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Analysis of natural dyes and metal threads used in 16th -18th century Persian/Safavid and Indian/Mughal velvets by HPLC-PDA and SEM-EDS to investigate the system to differentiate velvets of these two cultures

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Abstract

Introduction: Analyses of natural dyes and the metal of the metal-wrapping threads used in 16th -18th century Persian/Safavid and Indian/Mughal period velvets were performed on these textiles in the collection of The Metropolitan Museum of Art. The purpose was to determine whether velvets from the two cultures, which have shown problems in the past with attribution based on historical and iconographical studies, could be more precisely differentiated with the additional evidence from identification of their natural dyes and metals along with information of weaving techniques.
Dyes and metal of the metal-wrapped threads from fifteen Persian velvets and six Indian velvets were analyzed by high performance liquid chromatography with photo diode array detector and by scanning electron microscopy with energy dispersive X-ray spectrometry respectively.

Results: There seem to be types of dyes which specifically characterize the velvets of each culture, as well as types of dyes commonly found in velvets of both cultures. Dyes typical of Persian velvets are cochineal and yellow larkspur, while lac and turmeric are characteristic of Indian velvets. The dyes commonly found are a combination of yellow larkspur and indigo dye in green, as well as safflower, indigo dye, soluble redwoods, and tannin dye. There were exceptions however. Because of those exceptions, examining the range of dyes used in the velvets would be important in differentiating the velvets. Metal used for wrapping the threads was in all cases found to be silver of fairly high purity, the majority of which had been gilded. The silver from Persia metal threads showed very slightly higher copper content, while Indian threads showed nearly pure silver. This is the first extensive comparative study of dyes and metal threads of Safavid and Mughal velvets: the first evidence of yellow larkspur being the most used yellow dye in Persