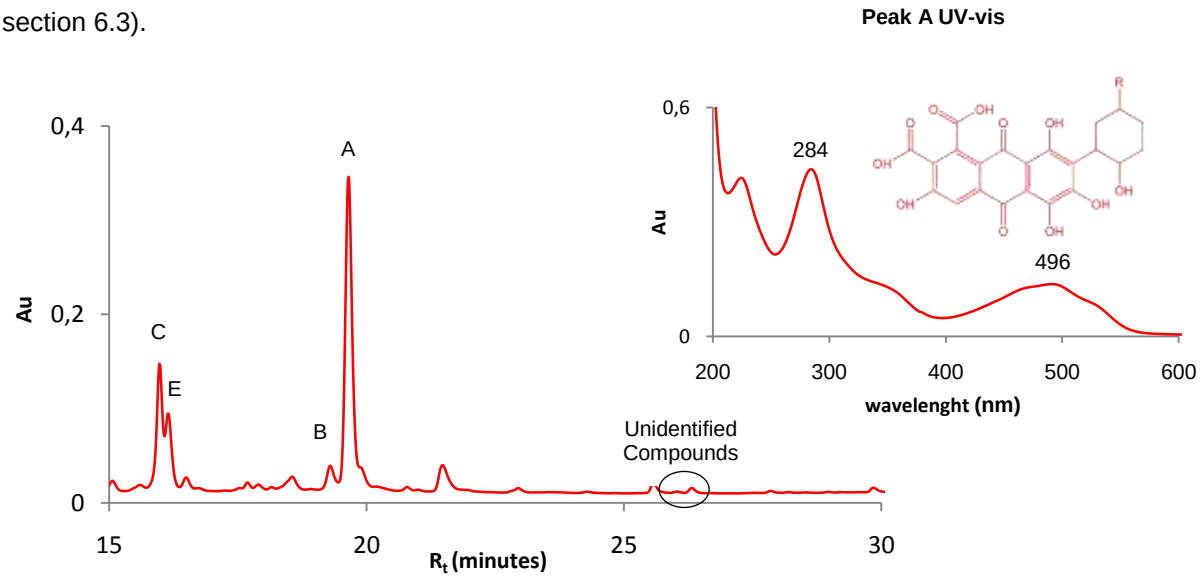


Figure 14: HPLC-DAD chromatogram acquired at 275 nm of of a red textile sample from rug PD77, were it is possible to identify: A) acid laccaic A; B) acid laccaic B; C) acid laccaic C and E) acid laccaic E. Two unidentified small compounds (black open circle) from the resinous lac matter were also identified. All the red and pink samples analysed have a similar elution profile to this chromatogram.

Although laccaic acid A was the main chromophore in the three red hues, in the *medium* and *darker red* hues, its relative percentage was usually around 70%, whereas in the *light red* hue for the Medallion Carpet (PD76) its relative percentage was around 30% (table 3). The relative percentage area of laccaic acid C and E was also considerable in the three red tones, ranging between 20-60%. The relative percentage of laccaic acid B in the three red hues is less than 10%, in contrast to what is reported in the literature (circa 30%) [8].

As the chromophores distribution in the three tones for all the carpets is similar within each carpet, with exception of the *light red* hue in the Medallion rug (PD76), probably the dyeing process used to obtain the three red hues was similar, or even the same for the three Guimarães carpets.

One of the most common methods used in the Middle Ages involves pre-mordanting [12], in which baths with different concentrations of metallic ions are applied to the textile fibres prior to immersion in the dye-bath. The advantage of this method is that the dye-bath is not altered by the addition of a metallic salt so that it can continue to be used until there is no more dye left in the bath, resulting in a series of gradually less saturated hues or tints [12], and this was probably explaining the results for the Guimarães carpets.

It is interesting to note that in the *darker red* hues of the *Benguiat* carpet (PD77), there was a higher amount of aluminium ion (circa 3.6 mg Al^{3+} /wool (g)) than in the *light red* hue (circa 2mg Al^{3+}/wool (g)) (table 3), which could promote a higher level of lac-dye absorption during repeated dye-baths. Indeed, the darker hues have at least twice as much lac-dye as observed in the *light red* hues (for more details, see normalized areas in table IV.1, Appendix IV). Higher amounts of alum and lac-dye in darker red hues have also been reported for other historical Persian carpets [9,35].

Table 3: Relative percentage area of the lac-dye chromophores measured at 275nm for the three red tones (light, medium and dark) found in carpets *PD76 (Medallion carpet), PD77 (Benguiat Prayer Rug)* e *PD78 (Duff Prayer Rug)*. For more details see Appendix IV.

Red hue CIELab (L*; a*; b*)	**Laccaic acids (%)** C R_t 16.37 $\lambda_{máx}$ 494	E R_t 16.46 $\lambda_{máx}$ 494	B R_t 19.72 $\lambda_{máx}$ 490	A R_t 20.10 $\lambda_{máx}$ 496	**Unidentified compounds (%)** R_t **C1:**25.80 **C2:**26.30 $\lambda_{máx}$ **C1:**432 **C2:**462	**Mordant (mg)/wool (g)** Average
Red samples – Medallion Carpet (PD76)						
Light **L*33.88±1.31; a*9.37±0.65; b*10.78±0.47**	11-66	12-66	1-5	27-45	1-3	8.6
Medium **L*26.77±0.01; a*11.68±0.07;b*6.28±0.02**	10-33	8-33	7-10	44-70	1-2	4.4
Dark **L*23.64±0.35; a*13.87±0.54; b*5.94±0.03**	13-49	7-23	5-10	44-71	1-6	8.5
Red samples – Benguiat Prayer Rug (PD77)						
Light	3-6	1-17	5-6	71-76	3-7	1.9
Medium	2	13-15	5-6	72-74	5	3.6
Dark **L*20.80±0.24; a*17.08±0.07;b*6.07±0.09**	2-3	8-14	5-10	53-78	1-7	3.3
Pink samples						
L*33.39±0.86; a*6.33±0.26; b*12.38±0.27	5-14	14	13-17	62-63	6-7	2.1
Red samples – Duff Prayer Rug (PD78)						
Dark	18-52	6-43	4-6	52-65	1	2.2

These results suggest that the three different red hues observed in the *Benguiat* Rug (PD77) reflect diverse mordant concentrations in the pre-mordant bath, and are possibly related to the number of occasions or length of time the textile fibres were immersed in the dye-bath. Furthermore, the difference in the three red hues does not appear to be due to the effect of prolonged light exposure, which, in the other hand, does appear to be responsible for generalized fading across the entire surface area of the carpets.

The pink colour observed in the *Benguiat* Rug (PD77) was also obtained with lac-dye and an alum mordant. The elution profiles of the pink and red textile samples are similar; and it is possible to identify the laccaic acids A and B, C and E. However, in the pink samples analyzed by HPLC-DAD, the C and E laccaic acids are co-eluted. As expected, the pink samples were dyed with lesser amounts of lac-dye than the darker red samples, approximately 6 times less. The amount of aluminium

ion is comparable to the *light red hue* in the *Benguiat* Rug (PD77). For more details see appendix IV, table IV.2.

6.2.2. Blues

The blues in the two prayer rugs are present in the borders of the cartouches, arabesque motifs, or irregularly-shaped areas that fill the upper corners of the *Benguiat* Rug. They are also found in the central medallion and arabesque motifs in the field in the Medallion Carpet.

In all three carpets, several hues of blue (*light, medium* and *dark blue*) with different *lightness* and *chromatic* coordinate values (L) were observed as reported above for the reds. The main difference is observed in the yellow component. For example, some blue hues have a significant value for the yellow component (b* around 7-11), and as a result are more greenish.

Nevertheless, indigo was identified in all the blue samples analysed (total of 26), detected by the presence of indigotin (figure 15) as the main chromophore, eluted at 24.85 min with a λ_{max}= 610 nm. In the darker blue tones in the Medallion Carpet, a higher amount of indigotin was present, approximately 35 times in comparison to lighter tones. For more details see appendix IV, table IV.3.

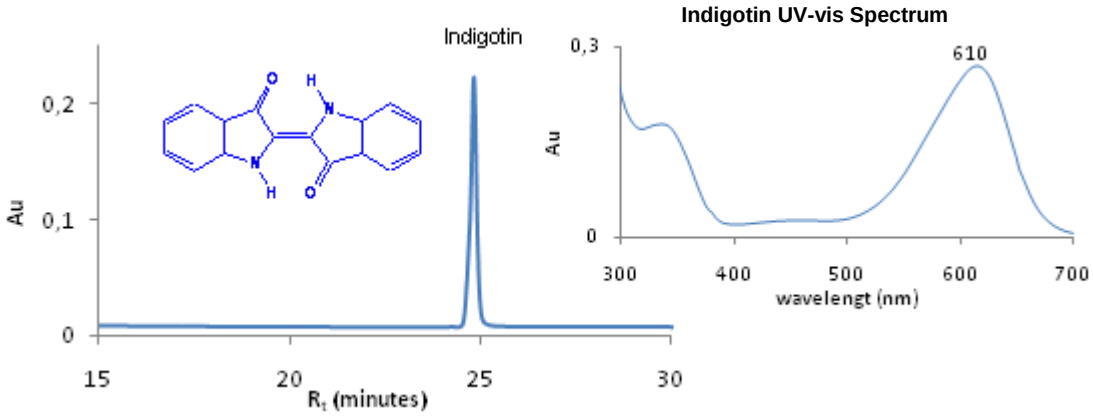


Figure 15: HPLC-DAD chromatogram acquired at 610 nm of a blue textile sample from *Duff* Rug, were it is possible to identify the main chromophore of indigo, indigotin.

Although at this point it is not possible to identify the exact plant dye source as only indigotin chromophore is captured by the fibres during the dyeing process [12,36]. Nevertheless, *Indigofera spp.* is known to have been largely used in the Middle East, Iran, Turkey and India, as it was locally produced [12,18]. The different hues observed in the blue colours are probably related mainly to the variable conditions of the dye bath, i.e. water temperature, rapidity of oxidation, length of immersion time [12,36].

6.2.3. Yellows

The yellows are only present in the two prayer rugs in very small motifs, such as flowers, and hence it was not possible to perform colorimetric measurements.

All the yellow samples (total of 10) analysed by HPLC-DAD and MS (total of 2) revealed the presence of luteolin-7-*O*-Gl (R_t= 18.30 min., λ_{max}=349nm, $[M-H]^-$= 447) as the main chromophore (>85%), apigenin-7-*O*-Gl with a R_t= 19.35 min., λ_{max}= 335nm and $[M-H]^-$ = 431, (<5%) and luteolin with a R_t= 21.40, λ_{max}= 349 nm and $[M-H]^-$ = 285, (<7%) (figure 16). In vestigial amounts (<1%), the presence of a flavonoid di-*O*-glucoside was detected, with a R_t= 17.30 min., λ_{max}= 345nm and $[M-H]^-$ =609; and a luteolin-di-*O*-Glucoside with a R_t=17.80, λ_{max}= 343nm and $[M-H]^-$=579. For more details see appendix IV, table IV.4.

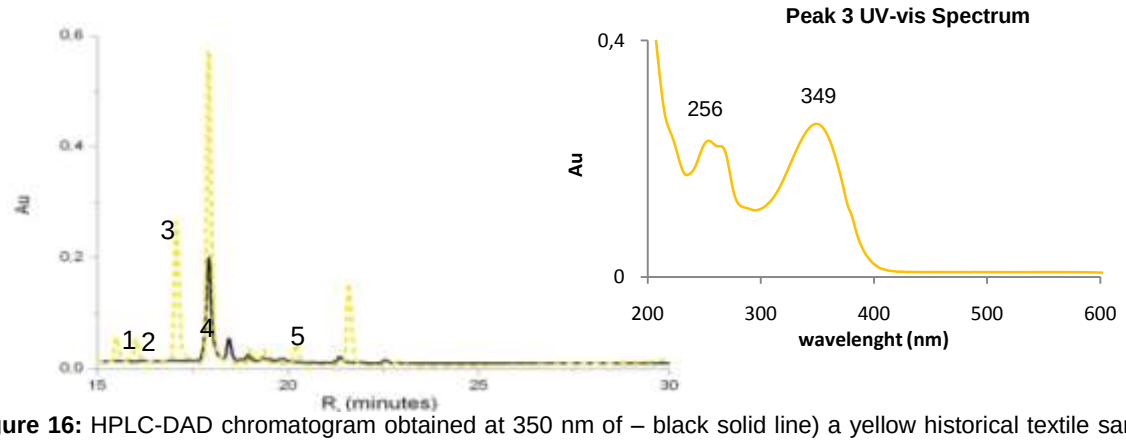


Figure 16: HPLC-DAD chromatogram obtained at 350 nm of – black solid line) a yellow historical textile sample from PD78 prayer rug extracted with H_2O: CH_3OH: H_2O/ $HClO_4$ (50:20:30, v/v/v): (1) Flavonoid di-O-glucoside [M-H]-=609; (2) Luteolin-di-*O*-Glucoside [M-H]- = 579, (3) Luteolin-7-O-glucoside [M-H]-=447, (4) Apigenin glucoside[M-H]-=431, (5) Luteolin [M-H]-=285; yellow dashed line) weld (Reseda luteola L.) extracted with water. The major chromophores are the same of the yellow historical textile sample.

These yellow chromophores can be found in weld (*Reseda luteola* L.), one of the most reported plant in the literature for yellow colours. However, the elution profile reported in (figure 16 - solid line) is slightly different from weld (figure 16 - dotted line) and the utilization of other similar glycosylated dye-plant cannot be excluded. Chromatograms obtained from previous analyses of Persian carpets, with animals and vine scrolls (16th century), and 'Indo-Persian designs' (17th century) in Portuguese collection revealed the same elution profile as for the Guimarães carpets [8-9]. Usually yellow dyes were obtained from local plants, and thus it seems very likely that the Guimarães carpets were produced in the same geographical area as those purchased by Portuguese merchants, possibly southern and central Iran. In all these studies, the yellow dye were also applied with alum mordant [9,34].

In other examples cited in the literature, in which aggressive extraction methods were applied, and as a consequence only luteolin was detected [10,11,27], it is also possible that a similar dye plant was used. However, this can only be confirmed through re-analysis of these historical textiles.

6.2.4. Oranges

The oranges are found only in main border and field of the two prayer rugs, and three hues were noted in the *Duff* Rug in the interlocking hexagons in the field, which have distinct *lightness* and red chromatic coordinate values, table 5.

Table 5: Average relative percentages of different chromophores found in the three orange tones (light, medium e dark) from prayer rugs. Yellow chromophores: (1) Luteolin-7-*O*-glucoside, (2) Apigenin-7-*O*-glucoside, (3) Luteolin; Red chromophores: (4) Alizarin, (5) Purpurin. For more details see Appendix IV, table IV.5.

Red hue CIELab (L*; a*; b*)	**Orange chromophores (%)**					**Mordant (mg)/wool (g)** Average **Al^{3+}**
	1 R_t 18.30 $\lambda_{máx}$ 349	**2** R_t 19.35 $\lambda_{máx}$ 335	**3** R_t 21.40 $\lambda_{máx}$ 349	**4** R_t 23.47 $\lambda_{máx}$ 430	**5** R_t 26.15 $\lambda_{máx}$ 480	
Orange samples – Benguiat Prayer Rug PD77						
Dark **L*** 29.18±0.16; **a*** 11.17±0.08; **b*** 15.51±0.11	55-62	2-6	8-9	7-24	5-7	2.7
Orange samples – Duff Prayer Rug PD78						
Light **L*** 38.13±0.15; **a*** 6.11±0.09; **b*** 18.81±0.16	57-61	1-7	25-30	3-16	0	2.7
Medium I **L*** 36.89±0.83; **a*** 8.41±0.30; **b*** 16.65±0.40	68-76	2-4	16-14	1-16		-
Medium II **L*** 34.26±1.60; **a*** 13.76±0.49; **b*** 18.68±0.61	66	0	7	7		2.3

The analyses performed (total of 13 samples) on the three orange hues revealed a mixture of yellow-dye reported previously, rich in luteolin-7-*O*-Gl (>50%), with red madder (>30%), which was applied to the fibres with alum mordant. It was also possible to identify the major chromophores of madder (probably *Rubia tinctorium*), namely alizarin with R_t= 23.47minutes and λ_{max}= 430nm and the vestigial presence of purpurin (less than 10%) with a R_t= 26.15 minutes and λ_{max}= 480nm (figure 17).

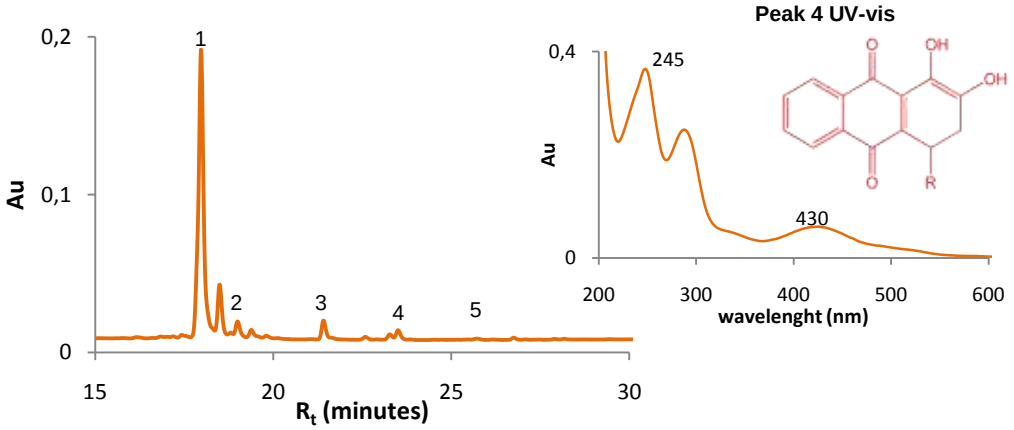


Figure 17: HPLC-DAD chromatogram of the chromophores for orange colours measured at 385 nm, for *PD77* and *PD78* prayer rugs. **Yellow chromophores -** (1) Luteolin-7-*O*-glucoside, (2) Apigenin-7-*O*-glucoside, (3) Luteolin; **Red chromophores** - (4) Alizarin, (5) Purpurin. For more details see Appendix III.

6.2.5. Greens

Greens were identified in both the field and main borders in the three carpets, with a considerable variety of hues, particularly in the *Duff* Rug which contains four different hues.

The greens were obtained with a mixture of luteolin glycosides and indigotin chromophores (a total of 21 samples were analysed by HPLC-DAD, see appendix IV, table IV.6).

In the different hues analysed, it was possible to distinguish luteolin-7-*O*-Gl (>40%) and indigotin (>50%) as the main chromophores, probably derived from the same yellow and blue sources, as reported above (table 6). Furthermore apigenin-7-O-Gl (< 3%) and luteolin (<5%) were also identified as minor chromophores. In the *Duff* Rug (PD78), there is a higher relative percentage of the yellow dye than observed in the others carpets, which is also reflected in a higher overall b* value in the colorimetric measurements (see table 6). Finally, in order to fix the yellow source, an alum mordant bath was applied.

Table 6: Average relative percentages of different chromophores found in the green tones (*light, medium* and *dark*) found in all Guimarães carpets. Yellow chromophores: (1) Luteolin-7-*O*-glucoside, (2) Apigenin-7-*O*-glucoside, (3) Luteolin; Blue chromophore (4) Indigotin. For more details see Appendix IV.

Red hue **CIELab (L*; a*; b*)**	**Green chromophores (%)** **1** R_t 18.30 $\lambda_{máx}$ 349	**2** R_t 19.35 $\lambda_{máx}$ 335	**3** R_t 21.40 $\lambda_{máx}$ 349	**4** R_t 24.85 $\lambda_{máx}$ 625	**Mordant (mg)/wool (g)** Average **Al^{3+}**
Green samples – Medallion Carpet PD76					
Medium II **L***32.21±0.04; **a*** -2.28±0.17; **b***10.96±0.13	25-64	1-2	1-4	31-76	3.9
Green samples – Benguiat Prayer Rug PD77					
Light II **L***34.22±0.18; **a*** 0.06±0.18;**; b*** 13.58±0.26	30-58	1-5	1-4	37-70	1.7
Dark **L***26.84±0.34;**a*** -1.88±0.29; **b*** 13.26±0.53	27-60	1	2	40-71	3.3
Green samples – Duff Prayer Rug PD78					
Light I **L***40.35±0.25; **a***0.93±0.01; **b***13.55±0.15	68-79	3-5	4-12	12-17	-
Medium I **L***34.26±1.60; **a***13.76±0.49; **b***18.68±0.61	34-62	0	4-15	32-49	3.7
Medium II **L***33.56±0.16; **a***-5.24±0.15;**b***6.74±0.79	68-76	2-4	16-14	1-16	-

6.2.6. Browns

Browns occurs in all three carpets (a total of 29 samples), with different hues (*light, medium* and *dark*), in the main border and field. In the Medallion Carpet (PD76), the presence of ellagic acid was detected, at R_t= 18.54min and λ_{max}= 366nm (figure 18), and not juglone, as reported in other Persian carpets (18), suggesting that a dye source rich in tannins was used.

In the prayer rugs, after several dye extractions using both soft extraction and aggressive methods, only colourless compounds were identified (figure 19). It is possible that natural wool with an iron mordant was used, or condensed tannins were applied (which are not included in the HPLC-DAD database) with an iron mordant. Nevertheless, the results suggest that darker hues are obtained with a higher amount of iron, than the lighter tones (consult table IV.6, Appendix IV).

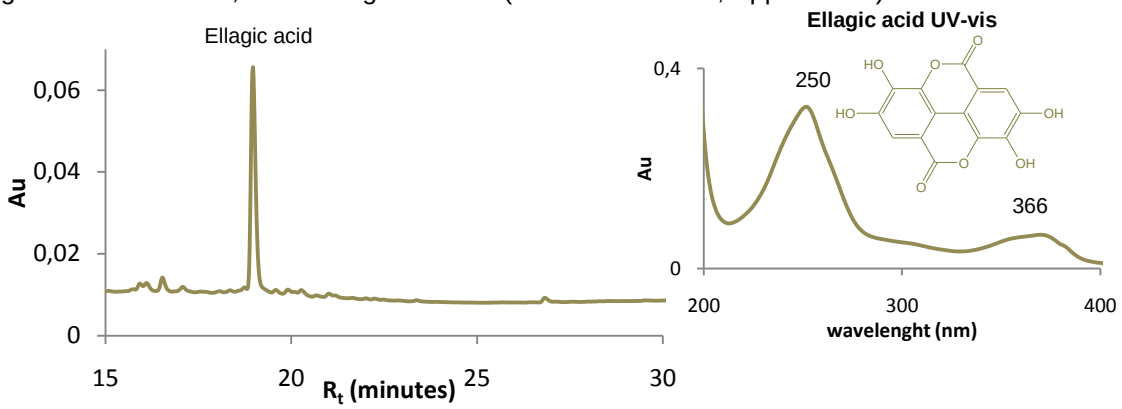


Figure 18: HPLC-DAD chromatogram obtained at 366 nm for brown historical textile from Medallion Carpet where it is possible to identify ellagic acid, R_t= 18.54min, $\lambda_{máx}$ 366.

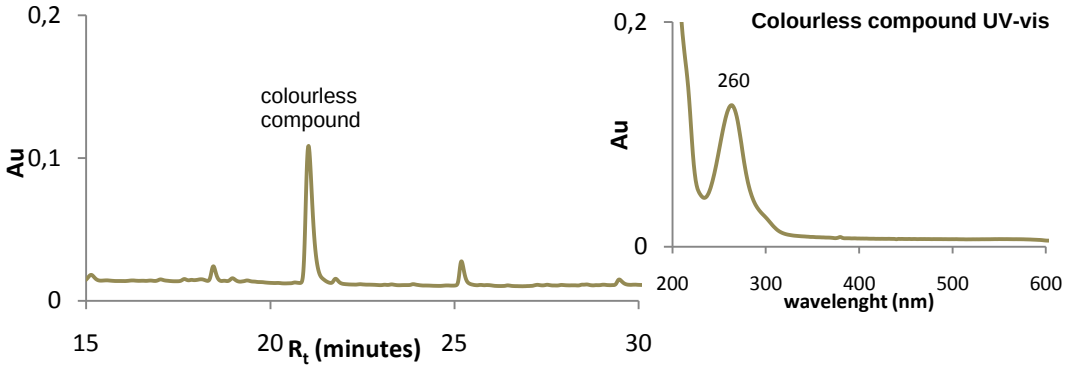


Figure 19: HPLC-DAD chromatogram obtained at 275 nm for brown historical textile samples from *Benguiat* carpet, where it is possible to observe colorless unidentified compounds.

6.2.7. Beiges

Beiges were identified in the three carpets in the central field and border areas, and colorimetric measurements were taken. For more details see appendix IV, table IV.7.

The HPLC-DAD chromatogram of beige samples (a total of 18 samples) revealed the presence of colourless compounds, at R_t=21.03min and λ_{max}= 265nm (figure 20). The presence of juglone chromophores was not identified, as reported for other Persian carpets [11]. The beige colours were obtained using natural wool as reported elsewhere for classical Persian carpets [8,9].

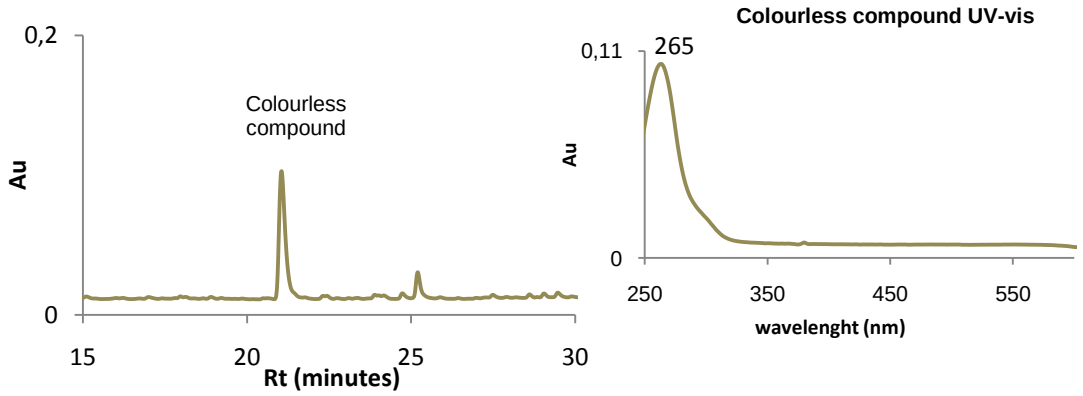


Figure 20: HPLC-DAD chromatogram obtained at 275 nm for beige historical textile samples from rug *PD78*, where it is possible to identify colorless unidentified compounds.

To summarize, the results confirm the use of natural dyes, and complete absence of synthetic dyes which could offer evidence of 19th- or 20th-century production. Furthermore, while the reds were obtained with lac-dye, the red source for the oranges is entirely different, and reflects the use of madder with a luteolin-based yellow. For the blues and greens, indigo was consistently present, with probably the same yellow added to the greens. Regarding the use of mordants, alum was found to be used to fix the dyes to the fibres in almost of all of the colours, with the exception of blues, browns and beiges, which were obtained using indigo (vat-dye), tannins and natural un-dyed wool, respectively.

6.3. Lac-dye and the HPLC-DAD Library

As mentioned above, the presence of lac-dye and the precise identification of its taxonomic and geographic source can provide potentially important evidence for provenance determination of historical textiles. A reference HPLC-DAD library was prepared to narrowing the lac-dye provenance as dyestuff identification afford information on trade routes, as well as for the provenance and past restoration of a historical textile. Therefore, in order to establish accurate species identification on textiles, it will be necessary to perform a more rigorous taxonomic study of the wide variety of insect species known to produce lac dye (over 20), followed by chemical analysis and comparison with a wider range of carpets.

6.3.1. Samples preparation

Prior to the analysis of unidentified historical samples with HPLC-DAD, several HPLC-DAD analyses were performed on known lac-dye species identified by entomologists: **(b)** 1 sample given by Dominic Cardon; and **(c)** 6 samples supplied by Penny Gullan.

Further analyses were conducted on unidentified historical lac-dye species: **(a)** 76 samples from different places (India, Australia, Taiwan, Vietnam, Laos, Singapore, Pakistan, Bangladesh Sri-Lanka and others), from the 19th and 20th centuries, provided by Royal Botanic Garden at Kew (London).

6.3.2. Lac-dye insect sources

All the lac-dye insect sources were extracted in 100% H_2O. However, better HPLC separations were achieved with H_2O: CH_3OH: H_2O/ $HClO_4$, pH=2 (50:20:30, v/v/v) in the final dye extract, than using H_2O or H_2O: CH_3OH (50:50) (figure 21) [6] and this result was applied in all the insect and textile specimens' preparations.

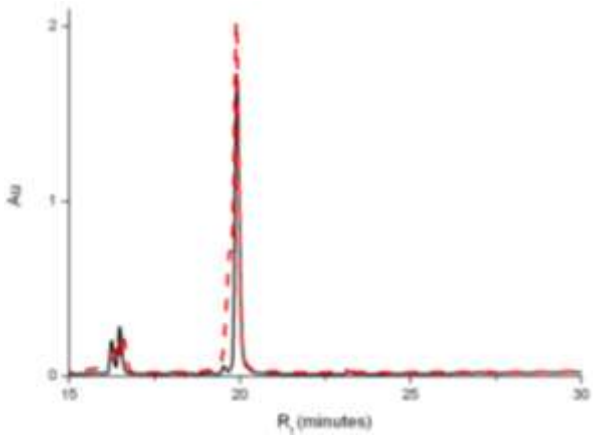


Figure 21: HPLC-DAD chromatogram acquired at 275 nm. **Red dashed line)** lac-dye extract from *Kerria lacca* insect from Taiwan with 100% H_2O and **black solid line)** lac-dye extract from *Kerria lacca* insect from Taiwan H_2O: CH_3OH: H_2O/ $HClO_4$, pH=2 (50:20:30, v/v/v).

6.3.3. Historical red-dyed textiles

As reported in the literature, the maximum amount of laccaic acid A extracted from dyed fibres has been obtained with oxalic acid. The results from performed tests revealed that oxalic acid extracted almost the same amount of laccaic acid as TFA solution in agreement with [37]. The oxalic acid method showed better chromatograms' resolution than extraction with other methods, with a higher separation of laccaic acid A and B, and, consequently, it was selected for all the fibres' extractions.

6.3.4. *Paratachardina* and *Kerria* genera – reference insect sources

The insect specimens which were identified with accurate taxonomic studies and supplied by the entomologist Penny Gullan (6 samples) for *Paratachardina* and *Kerria* genera, displayed different HPLC elution profiles, enabling the distinction of both genera, figure 22.

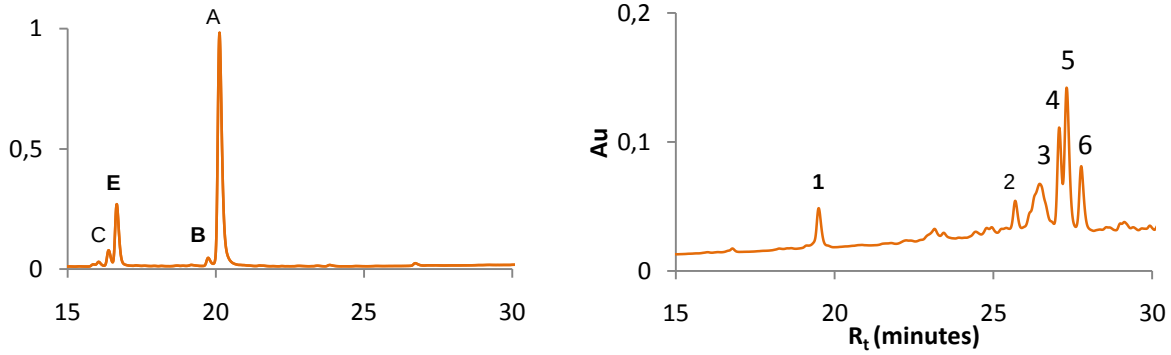


Figure 22: HPLC-DAD chromatogram obtained at 275 nm for: a) *Kerria sp.* from India and b) *Paratachardina xxxx* from India. Both samples were extracted with 100% water.

In the *Paratachardina* specimens, analysed for the first time by HPLC-DAD, unknown compounds were identified, **1** (R_t=19.44 λ_{max}= 495), **2** (R_t=25.62 λ_{max}= 465), **3** (R_t=26.33 λ_{max}= 465), **4** (R_t=26.99 λ_{max}= 465), **5** (R_t=27.21 λ_{max}= 300) and **6** (R_t=27.70 λ_{max}= 300). Laccaic acids were identified in small amounts in these specimens, excluding the utilization of *Paratachardina spp.* as the source of lac-dye. As expected in the *kerria* species, it were identified with LC-MS analysis the red chromophores of the lac-dye and already mentioned in section 6.2.1. The results obtained, were in agreement with the literature [26,34].

6.3.3. Lac-dye specimens from the collection of the Royal Botanical Garden at Kew – unidentified historical lac-dye species

The insect specimens from the Kew Garden Collection, collected in the 19th century, were labeled as *sticklac* (34%), *shellac* (12%), *grain/seed lac* (14%), *lac* (12%) and other types (20%). These specimens are from different geographical regions (India, Australia, Taiwan, Vietnam, Laos, Singapore, Pakistan, Bangladesh Sri-Lanka and others), as well as from different host plants (*Ficus spp.*, *Schleichera spp.*, *Butea spp.*, *Zizyphus spp. and Shorea sp.*).

Although the 76 samples analyzed by HPLC-DAD, displayed very heterogeneous chromatographic profiles, it was possible to obtain three reasonable clusters with PCA analysis, which had three different compositions: ***Cluster I)*** comprised by samples rich in laccaic acids that were designated as lac-dye (30%), ***Cluster II)*** samples composed by a mixture of laccaic acids and yellowish compounds from the resinous lac matter (named as a mixture of lac-dye and resin) (29%), ***Cluster III)*** samples composed only by the yellowish compounds from the resionous lac matter (named resin) (41%) (figure 23). For more details see appendices V and VI.

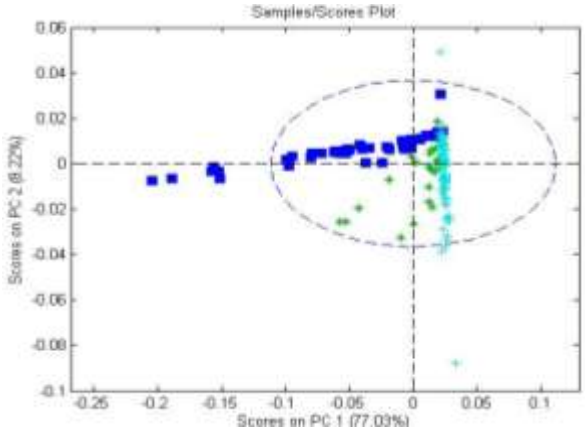


Figure 23: PCA scores obtained from mean centered Kerridae chromatograms acquired at 275nm: ***Cluster I)*** lac-dye (blue squares), ***Cluster II)*** a mixture of lac-dye and resin (green stars), and ***Cluster III)*** resin (blue stars).

All the samples present in *cluster I* were labeled previously by Kew Garden as *lac type*. However, the samples 73-76, 14, 50, 53, 57 and 63 also labeled as a *lac type* were indeed composed by a mixture of laccaic acids and/or yellowish compounds from the resinous lac matter. Therefore, these samples were not grouped in cluster I, but in clusters II and III. In *cluster II and III* were grouped only samples previously labeled by Kew Garden as *sticklac shellac grain/seed lac* types.

The samples grouped in *cluster I*, rich in laccaic acids were submitted to a PCA analysis in order to distinguish the specimens according to its local of provenance. Good relations were established with samples from Pakistan, East Indies, Laos, Mirtarpur, Bangladesh, Sri Lanka, Vietnam, Australia, Singapore, and Thailand, figure 24. However in samples from India there was a considerable variation and they had to be excluded from this analysis. This variation in the results from India reflects the importance of having reliable insect samples submitted to accurate taxonomic species characterization.

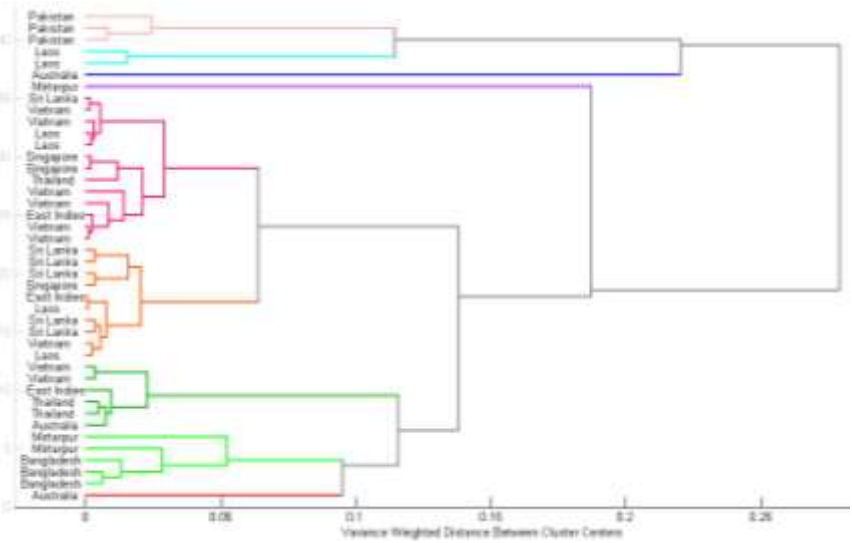


Figure 24: Dendrogram of lac dye samples from Pakistan, East Indies, Laos, Mirtarpur, Bangladesh, Sri Lanka, Vietnam, Australia, Singapore, and Thailand.

Nevertheless, the textile red samples from the Guimarães rugs appear to be more similar to insect samples from Pakistan (see appendix VII).

To summarize, it is possible to distinguish both genera, *Kerria and Paratarchadina* referred to in the literature as the source of lac and apparently only the Kerria genera has sufficient red dye to be used in textiles dyeing. In the Kew Garden collection it was possible to discriminate the samples according to their composition and eventually their provenance. In order to establish rigorous similarities between lac-dye red textiles and for identifying insect groups according to their provenance and host plants it will be necessary to have reliable insect samples submitted to molecular taxonomic studies.

6.4. Metal threads

Microscopic analyses indicated that the metal threads used in the three Guimarães carpets comprise a metal strip wound (S-direction) around a yellow silk core, so that the edges of the tape abut but do not overlap. This allows the colour of the substrate – in this case yellow silk -to play a greater role in the final visual effect, enhancing the golden sheen of the thread (figures 1 and 2, appendix VIII). This technique gives a smooth, as opposed to a rough, irregular surface to the thread [38]. Measurements for the metal strip for the Benguiat Rug (c. 0.23 mm wide and 0.015 mm thick) are in accordance with previous results reported for ‘Salting’ carpets (ca. 0.25 mm wide) [38].

XRF and SEM analyses demonstrate that the metal lamina of the Guimarães threads is composed mainly of silver (Ag), gold (Au) and copper (Cu) (figures 2 and 3, appendix VIII). In the prayer rugs, Ag was major element (circa 80%), followed by Au (circa 10%), Cu (circa 2%), with vestigial amounts of tin (Sn) and lead (Pb). Previous results for the ‘Saltings’, however, identified the presence of Pb, but not Sn [38].

The SEM analyses also show considerable degradation of the exterior surface, particularly in places where sulphur (S) and chlorine (Cl) were identified and probably the result of Ag corrosion products (figures 5 and 6, appendix VIII). By contrast, the inside of the strip, which is in direct contact with the silk core, and therefore protected from contact with environmental conditions, and is better preserved. Analyses here revealed the presence of Au in higher amounts, in contrast to the exterior where it presumably had been worn away.

It is difficult to establish from these analyses with certainty how the strips were made, but it is possible to identify the presence of a silver strip with a layer of gold. This is consistent with the method previously proposed by Eiland for the 'Saltings' and 'Polonaise' carpets, in which a silver sheet is covered with a thin layer of mercury (Hg) to create an amalgam for gilding, and then forged to a very thin gauge and hand-cut [38]. However, confirming the use of this technique requires further research.

6.5. AMS Radiocarbon dating

Finally, AMS Radiocarbon dating was used to establish the age of the Guimarães carpets; as six prayer carpets had been analysed previously, it was decided to concentrate on the extremely important and rediscovered Medallion Carpet.

The results point, with 95% confidence, to **1485-1604** (59,25%) Cal date and **1606-1668** (35,95%) Cal date as calibrated ages (figure 25).

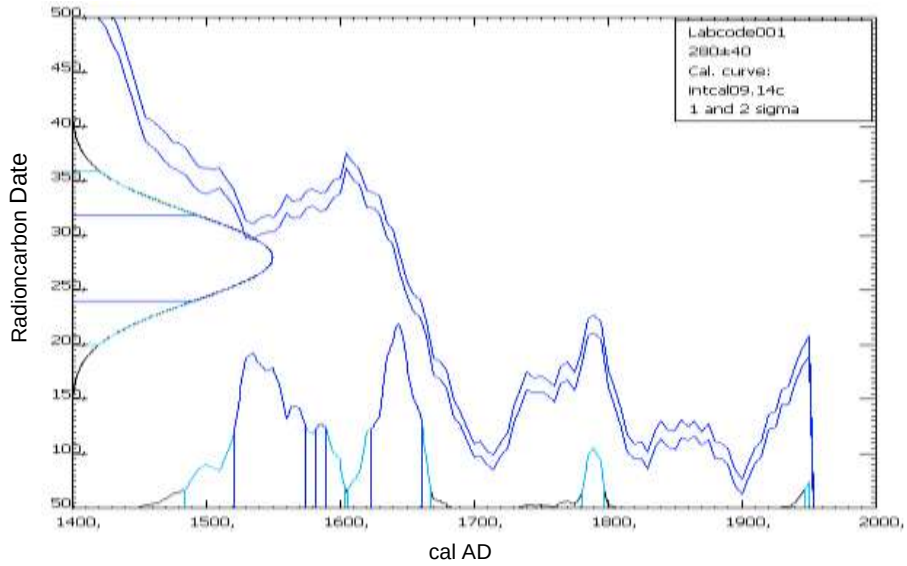


Figure 25: Radiocarbon Date versus Calibrated Date

Comparison of these results with other data published for Persian carpets (see appendix IX), confirms that this BP age is in line with those observed for other 'Salting' carpets (figure 26), as well as an important fragment related to the famous Ardebil carpet (which has an inscribed date confirming its manufacture in the year 1539-1540) [1].

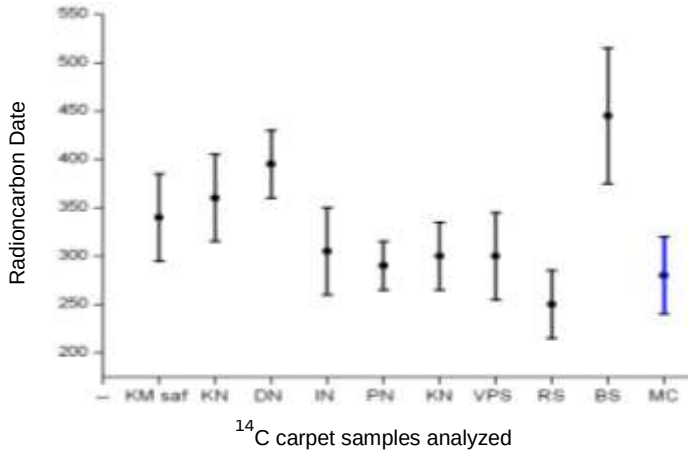


Figure 26: Textile samples from Persian carpets and fragments analysed by C14: *Khatif Muslihidd saf* (KM), *Kelekian niche rug* (KN), *Darmstadt niche rug* (DN), *Indjoudjian niche rug* (IN), *Paris niche rug* (PN), *Karlsruhe niche rug* (KN), *Von Pannwitz ´Salting` rug* (VPS), *Rothschild ´Salting` rug* (RS), *Benguiat ´Salting` rug* (BS), *Medallion Carpet* (MC)(blue line).

These results are extremely important as they confirm that the Medallion Carpet can now be associated with confidence to the period between the end of the 15th to first half of the 17th century, and that a 19th-century date can be excluded definitively.

7. CONCLUSIONS

The publication of the 'Salting' carpets in 1999 represented an important step in presenting the first corpus of identified carpets. However, doubts remained about their precise date and provenance. The rediscovery of two prayer carpets in Guimarães, and a third Medallion carpet which was not included in the corpus in 1999, offered a significant opportunity for returning to these questions using an interdisciplinary approach and the application of a wide range of analytical techniques.

The dyes identified in the three Guimarães carpets point consistently to an Iranian provenance. Use of lac-dye in the reds and pinks, but madder (and not lac) in the oranges, is consistent with other results for carpets associated with Iran in Portuguese collections. Together, these studies reinforce the notion that this palette is a classical characteristic of Persian (and not Turkish) dyeing practices, especially as the Medallion Carpet has an inscription written in Persian.

Through the development of the HPLC-DAD database for lac-dye, it was possible to distinguish Kerria and Paratachadina genera, for the first time, and to confirm that only Kerria has sufficient red-dye chromophores to be used for dyeing textiles. It was possible to discriminate the samples from the Kew Garden collection, according to their composition and eventually their origin. The red textile samples from the Guimarães rugs appear to be more similar to insect samples from Pakistan, in close proximity to Iran. Further development of the database is required to establish more rigorous comparisons between historical textiles and lac-insect sources. This can only be achieved with the collaboration of entomologists, and the identification of reliable Kerria insect samples which have been submitted previously to molecular taxonomic studies, and for which their precise origin and host plants are well documented.

For the browns and yellows in the carpets, tannins and probably weld, respectively, were found. As these are usually obtained from local sources, further research could offer additional information for narrowing the provenance of the carpets. In this respect, it is noteworthy that the brown used in the Medallion Carpet is comprised of ellagic acid, not encountered in the Guimarães prayer rugs or other 'Saltings' analysed [11], but previously identified in the 'small silk Kashan' in the Museu Nacional de Machado Castro [20]. This latter carpet can be dated to the second half of the 16th century and represents the height of Safavid carpet production. The presence of this compound draws attention to the importance of further study of the browns in Islamic carpets, something which has rarely been considered in the past, owing to the apparent insignificance of this colour to the overall visual effect. No significant difference, however, was observed between the three carpets in relation to the mordants used, which it was hoped would be a distinguishing feature of provenance. The *abrash* observed reflects differences in dye procedures, and the concentration of alum present, and not degradation for light exposure.

As for the chronology of the carpets, all the data presented here supports an early date, such as the exclusive use of natural dyes and the non-industrial construction techniques used to make the metal threads, which have also been identified in other classical Persian carpets. Moreover, as "a carpet can only be as old as its design" [10], all of the stylistic features are also consistent with Safavid

art. Although these few elements are significant, they are not necessarily conclusive, of course, and only the AMS Radiocarbon results for Medallion Carpet confirms a more precise date between the late 15th and mid-17th century. This result is extremely important, as it confirms that it is an authentic Safavid rug, as expected from its extraordinarily high quality (11.155 knots/dm^2), rarely seen in wool carpets. However, Reed's proposal that the carpet was intended to be placed "under the feet" of the Persian Shah Suleiman I (r. 1666-1694) is not directly confirmed, as the dates of this Shah are slightly outside the parameters of the AMS Radiocarbon results. Instead, a date for the carpet in the 16th century seems more likely, which raises the possibility that it could have been made especially for the Ottoman Sultan Suleyman the Magnificent (r. 1520-1566), and possibly sent in 1556, as originally proposed by Mills and Franses [1]. This proposal, if it can be supported by additional scientific or historical evidence, would make this carpet extremely important and only the second example, besides the Ardebil (V&A), to offer a historical name and related date.

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Three ‘Salting’ carpets discovered in the Palace of the Dukes of Braganza, Portugal
Submitted to the International Conference on Oriental Carpets, ICOC XII, Stockholm, 16-19 June 2011.

APPENDICES

APPENDIX I

Medallion Carpet inscriptions

With its proximity and lofty station, the carpet of regal fortune, which resides upon the earth, can hurl a hundred taunts at the sublime celestial sphere.

Fallen beneath the feet of a monarch and happy that around it are beautiful damsels of paradise with brooms in hand.

Why should this exalted carpet not vie with the zephyr when the day may come when it has its forehead on the foot of a Solomon?

The king of kings resides on a lofty carpet because he is surrounded by victory and triumph through divine grace.

Every evening the celestial sphere becomes a reflection of the gathering of that just king, who possesses on his signet the kingdom of a hundred Solomons through justice.

Source: Professor W. M. Thackston, Harvard University

(Cf. Stanley, R. *Oriental Rugs and Carpets, pleasures and treasures.* London: George Weidenfeld and Nicolson Ltd, (1967))

APPENDIX II

Kerria species found in literature

Species analysed by HPLC-DAD

1. ***Kerria lacca*** (Kerr, 1782)
DISTRIBUTION: **Neotropical**: Guyana [Cocker1893r]. **Oriental**: Bangladesh [Varshn1976]; Burma (=Myanmar) [Varshn1976]; China (Hunan [HuHeWa1992]); India (Andhra Pradesh [Varshn1976], Bihar [Varshn1976], Gujarat [Varshn2000], Karnataka [Varshn1976], Tamil Nadu [JalaluMoSa1999], West Bengal [Varshn1976]); Malaysia [Varshn1997]; Nepal [Varshn1976]; Pakistan [Varshn1976]; Sri Lanka [Varshn1976]; Taiwan [HsiehHw1983]. **Palaearctic**: Azerbaijan [Hadzib1983]; Georgia (Georgia [Hadzib1983, Varshn1997]).

Kerria species never analysed by HPLC-DAD

2. ***Kerria chinensis*** (Varshney, 1966)
DISTRIBUTION: **Oriental:** Bhutan [Varshn1976]; Burma (=Myanmar) [Varshn1976]; India (Assam [Misra1930, Varshn1976], West Bengal [Varshn1976]); Kampuchea (=Cambodia) [Varshn1997]; Nepal [Varshn1976]; Thailand [Takaha1941]; Vietnam [Varshn1997]. Palaearctic: China (Xizang (=Tibet) [Varshn1976]).

3. ***Kerria albizziae*** (Green, 1911)
DISTRIBUTION: **Oriental**: India (Bihar [Ali1967a, Varshn1976], Uttar Pradesh [Varshn1976], West Bengal [Varshn1976]); Sri Lanka [Green1911].

4. ***Kerria brancheata*** (Varshney, 1966)
DISTRIBUTION: **Oriental:** India (Bihar [Varshn1966b, Varshn1976]).

5. ***Kerria chamberlini*** (Varshney, 1966)
DISTRIBUTION: **Oriental**: India (Rajasthan [Varshn1966b, Varshn1976]).

6. ***Kerria ebranchiata*** (Chamberlin, 1923)
DISTRIBUTION: **Oriental**: India [Chambe1923] (Bihar [Ali1967a], Karnataka [Chambe1925JC, Kapur1958]); Pakistan [Varshn1997].

7. ***Kerria greeni*** (Chamberlin, 1923)
DISTRIBUTION: **Oriental**: Hong Kong [SchroePeCo2008]; Philippines (Luzon [Chambe1923, Varshn1976]); Taiwan [Varshn1976]; Thailand [Takaha1941, Varshn1976].

8. ***Kerria indicola*** (Kapur, 1958)
DISTRIBUTION: **Oriental:** India (Bihar [Misra1930, Ali1967a]).

9. ***Kerria javana*** (Chamberlin, 1925)
DISTRIBUTION: **Oriental**: Indonesia (Java [Chambe1925JC]); Malaysia [Varshn1976].

10. ***Kerria mendingonsis*** (Zhang, 1993)
DISTRIBUTION: **Oriental**: China (Yunnan [Zhang1993a]). **Palaearctic**: China [Varshn1997].

11. ***Kerria meridionalis*** (Chamberlin, 1923)
DISTRIBUTION: **Australasian**: Australia [Chambe1923].

12. ***Kerria nagotiensis*** (Mahdihassam, 1923)
DISTRIBUTION: **Oriental**: India (Madhya Pradesh [Mahdih1923, Varshn1976 and Varshn1984b]).

13. ***Kerria nepalensis*** (Varshney, 1976)
DISTRIBUTION: **Oriental**: India (Bihar [Varshn1976]); Nepal [Varshn1976].

14. ***Kerria pusana*** (Misra, 1930)
DISTRIBUTION: **Oriental**: India (Bihar [Misra1930, Varshn1976]).

15. ***Kerria rangoonensis*** (Chamberlin, 1925)
DISTRIBUTION: **Oriental:** Burma (=Myanmar) [Chambe1925JC]; India (Assam [Varshn1976]); Indonesia (Sumatra [Green1930c]).

16. ***Kerria ruralis*** (Wang, Yao, Teiu & Liang, 1982)
DISTRIBUTION: **Oriental**: China (Yunnan [WangYaTe1982]).

17. ***Kerria sharda*** (Mishra & Sushil, 2000)
DISTRIBUTION: **Oriental**: India (Orissa [MishraSu2000]).

18. ***Kerria sindica*** (Mahdihassam, 1923)
DISTRIBUTION: **Oriental**: Pakistan [Kapur1958, Varshn1976].

19. ***Kerria yundanensis*** (Ou & Hong, 1990)
DISTRIBUTION: **Oriental**: China (Yunnan [OuHo1990]).

20. ***Kerria chinesis kydia*** (Varshney, 1966)
DISTRIBUTION: **Oriental**: India (Assam [Misra1930, Kapur1958 and Varshn1976]).

21. ***Kerria communis*** (Mahdihassam, 1923)
DISTRIBUTION: **Oriental**: India (Karnataka [Mahdih1923]).

22. ***Kerria fici fici*** (Green, 1903)
DISTRIBUTION: **Oriental**: India (Bihar [Ali1967a, MishraBhSu1998], Rajasthan [Varshn1976], Tamil Nadu [Varshn1976], Uttar Pradesh [Varshn1976], West Bengal [Varshn1976]); Pakistan [Varshn1997]; Thailand [Varshn1976]. **Palaearctic**: China [Varshn1976].

23. ***Kerria fici jhansiensis*** (Misra, 1930)
DISTRIBUTION: **Oriental**: India (Uttar Pradesh [Misra1930]).

24. ***Kerria mysorensis*** (Mahdihassem, 1923)
DISTRIBUTION: **Oriental**: India (Karnataka [Kapur1958]).

25. ***Kerria lacca takahashii*** (Varshney, 1974)
DISTRIBUTION: **Oriental**: Thailand [Varshn1976].

26. ***Kerria lacca ambigua*** (Misra, 1930)

Source: United States Department of Agriculture – Systematic entomology Laboratory
Compiled in Catalogue Query: http://www.sel.barc.usda.gov/catalogs/kerriida/KerriaAll.htm

APPENDIX III

Experimental Details

1. SOLVENTS

Water from *Millipore Simplicity Simpak* 2, *R* = 18.2MΩ cm (USA), methanol, CH_3OH 99,9%, from *Panreac* (Barcelona, Spain) and perchloric acid from *Riedel-de-Haën* (Seelze, Germany) were applied in all extraction and mobile phase preparation, in dyes analyses performed in HPLC. Formic acid from *Riedel-de-Haën* (Seelze, Germany), acetone, C_3H_6O, from *Aga* (Prior Velho, Portugal), hydrochloric acid from *Pancreac* (Barcelona, Spain); oxalic acid from *BDH* (Poole, England) and TFA from *Riedel-de-Haën* (Seelze, Germany) were used in dyed textile samples extractions solutions. For dyes extraction from blue textile samples, DMF from *Sigma-Aldrich* (Steinheim, Germany) was used. Glycerol from *Sigma-Aldrich* was used to perform optical microscopy.

Aluminium and multielementar (Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Sn, and Zn) standards from *Fluka* (Steinheim, Switzerland), nitric acid from *Merck* (Darmstatt, Germany) and deionizer water were used in all extractions and standards solutions in mordent analysis.

2. OPTICAL MICROSCOPY – Fibers identification

2.1 Historical textile samples

For optical microscopy characterization, 22 fibre samples were selected from each colour, 1 from weft, 1 warp, 1 from safety warp and finally 1 from silk core (metallic thread).

2.2 Sample preparation

Fibre identification was carried out on longitudinal sections; a single fibre was placed between a lamina and a lamella with a small proportion of Glycerol.

2.3 Instrumentation

For fiber analysis was used a Zeiss Axionplan Z optical microscope with a Nikon DXM1200F digital camera.

3. COLORIMETRY – colour measurements

Color coordinate measurements (L*, a*, b* - CIELAB) were taken for the sample-collecting areas, either in front or the back of each rug (total 86) with three measurements for each area, with a portable spectrophotometer *Datacolor International*. Conditions used for measurements were: Xenon lamp with a 22 mm illumination area; 18 mm measurement area D65; 10º of observation angle.

4. HPLC-DAD-MS ANALYSIS – Dyes

HPLC-DAD reference library

4.1 Dyestuffs standards

Several HPLC standards were analyzed, namely apigenin, luteolin, luteolin-7-O-glucoside and luteolin-3'7-di-O-glucoside from *Extrasynthèse* (Genay, France); laccaic acid A from *Wako Pure Chemicak Industries Ltd*, indigo, isatin, purpurin and ellagic acid from Sigma-Aldrich (Steinheim, Germany); juglone, Alizarin from *Kremer* (Aichstetten, Germany). Moreover, analysis from dyes extracts from plants as weld (*Reseda luteola L*.) from *Zecchi* (Florence, Italy) and Asbarg (*D. semibarbatum*) gently provided from Richard Laursen were also preformed.

4.2 Lac-dye insect sources

Prior to the analysis of historical samples with HPLC-DAD, several HPLC-DAD analyses were performed on known lac-dye species identified by entomologists: **(b)** 1 sample given by Dominic Cardon; and **(c)** 6 samples supplied by Penny Gullan.

Further analyses were conducted on unidentified historical lac-dye species: **(a)** 76 samples from different places (India, Australia, Taiwan, Vietnam, Laos, Singapore, Pakistan, Bangladesh Sri-Lanka and others), from 19th and 20th centuries and provided by Royal Botanic Garden at Kew.

4.3 Historical dyed textiles

Analyses were carried out in a total of 180 coloured wool fibres, with 0.3-0.4mg each, collected field and main border of each carpets; namely light red, mid red, dark red, light pink, dark pink, yellow, light orange, mid orange, dark orange, light blue, mid blue, dark blue, light green, mid green, dark green, light brown, mid brown, dark brown, light beige and beige colours from both **Prayer Rugs** (table II.1); and light red, mid red, dark red, light blue, dark blue, green, light brown and dark brown and beige colours from the **Medallion Carpet** (table II.1).

Table II.1: Total of fibers samples analyzed by HPLC-DAD from each rug.

Main Colours	Red		Pink		Yellow		Orange		Green		Blue		Brown		**Beige**	
Area	**field**	**border**	**field**	**border**	**field**	**border**	**field**	**border**	**field**	**border**	**field**	**border**	**field**	**border**	**field**	**border**
	Benguiat Prayer Rug (*PD77*)															
Light	4	-	-	-	-	-	-	-	2	3	2	2	-	-	3	3
Medium	4	-	3	3	1	1	3	3	2	-	4	4	3	3	-	-
Dark	7	3	-	-	-	-	-	-	-	-	2	2	3	3	-	2
Total:	**15**	**3**	**3**	**3**	**1**	**1**	**3**	**3**	**4**	**3**	**8**	**8**	**6**	**6**	**3**	**5**
	Duff Prayer Rug (*PD78*)															
Light	-	-	-	-	-	-	2	2	2	-	3	3	-	3	3	3
Medium	-	-	3	3	2	1	3	3	4	-	-	-	3	3	-	-
Dark	3	3	3	-	-	-	2	-	3	3	2	-	3	3	-	-
Total:	**3**	**3**	**6**	**3**	**2**	**1**	**7**	**5**	**9**	**3**	**5**	**3**	**6**	**9**	**3**	**3**
	Medallion Carpet (*PD76*)															
Light	3	3	-	-	-	-	-	-	-	-	2	-	-	3	-	-
Medium	3	3	-	-	-	-	-	-	2	-	-	-	-	-	-	3
Dark	3	3	-	-	-	-	-	-	-	-	1	-	3	3	-	-
Total:	**9**	**9**	**-**	**-**	**-**	**-**	**-**	**-**	**2**	**-**	**3**	**-**	**3**	**6**	**-**	**3**

4.4 Extraction methods and sample preparation

Prior to the analysis of180 coloured historical wool textile samples and 174 historical lac-dye sources HPLC-DAD analysis; several tests were performed on 30 lac-dyed wool fibre references, 0.3 mg each, in order to evaluate the best extraction method and textile samples preparations. Historical lac-dye sources were tested with several solvent proportions in lac-dye brand from *Kremer* extract: **(a)** H_2O; **(b)** H_2O: CH_3OH (90:10); **(c)** H_2O: CH_3OH (70:30); **(d)** H_2O: CH_3OH: $H_2O/HCLO_4$, pH=2 (70:30:20). Owing to their heterogeneity, three samples were removed from different areas of same source (interior, middle and exterior), circa 0.1mg each, in order to obtain representative results for comparison and try to characterize their heterogeneity; Red historical samples from carpets were compared with Kerridae historical samples using HPLC-DAD and chemometrics studies to identify the insect species involved.

Lac-dyed wool fibre reference samples were obtained from a wool skein dyed with lac-dye brand from *Kremer*. Dyeing and mordanting procedures were adapted from lac dyeing recipes: 1 g wool was

washed with soap and pre-mordanted with alum and tartar cream at 80ºC; and dyed with 1 g/L extracted lac-dye from *Kremer* with T=80ºC, during 30-40 min, at pH=2-3 and constant mechanical agitation [9,12].

Four different extraction solutions were undertaken on the Lac-dyed wool fiber references, to optimize the best extraction method for the lac dyestuff: **(a)** Formic acid method - HCOOH: CH_3OH (5: 95, v/v) [40]; **(b)** HCl method - HCl 37%: CH_3OH: H_2O (2:1:1, v/v/v) [40]; **(c)** Oxalic acid method - $C_2O_4H_2$ (0,2M): C_3H_6O: CH_3OH: H_2O (0,1: 3: 3: 4, v/v/v/v) [41]; and **(d)** TFA method **-** TFA 2M [24]. Blue samples were extracted with DMF as reported in literature [4,8,9,31].

The analyses were performed in six replicates, for each extraction method. Fiber' samples, with circa 0,2-0,3 mg, collected from the red cochineal-dyed silk fiber references were extracted in 400 µl extraction solution, at 60ºC for 30 min, with constant mechanical agitation. After extraction, each extract was dried in a vacuum system, where the resulting dry residues were reconstituted with H_2O: CH_3OH: $H_2O/HClO_4$, pH=2 (50:20:30, v/v/v).

4.5 Instrumentation

HPLC-DAD

The dye analyses were carried out in a *Thermofinnigan Surveyor* HPLC-DAD system with a *Thermofinnigan Surveyor PDA 5* diode-array detector (Thermofinnigan, USA), an autosampler and a pump. The samples' separations were performed in a reversed-phase column, Eclipse Plus C18 with 100Å – 5 µm particle size and 150 x 2,1 mm dimensions, with a flow rate of 0.5 ml/min at 35ºC constant temperature, and were injected onto the column by a Rheodyne injector with a 25 µL loop. A solvent gradient of A-pure methanol and B-0,3% (v/v) aqueous perchloric acid (v/v) adapted from [41] was applied to the insect extracts and textiles: 0-2 min 7A:93B isocratic, 8 min 15A:85B linear, 25 min 75A:25B linear, 27 min 80A:20B linear, 29 min 95A:5B linear, and 33-40 min 7A:93B isocratic.

HPLC-MS

The LC-ESI-MS analysis were performed with a ProStar 410 autosampler, two 210-LC chromatograph pumps, a ProStar 335 diode array detector and a 500-MS ion trap mass spectrometer with an electrospray ionisation (ESI) ion source (Varian Inc., Palo Alto, CA, USA). Data acquisition and processing were performed using Varian MS Control 6.9 software. . The separations were carried out using a Zorbax Eclipse Plus (Agilent, USA) with 5 µm particle size column (2.1 mm x 150 mm). The column was kept at controlled temperature (30ºC). The samples were injected onto the column via a Rheodyne injector with a 20 µL loop. The mobile phase was delivered at a flow rate of 200 µL/min using a 2-min isocratic elution with 5% acetonitrile in 0.1% aqueous formic acid, followed by a 30-min linear gradient from 5-60% acetonitrile, a 5-min linear gradient to 100% acetonitrile. The mass spectrometer was operated in negative ESI mode; the optimized operating parameters were: ion spray voltage, -4.8 kV; capillary voltage, 60 V; and RF loading, 80%. Nitrogen was used as the nebulizing and drying gas, at pressures of 35 and 10 psi, respectively; the drying gas temperature was 350°C.

5. PCA – Lac-dye insect sources and historical red-dyed textiles (Statistical analysis of data)

Given the multivariate nature of the lac-dye insect sources and historical red-dyed textiles samples' chromatograms, multivariate data analysis was required in order to analyse samples. Principal

components analysis (PCA) was selected to perform a similarity analysis [42]. PCA results were analysed on the basis of the principal components retaining the major part of the original chromatogram data variance. Since principal components represent the original chromatograms in a smaller dimension, space scatter plots can be used to visualize the original data. PCA calculations were carried out using Matlab version 7.4 release 2007a (MathWorks, Natick, MA) and the PLS toolbox version 4.2.1 (Eigenvector Research, Wenatchee, WA). The algorithm for PCA was written using the method described in Naes et al. [42]. It is based on the singular value decomposition of the chromatographic data covariance matrix. Each row in the chromatographic data matrix corresponds to a chromatogram of a cochineal sample (signal intensity over time). Model scores and loadings were obtained from the covariance matrix eigenvectors.

Similarity between the cochineal samples was assessed with the chromatogram data. A preliminary analysis was made for samples belonging to the same species and it was found that retention times were consistent (no retention time shifts were observed). Therefore, no retention time correction was adopted as a pre-processing step.

The PCA models were estimated using the chromatographic data (absorbance at 275 nm) obtained from 19 to 27 min (retention time) since all peaks were found to be within this region. For each chromatogram, 600 points were available for the selected retention time region (1 second intervals). Prior to PCA modelling, all chromatograms were pre-processed using the standard normal variate method (SNV) and mean centering. The consistence between replicates and adjustment of analyzed samples was assessed and guaranteed through the analysis of scores and Hotelling T2/residuals statistics [43].

The analysis of red textiles samples (of unknown origin) was performed by projecting the correspondent chromatograms onto PCA models developed using known origin samples of Kerria. Therefore, textile samples on score plots were never used to calibrate the model. The matching of these samples to the calibration samples (known origin) was assessed by evaluating the Hotellin T2/residuals statistics. These statistics for the textile samples must be below the confidence level obtained for the calibration samples, in order to validate the projection. The extraction methods produced additional peaks on the chromarograms. This was circumvented by restricting the PCA analysis to elution time regions where chromatograms are consistent.

6. ICP-AES – mordant

6.1 Historical dyed textiles

Mordant identification was conduct on 60 coloured wool fibres, 0.4-0.5 mg each; different colours were selected from different areas of field and main border (three for each colour); aiming to understand the different shades of colours (*abrash*), one sample was also removed from the back of the carpet, on both right and left sides of the carpet along to the symmetrical design (table II.2). Weft from *Duff* Prayer Rug (PD78) was also analysed.

Table II.2: Total of fiber samples analyzed by ICP-AES from each rug

Main Colours	Red			Pink	Yellow	Orange	Green		Blue	Brown		Beige	Weft
Abrash	left	right	field				left	right		left	right		
	Benguiat Prayer Rug (*PD77*)												
Light	1	1	-	-		-	1	1	-	-		1	-
Medium	1	1		3	1	3	1	1	-	3		-	-
Dark	1	1	3	-		-	-	-	-	3		2	-
Total:	**3**	**3**	**3**	**3**	**1**	**3**	**2**	**2**	**-**	**6**		**3**	**-**
	Duff Prayer Rug (*PD78*)												
Light	-			-	-	3	-		-	1	1	1	
Medium	-			1	1	-	3		-	-	-	1	1
Dark	1			1	-	3	3		-	1	1	-	
Total:	**1**			**2**	**1**	**6**	**6**		**-**	**2**	**2**	**2**	**1**
	Medallion Carpet (*PD76*)												
Light	1			-	-	-	-	-	-	-	1	1	-	-
Medium	1			-	-	-	-	-	2	-	-	-	1	-
Dark	1			-	-	-	-	-	-	-	1	1	-	-
Total:	**3**			**-**	**-**	**-**	**-**	**-**	**2**	**-**	**2**	**2**	**1**	**-**

6.2 Samples preparation

Fibre samples were subjected to acid digestion with a solution of 9.1% HNO_3/H_2O. Being subjected to an ultrasound bath for about 90 minutes (~ 45ºC) only with acid, where they remain for the next 24 hours. Quantification of elements was based on calibration lines: with concentrations of 0.2-1 ppm for the lines corresponding to the Iron and Copper, 1-5 ppm for Aluminium.

6.3 Instrumentation

Mordant analyses were performed in a Jobin-Yvon Ultima Inductively Coupled Plasma with Atomic Emission Spectrometry, with RF 40.68 MHz generator and a Czerny-Turner 1.00 m monochromator. Conditions used were: 1000 kW potency; 12 L/min of argon flow, Meinhard nebulisator with 3 bar pressure; pump velocity of 20 rpm; 10 ml/ min of sample flow debit; and three analyses for each sample.

7. EDXRF and SEM-EDS[15] – metal threads

7.1 Historical metal samples

Metal threads from each rug were carefully observed; areas where were macroscopically observed different colours or techniques were selected. Analyses to 2 sub-areas with similar characteristics (different colour or technique) were performed whenever possible. For each, 3 analyses were carrying out for future comparison of results.

7.2 Samples preparation

To µ-EDXRF it was not necessary any special preparation of samples, only a video camera and a red diode laser, which allow select and fix the distance between detector and surface areas of analysis.

SEM-EDX samples did not suffer any previous preparations, were fixed to adhesive metallic tape (Al), in order to be applied on SEM sample holder; to samples with strong surface alteration, with lower electrical conduction were gold coated in plating.

[15] According to Professor Nuno Leal, responsible for the SEM-EDX analyses.

7.3 Instrumentation

μ-EDXRF

Identification of the metal threads was performed with a ARTAX Spectrometer, equipped with Molybdenum ampoule with a maximum potential of 50 kV; maximum intensity of 600 μA and potencial 30 Watt. It is prepared with a solid state detector (Si) among a resolution of 160 keV a 5,9 keV; Conditions used were: 40 kV potency, 600 μA intensity during 12 seconds of time exposure. Analyses a JEOL JSM-T330A Scanning Microscope was used; maximum intensity of 5-6 μA and potential difference 25 kV.

SEM-EDX

Analyses were conducted in a JEOL JSM-T330A Scanning Microscope with maximum intensity of 5-6 μA and potential difference of 25 kV.

8. C14-AMS

8.1 Historical dyed textiles

Analyses were conduct in AMS division from Beta Analytics Inc. on coloured wool fibres, 3mg, collected from Medallion carpet (PD76). The sample used was obtained with loose knots from different areas of field and main border, on both right and left sides of the carpet.

8.2 Sample preparation[16]

The sample was subjected to a series of solvent baths typically consisting of benzene, toluene, hexane, pentane, and/or acetone prior to C14 analysis. Pre-treatment of submitted material was also performed, in order to remove small percentages of Carbon. The sample was first gently dispersed in deionized water. It was then given hot HCI acid and NaOH alkali washes. The alkali washes were followed by a final acid rinse to neutralize the solution prior to drying. Chemical concentrations, temperatures, exposure times, and number of repetitions, were applied accordingly with the uniqueness of the sample.

8.3 Instrumentation

The comparable context age of the Medallion Carpet fibre sample was determined by AMS Radiocarbon dating; 280±40 BP[17] is presented as conventional ^{14}C date (Beta-279893[18]) and also as calendar dates using the program CALIB 6.0.1 [44] and the associated IntCal09. Calibrated ranges have been calculated; due to the shape of calibration curve in the region of interest, more than one age range is possible.

[16] According to Beta Anatytic Inc. laboratorial report.
[17] Before Present
[18] Laboratory number.

APPENDIX IV

Experimental results from HPLC-DAD-MS, ICP-AES and colorimetric analyses performed to all dyes and correspondent colours identified.

Table IV.1: Red samples – Medallion Carpet[19](PD76) (17 samples)

Al^{3+}	Area	Weight (mg)	(1) Laccaic acid C Rt (min.) = 16.37 λmáx (nm) = 284 494 $[M-H]^-$ =538		(2) Laccaic acid E Rt (min.)= 16.64 λmáx (nm)= 284 494 $[M-H]^-$ = 494		(3) Laccaic acid B Rt (min.)= 19.72 λmáx (nm)= 288 490 $[M-H]^-$ = 495		(4) Laccaic acid A Rt (min.)= 20.10 λmáx (nm)= 284 496 $[M-H]^-$ = 536		5) unidentified compounds C1 and C2 Rt = **C1:**25.80 **C2:**26.30 λmáx= **C1:**432 **C2:**462		Colorimetric values - **CIELAB, D65/10 –** (Average±STD)	ICP[20] (Average)	
			Normalized %	Relative[21] %	Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %		Al^{3+} (mg)/wool (g)	Fe^{2+} (mg)/wool (g)
Red (light)															
V1C1	field	0,24	Normalized =14.7; Relative = 65.6				1.1	4.8	6.1	27.2	0.6	2.5	**L*** 33.88±1.31 **a*** 9.37±0.65 **b*** 10.78±0.47	8.6	0.57
V1C2	field	0,15	Normalized = 21.0; Relative = 65.8				1.3	4.1	9.2	28.9	0.3	1.1			
V1B5	border	0,16	0.7	11.2	3.5	55.9	0.2	3.6	1.7	26.5	0.2	2.8			
V1B6	border	0,12	16.6	41.7	4.2	55.5	4.2	1	31.1	44.7	1.1	1.6			
Red (medium)															
V2C1	field	0,16	3.5	13.2	4.0	15.1	2.1	7.7	16.7	62.7	0.4	1.3	**L*** 26.77±0.01 **a*** 11.68±0.07 **b*** 6.28±0.02	4.4	0.65
V2C2	field	0,2	4.0	10.2	4.5	11.6	2.8	7.2	26.8	69.5	0.6	1.5			
V2C3	field	0,2	3.4	18.8	1.4	7.9	1.3	7.1	11.4	64.0	0.4	2.1			
V2B4	border	0,18	Normalized = 20.3; Relative = 32.8				2.6	6.2	17.9	43.5	0.4	0.9			
V2B5	border	0,09	2.9	24.2	6.0	9.7	5.7	9.2	40.4	65.1	1.0	1.6			
V2B6	border	0,17	6.8	15.6	3.5	16.9	1.0	10.1	9.3	61.1	0.3	1.2			
Red (dark)															
V3C1	field	0,07	28.6	49.3	7.8	6.6	12.0	10.1	59.5	50.4	10.2	1.4	**L*** 23.64±0.35 **a*** 13.87±0.54 **b*** 5.94±0.03	8.5	0.45
V3C2	field	0,17	5.2	14.5	4.9	14.7	2.9	7.1	20.5	61.1	0.5	1.4			
V3C3	field	0,2	5.6	32.8	3.1	8.9	2.0	5.7	21.4	61.4	0.4	5.5			
V3B4	border	0,14	8.8	24.2	16.3	11.6	7.6	5.4	100.0	71.2	7.8	5.5			
V3B5	border	0,22	2.0	15.6	5.5	13.5	5.1	7.9	28.6	70.1	0.7	1.7			
V3B6	border	0,2	Normalized = 12.9; Relative = 22.5				1.2	4.5	11.1	43.6	0.4	1.5			

[19] All colorimetric values were measured only from the front of the carpet, since full support and stitches from the back were not removed at the time.
[20] Only one analysis was performed for each hue.
[21] The relative percentage area for each compound was the area of an individual peak calculated as a percentage of the total areas recorded in the chromatogram for the selected wavelength.

Red samples – Benguiat Prayer Rug (PD77) (6 samples)															
Sample	Area	Fibre weight (mg)	(1) Laccaic acid C Rt (min.) = 16.37 λmáx (nm) = 284 494 $[M-H]^-$ =538		(2) Laccaic acid E Rt (min.)= 16.64 λmáx (nm)= 284 494 $[M-H]^-$ = 494		(3) Laccaic acid B Rt (min.)= 19.72 λmáx (nm)= 288 490 $[M-H]^-$ = 495		(4) Laccaic acid A Rt (min.)= 20.10 λmáx (nm)= 284 496 $[M-H]^-$ = 536		5) unidentified compounds C1 and C2 Rt = **C1:**25.80 **C2:**26.30 λmáx= **C1:**432 **C2:**462		Colorimetric values - CIELAB, D65/10 – (Average±STD)	ICP[22] (Average±STD)	
			Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %		Al^{3+} (mg)/wool (g)	Fe^{2+} (mg)/wool (g)
Red (light)															
V1**left**1	field	0,1	0.9	5.8	1.8	0.9	0.9	5.5	11.5	71.2	1.1	6.6	-	1.9±0.0	1.2±0.8
V1**right**1		0,1	0.9	2.6	5.1	14.1	1.9	5.3	27.2	75.5	0.9	2.5			
V1**left**2		0,1	0.7	3.1	3.8	16.5	1.1	4.7	16.8	72.3	0.8	3.3			
V1**right**2		0,1	0.8	2.8	4.0	14.0	1.5	5.5	21.1	74.8	0.8	2.9			
Red (medium)															
V2**left**1	field	0,1	0.3	2.1	2.3	15.4	0.8	5.6	10.5	71.7	0.8	5.1	-	3.6±2.4	1.1±0.3
V2**right**1		0,1	0.3	1.6	2.4	13.6	1.0	5.9	12.9	73.6	0.9	5.3			
V2**right**.2		0,1	0.3	2.2	2.1	13.3	0.8	5.3	11.8	73.8	0.9	5.4			
Red (dark)															
V3**left**1	field	0,1	0.3	2.3	4.2	11.2	2.2	5.9	29.5	77.8	1.1	2.8	**L*** 20.80±0.24 **a*** 17.08±0.07 **b*** 6.07±0.09	3.8±0.0	0.9±0.1
V3**right**1		0,1	0.3	1.9	1.6	10.9	0.9	6.1	10.7	74.8	1.0	6.9			
V3**right**2		0,1	0.3	2.0	1.8	11.2	1.2	7.4	12.3	76.1	0.5	3.3			
VC1	field	0,2	16.1	30.7	4.2	7.9	3.6	6.9	28.0	53.4	0.5	1		2.7±0.2	0.6±0.5
VC2		0,1	30.6	24.7	12.4	10	6.6	5.3	73.5	59.4	0.7	0.6			
VC3		0,1	3.5	5.5	8.8	13.9	5.0	7.9	42.9	67.5	3.3	5.2			
VB4	border	0,2	1.2	14.0	2.8	11.7	2.1	9.9	16.1	77.6	0.6	2.6			
VB5		0,1	11.5	17.3	6.4	9.6	3.5	5.3	43.9	66.1	1.1	1.6			
VB6		0,1	20.9	14.0	17.5	11.7	9.4	6.3	100.00	67.1	1.2	0.8			

[22] To colours in which was performed a single analysis, it is shown just the correspondent value.

Red samples – Duff Prayer Rug (PD78) (5 samples)

Sample	Area	Weight (mg)	(1) Laccaic acid C Rt (min.) = 16.37 λmáx (nm) = 284 494 $[M-H]^-$ =538		(2) Laccaic acid E Rt (min.)= 16.64 λmáx (nm)= 284 494 $[M-H]^-$ = 494		(3) Laccaic acid B Rt (min.)= 19.72 λmáx (nm)= 288 490 $[M-H]^-$ = 495		(4) Laccaic acid A Rt (min.)= 20.10 λmáx (nm)= 284 496 $[M-H]^-$ = 536		5) unidentified compounds C1 and C2 Rt = **C1:**25.80 **C2:**26.30 λmáx= **C1:**432 **C2:**462		Colorimetric values - CIELAB, D65/10 – (Average±STD)	ICP (Average)	
			Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %		Al^{3+} (mg)/wool (g)	Fe^{2+} (mg)/wool (g)
Red (dark)															
VC1	field	0,1	20	26.2	4.17	5.5	4.3	5.6	46.9	61.4	1.1	1.4	**L*** 17.59±0.98 **a*** 15.92±0.13 **b*** 5.36±0.27	2.2	0.9
VC3		0,2	Normalized = 51.8; Relative = 42.8				8.1	4.6	62.4	51.5	1.5	1.2			
VB4	border	0,2	22.2	17.8	14.1	9.8	5.6	3.9	71.1	62.2	1.3	1.1			
VB5		0,2	32.3	26	13.1	12.4	6.2	5	71.5	57.6	1	0.8			
VB6		0,2	27.4	17.8	16.2	10.5	8.7	5.6	100	64.7	2.2	1.4			

Table IV.2: Pink samples - Benguiat Prayer Rug (PD77) (2 samples)

Sample	Area	Weight (mg)	(1) Laccaic acid C Rt (min.) = 16.37 λmáx (nm) = 284 494 $[M-H]^-$ =538		(2) Laccaic acid E Rt (min.)= 16.64 λmáx (nm)= 284 494 $[M-H]^-$ = 494		(3) Laccaic acid B Rt (min.)= 19.72 λmáx (nm)= 288 490 $[M-H]^-$ = 495		(4) Laccaic acid A Rt (min.)= 20.10 λmáx (nm)= 284 496 $[M-H]^-$ = 536		5) unidentified compounds C1 and C2 Rt = **C1:**25.80 **C2:**26.30 λmáx= **C1:**432 **C2:**462		Colorimetric values - CIELAB, D65/10 – (Average±STD)	ICP (Average±STD)	
			Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %		Al^{3+} (mg)/wool (g)	Fe^{2+} (mg)/wool (g)
RosaC3	field	0,1	0.5	5.0	2.0	13.5	1.9	13.4	8.9	61.7	1.5	6.3	**L*** 33.39±0.86 **a*** 6.33±0.26 **b*** 12.38±0.27	2.1±0.2	0.6±0.1
RosaB5	border	0,1	Normalized = 0.9; Relative = 13.9				1.7	16.5	6.5	63	1.1	6.6			

Table IV.3: Blue samples – Medallion Carpet (PD76) (3 samples)

Sample	Area	Weight (mg)	**(1) indigotin** Rt (min.) = 24.85 λmáx (nm) = 610 Normalized %	**Colorimetric values - CIELAB, D65/10 –** (Average±STD)	**ICP** (Average) Al^{3+} (mg)/wool (g)	**ICP** (Average) Fe^{2+} (mg)/wool (g)
Blue (medium)						
A1C1	field	0,1	36	**L*** 32.20±0.19 **a*** -2.29±0.02 **b*** 3.82±0.05	1.5	0.9
A1C2	field	0,2	23			
Blue (dark)						
A4C1	field	0,1	100	**L*** 18.38±0.28 **a*** -2.01±0.21 **b*** -3.48±0.25	1.4	0.8

Blue samples – Benguiat Prayer Rug (PD77) (16 samples)

Sample	Area	Weight (mg)	**(1) indigotin** Rt (min.) = 24.85 λmáx (nm) = 610 Normalized %	**Colorimetric values - CIELAB, D65/10 –** (média±desvio padrão)	**ICP** Al^{3+} (mg)/wool (g)	**ICP** Fe^{2+} (mg)/wool (g)
Blue (light)						
A1C1	field	0,3	5	**L*** 36.41±1.06 **a*** -1.19±0.12 **b*** 8.37±0.17	-	-
A1B4	border	0,6	1			
A1B5	border	0,8	3			
Blue (medium I)						
A2C1	field	0,4	25	**L***32.92±0.49 **a*** -2.21±0.03 **b*** 5.38±0.21	-	-
A2C2	field	0,4	16			
A2B4	border	0,8	2			
A2B5	border	0,6	41			
Blue (medium)						
A3C1	field	0,1	5	**L***35.14±0.63 **a*** -0.22±0.49 **b*** 8.66±0.12	-	-
A3C2	field	0,1	7			
A3B4	border	0,4	21			
A3B5	border	0,2	1			
Blue (dark)						
A4C1	field	0,3	100	**L***29.20±0.52 **a*** -3.40±0.27 **b*** 2.48±0.76	-	-
A4C2	field	0,9	27			
A4B4	border	0,8	10			
A4B5	border	0,3	33			

Blue samples – Duff Prayer Rug (PD78) (7 samples)						
Sample	Area	Weight (mg)	**(1) indigotin** Rt (min.) = 24.85 λmáx (nm) = 610 Normalized %	**Colorimetric values** - **CIELAB, D65/10 –** (média±desvio padrão)	**ICP** Al^{3+} (mg)/wool (g)	**ICP** Fe^{2+} (mg)/wool (g)
Blue (light)						
A1C2	**field**	0,4	11	**L*** 38.70±0.18 **a*** 0.10±0.10 **b*** 7.32±0.16	-	-
A1C3		0,3	3			
A1B4	**border**	0,4	2			
A1B5		0,4	7			
A1B6		0,3	17			
Blue (dark)						
A2C1	**field**	0,3	86	**L*** 18.45±0.36 **a*** -3.03±0.17 **b*** -4.56±0.33	-	-
A2C2		0,4	100			

Table IV.4: Yellow samples – Benguiat Prayer Rug (PD77) (2 samples)

Sample	Area	Weight (mg)	(1) Flavonoid di-*O*-glucoside R_t (min.) = 17.30 $\lambda_{máx}$ (nm) = 259 345 $[M-H]^-$ = 609		(2) Luteolin-di-*O*-Glicose (?) R_t (min.) = 17.80 $\lambda_{máx}$ (nm) = 256 343 $[M-H]^-$ = 579		(3) Luteolin-7-O-Gl R_t (min.) = 18.30 $\lambda_{máx}$ (nm) = 256 349 $[M-H]^-$ = 447		(4) Apigenin-7-O-Gl R_t (min.) = 19.35 $\lambda_{máx}$ (nm) = 263 335 $[M-H]^-$ = 431		(5) Luteolin R_t (min.) = 21.40 $\lambda_{máx}$ (nm) = 256 349 $[M-H]^-$ = 285		Colorimetric values - CIELAB, D65/10 – (média±desvio padrão)	ICP (Average)	
			Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %		Al^{3+} (mg)/wool (g)	Fe^{2+} (mg)/wool (g)
Yellow															
AmC2	field	0,3	0.8	2.5	0.4	1.3	30.6	90.9	1.1	3.3	1.9	5.7	-	2.0	0.4
AmB5	border	0,3	3.5	21.0	2.9	17.4	100.0	89.4	4.9	4.4	6.9	6.2			

Yellow samples – Duff Prayer Rug (PD78) (5 samples)

Sample	Area	Weight (mg)	(1) Flavonoid di-*O*-glucoside R_t (min.) = 17.30 $\lambda_{máx}$ (nm) = 259 345 $[M-H]^-$ = 609		(2) Luteolin-di-*O*-Glicose (?) R_t (min.) = 17.80 $\lambda_{máx}$ (nm) = 256 343 $[M-H]^-$ = 579		(3) Luteolin-7-O-Gl R_t (min.) = 18.30 $\lambda_{máx}$ (nm) = 256 349 $[M-H]^-$ = 447		(4) Apigenin-7-O-Gl R_t (min.) = 19.35 $\lambda_{máx}$ (nm) = 263 335 $[M-H]^-$ = 431		(5) Luteolin R_t (min.) = 21.40 $\lambda_{máx}$ (nm) = 256 349 $[M-H]^-$ = 285		Colorimetric values - CIELAB, D65/10 – (média±desvio padrão)	ICP (Average)	
			Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %		Al^{3+} (mg)/wool (g)	Fe^{2+} (mg)/wool (g)
Yellow															
AmC2	field	0,4	0	1.3	0	2.9	71.9	91.6	2.6	3.3	3.9	5.0	-	3.4	0.4
AmC3		0,3	1.5	1.3	3.4	2.9	66.3	92.4	2.0	2.8	3.5	4.9			
AmB5	border	0,4	1.7	2.2	3.8	4.7	100.0	93.5	2.0	1.9	4.9	4.6			

Table IV.5: Orange samples – Benguiat Prayer Rug (PD77) (2 samples)

Sample	Area	Weight (mg)	(1) Luteolin-7-O-Gl R_t (min.) = 18.30 $\lambda_{máx}$ (nm) = 256 349		(2) Apigenin-7-O-Gl R_t (min.) = 19.36 $\lambda_{máx}$ (nm) = 260 337		(3) Luteolin R_t (min.) = 21.40 $\lambda_{máx}$ (nm) = 256 349		(3) Alizarin R_t (min.) = 23.47 $\lambda_{máx}$ (nm) = 245 430		(4) Purpurin R_t (min.) = 26.15 $\lambda_{máx}$ (nm) = 245 480		Colorimetric values - CIELAB, D65/10 – (média±desvio padrão)	ICP (Average±STD)	
			Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %		Al^{3+} (mg)/wool (g)	Fe^{2+} (mg)/wool (g)
Orange (dark)															
LC1	field	0,4	100.0	62.4	3.7	2.3	14.9	9.3	30.9	6.7	10.7	6.7	**L*** 29.18±0.16 **a*** 11.17±0.08 **b*** 15.51±0.11	2.7±0.8	0.6±0.2
LB5	border	0,4	31.7	54.9	3.3	5.8	3.9	6.7	13.9	24.1	8.5	4.9			
Orange samples – D78 Duff Prayer Rug (PD78) (11 samples)															
Sample	Area	Weight (mg)	(1) Luteolin-7-O-Gl Tr (min.) = 18.30 λmáx (nm) = 256 349		(2) Apigenin-7-O-Gl Tr (min.) = λmáx (nm) =		(3) Luteolin Tr (min.) = 21.40 λmáx (nm) = 256 349		(3) Alizarin R_t (min.) = 23.47 $\lambda_{máx}$ (nm) = 245 430		(4) Purpurin Tr (min.) = 26.15 λmáx (nm) = 245 480		Colorimetric values - CIELAB, D65/10 – (média±desvio padrão)	ICP (Average±STD)	
			Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %		Al^{3+} (mg)/wool (g)	Fe^{2+} (mg)/wool (g)
Orange (light)															
L1C1	field	0,4	70.7	55.8	1.4	1.1	17.7	13.9	37.0	29.2	n.d.		**L*** 38.13±0.15 **a*** 6.11±0.09 **b*** 18.81±0.16	2.7±0.3	-
L1C2		0,4	36.3	58.4	1.0	1.7	23.0	37.0	1.9	3.0	n.d.				
L1B4	border	0,4	100.0	91.8	2.5	2.3	5.4	5.0	1.0	0.9	n.d.				
L1B5		0,4	13.8	29.3	5.1	11.0	25.9	55.3	2.1	4.4	n.d.				
Orange (medium I)															
L2C1	field	0,4	67.3	88.0	5.8	7.6	3.1	4.0	0.3	0.4	n.d.		**L*** 36.89±0.83 **a*** 8.41±0.30 **b*** 16.65±0.40	-	-
L2C2		0,4	84.4	55.7	1.4	0.9	45.4	30.0	19.8	13.1	0.5	0.3			
L2C3		0,3	19.5	82.9	0.8	3.3	2.9	12.4	0.3	1.3	n.d.				
L2B4	border	0,4	46.9	56.3	0.6	0.8	22.9	27.4	13.0	15.5	n.d.				
L2B5		0,3	44.6	84.8	2.5	4.7	3.4	6.4	2.1	4.0	n.d.				
L2B6		0,3	11.3	62.1	0.2	1.3	1.7	9.1	5.0	27.5	n.d.				
Orange (medium II)															
L3C1	field	0,3	70.9	65.6	0.6	0.5	28.7	26.6	8.0	7.4	n.d.		**L*** 34.26±1.60 **a*** 13.76±0.49 **b*** 18.68±0.61	2.3±0.5	0.7±0.3

Table IV.6: Green samples – Medallion Carpet (PD76) (2 samples)

Sample	Area	Weight (mg)	(1) Luteolin-7-O-Gl R_t (min.) = 18.30 $\lambda_{máx}$ (nm) = 256 349		(2) Apigenin-7-O-Gl R_t (min.) = 19.36 $\lambda_{máx}$ (nm) = 260 337		(3) Luteolin R_t (min.) = 21.40 $\lambda_{máx}$ (nm) = 256 349		(4) indigotin R_t (min.) = 24.85 $\lambda_{máx}$ (nm) = 610		Colorimetric values - **CIELAB, D65/10 –** (média±desvio padrão)	ICP (Average)	
			Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %		Al^{3+} (mg)/wool (g)	Fe^{2+} (mg)/wool (g)
Green (medium II)													
VC1	field	0,4	33	25	1	1	1	1	100	74	**L*** 32.21±0.04 **a*** -2.28±0.17 **b*** 10.96±0.13	3.9	1.7
VC2		0,4	24	64	1	2	2	4	12	31			

Green samples – Benguiat Prayer Rug (PD77) (7 samples)

Sample	Area	Weight (mg)	(1) Luteolin-7-O-Gl Tr (min.) = 18.30 λmáx (nm) = 256 349		(2) Apigenin-7-O-Gl Tr (min.) = 19.36 λmáx (nm) = 260 337		(3) Luteolin Tr (min.) = 21.40 λmáx (nm) = 256 349		(4) indigotin Tr (min.) = 24.85 λmáx (nm) = 625		Colorimetric values - **CIELAB, D65/10 –** (média±desvio padrão)	ICP (Average±STD)	
			Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %		Al^{3+} (mg)/wool (g)	Al^{3+} (mg)/wool (g)
Green (light II)													
V1C1	field	0,3	98	52	1	1	1	1	84	47	**L*** 34.22±0.18 **a*** 0.06±0.18 **b*** 13.58±0.26	1.7±0.3	1.7±0.4
V1C2		0,4	26	30	1	1	1	1	55	68			
V1B4	border	0,4	31	29	1	1	2	2	70	69			
V1B5		0,4	86	58	1	1	5	4	52	37			
V1B6		0,4	32	29	5	5	2	2	66	64			
Green (dark)													
V2C1	field	0,3	38	27	2	1	2	2	100	71	**L*** 26.84±0.34 **a*** -1.88±0.29 **b*** 13.26±0.53	3.3±0.7	0.9±0.1
V2B5	border	0,3	94	59	2	1	1	2	63	39			

Green samples – Duff Prayer Rug (PD78) (12 samples)												
Sample	Area	Weight (mg)	(1) Luteolin-7-O-Gl Tr (min.) = 18.30 λmáx (nm) = 256 349		(2) Apigenin-7-O-Gl Tr (min.) = 19.36 λmáx (nm) = 260 337		(3) Luteolin Tr (min.) = 21.40 λmáx (nm) = 256 349		(4) indigotin Tr (min.) = 24.85 λmáx (nm) = 625		Colorimetric values - **CIELAB, D65/10 –** (média±desvio padrão)	ICP (Average±STD)	
			Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %	Normalized %	Relative %		Al^{3+} (mg)/wool (g)	Al^{3+} (mg)/wool (g)
Green (light I)													
V1C1	field	0,4	8	79	0	5	0	4	1	12	**L*** 40.35±0.25 **a*** 0.93±0.01 **b*** 13.55±0.15	-	-
V1C2		0,4	8	68	0	3	1	12	2	17			
Green (medium I)													
V3C1	field	0,3	6	34	0	0	3	15	9	49	**L*** 37.16±0.51 **a*** -4.95±0.24 **b*** 7.52±0.79	3.7±0.5	0.9±0.1
V3C2		0,4	10	62	0	0	1	4	5	32			
Green (medium II)													
V2C1	field	0,4	13	44	0	0	2	7	14	47	**L*** 33.04±0.16 **a*** -4.91±0.15 **b*** 8.62±0.16	-	-
V2C2		0,4	13	60	0	0	1	6	7	32			
V4C1	field	0,4	8	73	0	3	1	12	1	11	**L*** 34.08±0.08 **a*** -5.56±0.10 **b*** 4.86±0.07	-	-
V4C2		0,4	100	91	5	5	3	3	1	1			
V4C3		0,3	0	5	0	0	0	1	7	93			
V4B4	border	0,4	1	3	0	0	0	1	29	96			
V4B5		0,4	1	3	0	0	1	2	27	95			
V4B6		0,4	1	3	0	0	1	2	25	95			

Table IV.7: Brown samples – Medallion Carpet (PD76) (9 samples)						
Sample	Area	Weight (mg)	**(1) Ellagic acid** R_t (min.) = 18.54 λ_{max} (nm) = 366 Normalized %	**Colorimetric values - CIELAB, D65/10 –** (Average±STD)	**ICP** (Average) Al^{3+} (mg)/wool (g)	**ICP** (Average) Fe^{2+} (mg)/wool (g)
Brown (light)						
C1B2	border	0,3	57	-	1.3	0.78
C1B4		0,4	100			
Brown (dark)						
C3C1	field	0,4	52	**L*** 14.62±0.99 **a*** 0.35±0.07 **b*** 0.98±0.31	3.5	3.8
C3C2		0,4	100			
C3C3		0,3	41			
C3B4	border	0,4	51			
C3B5		0,3	97			

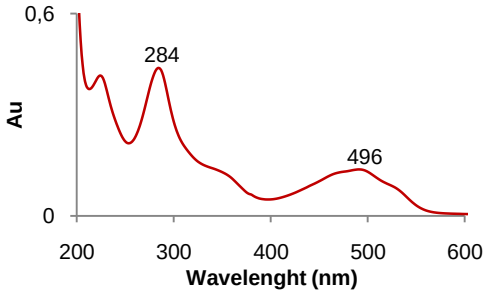
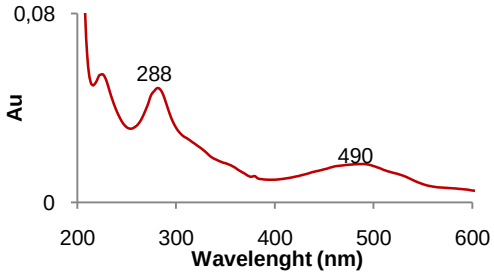
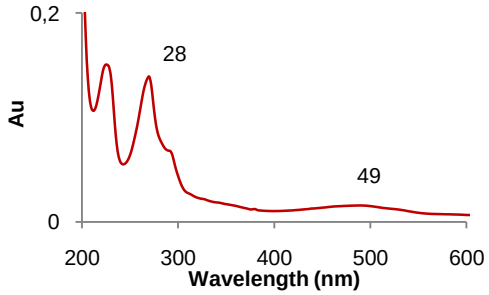
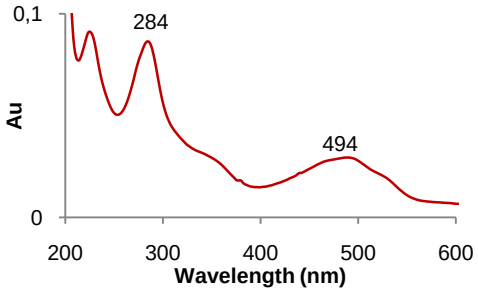
Brown samples – Benguiat Prayer Rug (PD77) (8 samples)						
Sample	Area	Weight (mg)	**(1) colourless compounds** R_t (min.) = 21.01 λ_{max} (nm) = 360 Normalized %	**Colorimetric values - CIELAB, D65/10 –** (média±desvio padrão)	**ICP** (Average) Al^{3+} (mg)/wool (g)	**ICP** (Average) Fe^{2+} (mg)/wool (g)
Brown (light I)						
C1C1	field	0,4	-	**L*** 38.63±0.97 **a*** 5.63±0.04 **b*** 15.98±0.20	1.6	1.4
C1C2		0,4				
C1C3		0,4				
Brown (medium I)						
C2C1	field	0,3	-	**L*** 27.22±0.91 **a*** 3.32±0.07 **b*** 10.83±0.54	3.5	3.8
C2C2		0,3				
B2C1	border	0,3				
B2C2		0,4				
B2C3		0,3				

Brown samples – Duff Prayer Rug (PD78) (12 samples)						
Sample	Area	Weight (mg)	**(1) colourless compounds** R_t (min.) = 21.01 λ_{max} (nm) = 660 Normalized %	**Colorimetric values** - **CIELAB, D65/10 –** (média±desvio padrão)	**ICP** (Average) Al^{3+} (mg)/wool (g)	**ICP** (Average) Fe^{2+} (mg)/wool (g)
Brown (light II)						
C1C1	field	0,4	-	**L*** 30.71±3.23 **a*** 3.92±0.42 **b*** 13.01±2.32	1.3	3.7
C1C2	field	0,4				
C1C3	field	0,4				
C1B1	border	0,4				
C1B2	border	0,4				
C1B3	border	0,4				
Brown (medium II)						
C2B1	border	0,3	-	**L*** 25.81±0.29 **a*** 3.47±0.09 **b*** 10.26±0.14	1.5	7.2
C2B2	border	0,4				
C2B3	border	0,3				
Brown (dark)						
C3B1	border	0,4	-	**L*** 15.61±1.06 **a*** 2.06±0.06 **b*** 3.73±0.15	-	-
C3B2	border	0,3				

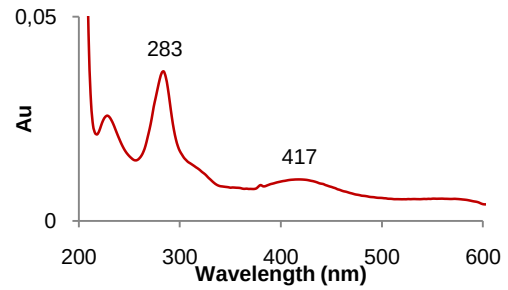
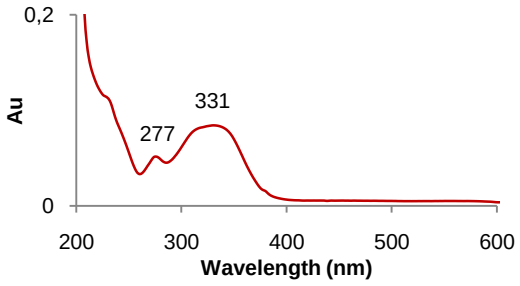
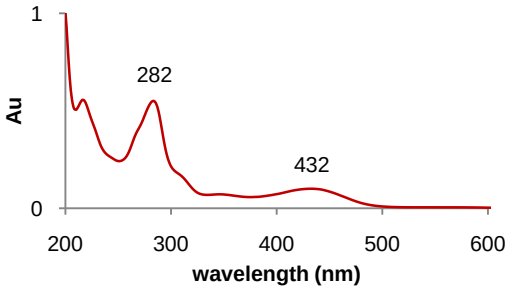
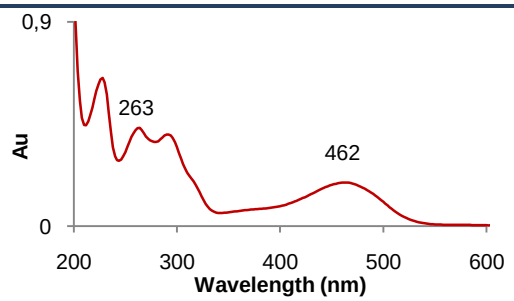
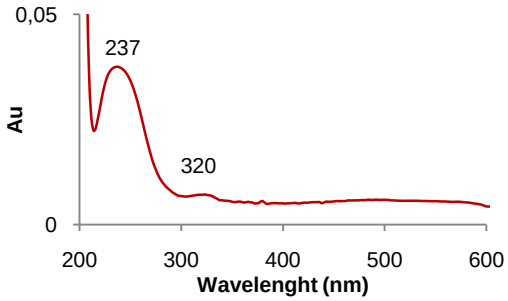
Table IV.7: Beige samples – Medallion Carpet (PD76) (3 samples)						
Sample	Area	Weight (mg)	**(1) colourless compounds** R_t (min.) = 18.54 λ_{max} (nm) = 366 Normalized %	**Colorimetric values - CIELAB, D65/10 –** (Average±STD)	**ICP** (Average) Al^{3+} (mg)/wool (g)	**ICP** (Average) Fe^{2+} (mg)/wool (g)
Beige II						
B1B1	**border**	0,4	-	**L*** 39.81±0.19 **a*** 1.62±0.05 **b*** 10.68±0.57	1.5	0.9
B1B2		0,3				
B1B3		0,4				
Beige samples – Benguiat Prayer Rug (PD77) (8 samples)						
Sample	Area	Weight (mg)	**(1) colourless compounds** R_t (min.) = 21.01 λ_{max} (nm) = 360 Normalized %	**Colorimetric values - CIELAB, D65/10 –** (média±desvio padrão)	**ICP** (Average) Al^{3+} (mg)/wool (g)	**ICP** (Average) Fe^{2+} (mg)/wool (g)
Beige II						
C1C1	**field**	0,4	-	**L*** 40.89±0.23 **a*** 1.82±0.02 **b*** 12.02±0.08	1.5	1
C1C2		0,4				
C1C3		0,4				
Beige I						
C2C1	**field**	0,3	-	**L*** 42.01±0.36 **a*** 2.05±0.08 **b*** 14.82±0.17	-	-
C2C2		0,3				
B2C1	**border**	0,3				
B2C2		0,4				
B2C3		0,3				
Beige samples – Duff Prayer Rug (PD78) (7 samples)						
Sample	Area	Weight (mg)	**(1) colourless compounds** R_t (min.) = 21.01 λ_{max} (nm) = 660 Normalized %	**Colorimetric values - CIELAB, D65/10 –** (média±desvio padrão)	**ICP** (Average) Al^{3+} (mg)/wool (g)	**ICP** (Average) Fe^{2+} (mg)/wool (g)
Beige I						
C1C1	**field**	0,4	-	**L*** 43.24±0. 64 **a*** 1.78±0.12 **b*** 13.42±0.42	0.8	0.7
C1C2		0,4				
C1C3		0,4				
C1B1	**border**	0,4				
C1B2		0,4				
C1B3		0,4				
C3B2		0,3				

APPENDIX V

Lac dye and resin markers database

Lac product	Compound	Rt (min.)	$[M-H]^-$ [23]	λ_{max} (nm)	UV-Vis Spectrum
DYE	Laccaic acid A	20.10	536	284 496	
	Laccaic acid B	19.72	495	288 490	
	Laccaic acid C	16.37	538	284 494	
	Laccaic acid E	16.64	494	284 494	

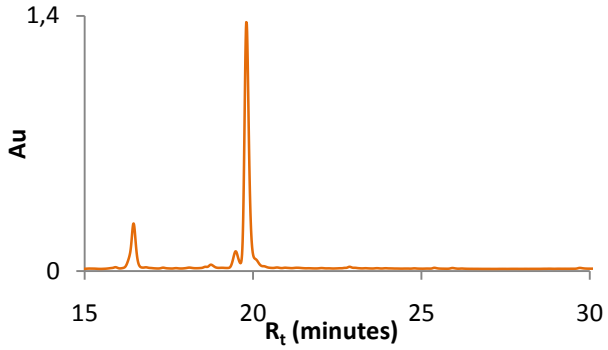
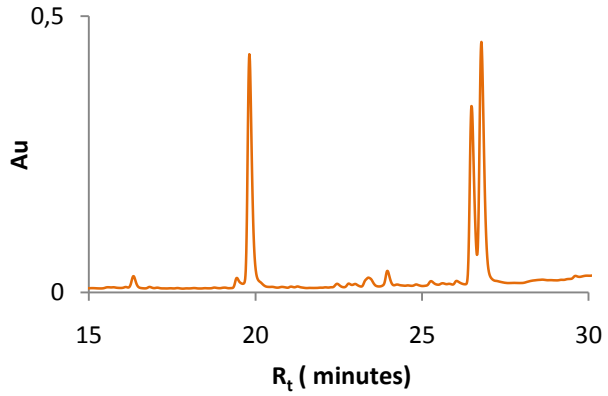
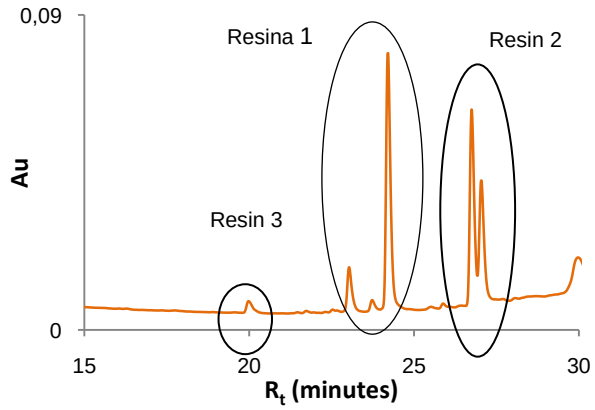
[23] In agreement with the literature [34].

Lac product	Compound	Rt (min.)	[M-H]⁻	λmax (nm)	UV-Vis Spectrum
RESIN	Resin 1	**Peak 1** 23.51	?	283 417	
		Peak 2 24.01	?	277 331	
	Resin 2	**Peak 1** 26.74min	?	282 432	
		Peak 2 27.05min	?	263 462	
	Resin 3	21.23	?	237 320	

APPENDIX VI

Chromatographic profiles from lac-dye insect sources

Table VI: HPLC-DAD chromatograms acquired at 275 nm to each composition displayed on all clusters obtained with PCA analyses.

Cluster I lac-dye

Cluster II Mixture of lac-dye and resin

Cluster III Resin


APPENDIX VII

PCA analyses: Insects sources origin VS Historical textile fibre

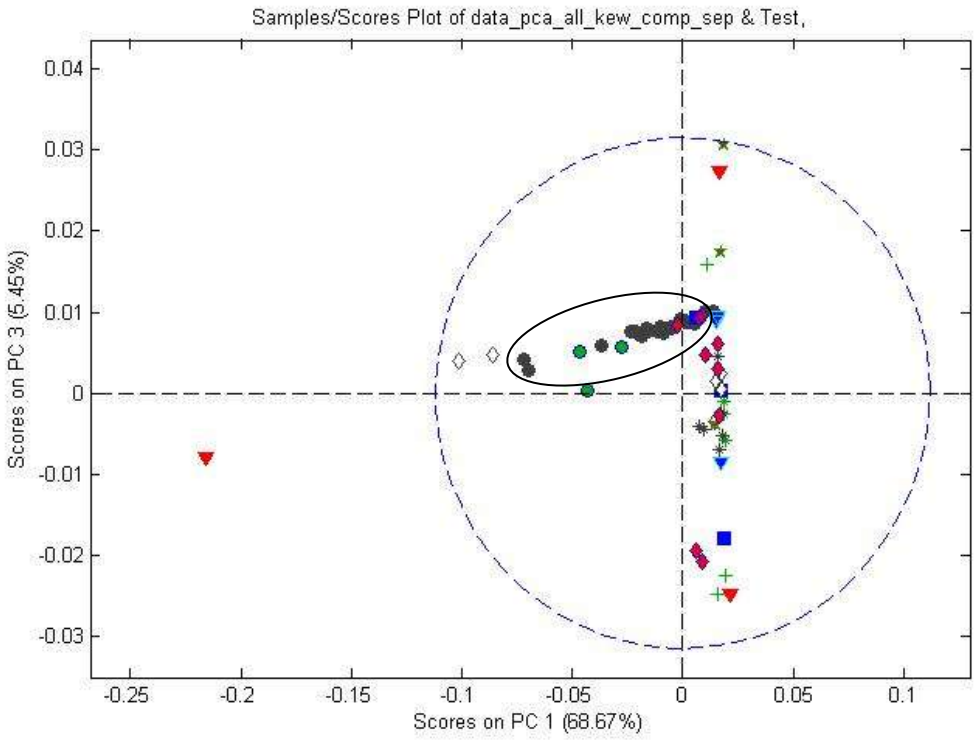


Figure 1: PCA scores obtained from mean centered Kerridae chromatograms acquired at 275nm: **black circles)** historical textile fibres; **green circles)** lac-dye sources from Pakistan.

APPENDIX VIII

Metal threads

Figura 1: Detailed view of metal strip wounded around the core of silk thread from *Benguiat* Prayer Rug SOURCE: Ana Serrano (18/5/2010).

Figura 2: Detailed view of metal strip wounded without core.

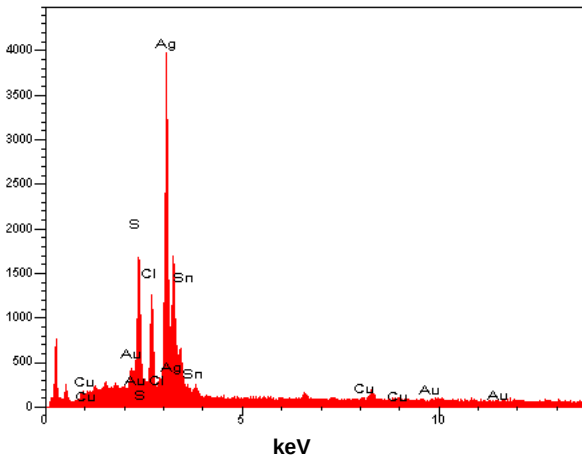


Figure 3 – SEM-EDX spectrum from the metal strip surface from *Benguiat* Prayer Rug

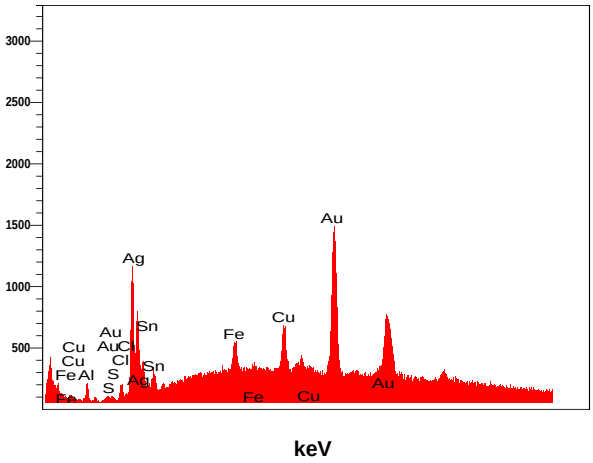


Figure 4 - SEM-EDX spectrum from the metal strip inner surface from *Benguiat* Prayer Rug.

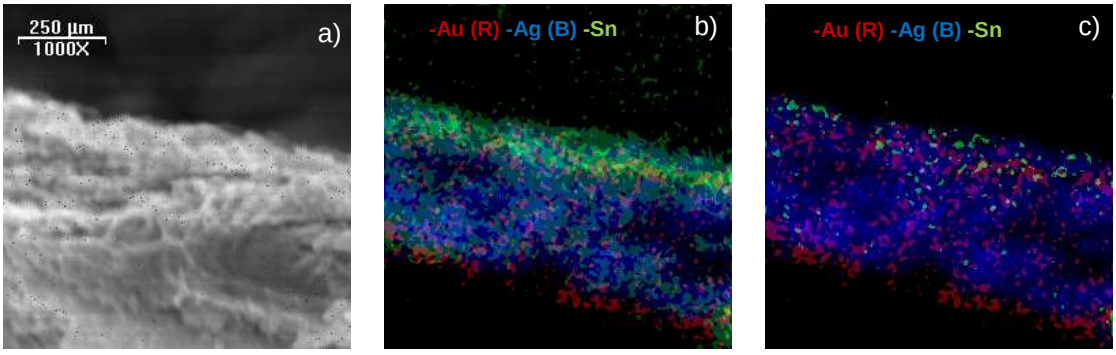


Figure 5: SEM micrographs of dirty and deteriorated metal strip surface from *Duff* Prayer Rug a) general view, b) chemical mapping of Au, Ag and Sn at the surface and c) chemical mapping from *Duff* Prayer Rug.

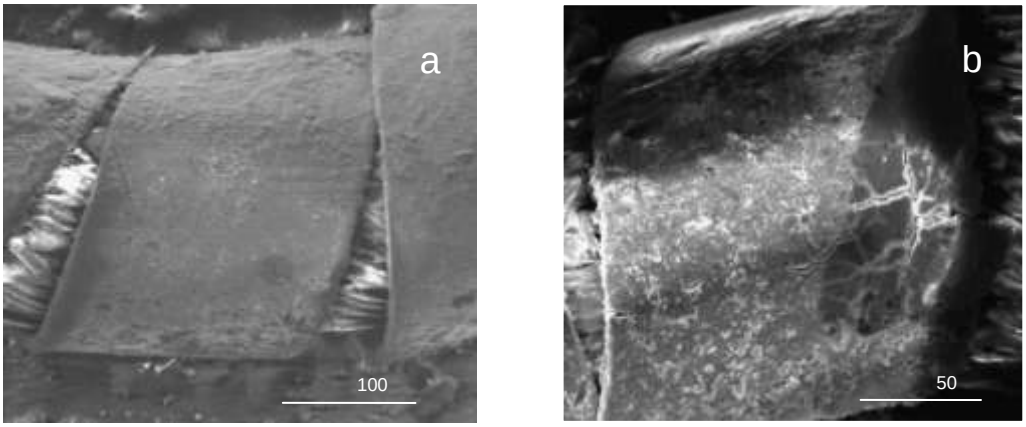


Figura 6: SEM micrographs of dirty and deteriorated metal strip surface a) and b).

APPENDIX IX

Radiocarbon Analysis

Carbon-14 Results for 'Saltings'

Type	Item	Laboratory number	AMS-^{14}C Age *(y BP)*	Calibrated. Age (AD) *95% confidence*	Catalog number
NICHE RUGS	 Khatif Muslihidd *saf* (KM)	ETH - 19085	340±45	1466-1650 (100%)	1d
	 *Kelekian niche rug* (KN)	ETH - 19085	360±45	1454-1641 (100%)	13
	 *Darmstadt niche rug* (DN)	NZA-4494.1 NZA-4494.2 NZA-6497 NZA-6491	392±76 408±72 402±67 386±66	-	22
		Weight mean:	395±35	1439-1527 (63.4%) 1554-1633 (36.6%)	

	 *Indjoudjian niche rug* (IN)	ETH-19084	305±45	1474-1667 (99.3%)	24
	 *Paris niche rug* (PN)	NZA-5973.1 NZA-5973.2 NZA-6489 OxA-6771 ETH-19087	197±61 257±71 323±70 335±45 295±45	-	30
		Weight mean:	290±25	1516-1591 (50.4%) 1622-1633 (49.6%)	
	 *Karlsruhe niche rug* (KN)	NZA-5972.1 NZA-5972.2 ETH-19086	282±58 383±68 270±45	-	47
		Weight mean:	300±35	1488-1607 (66.6%) 1612-1662 (33.4%)	

Source: Mills, J.and Franses, M. Salting Carpets. Oriental Carpets and Textile Studies. Danville: International Conference on Oriental Carpets, 1999, Vol. V.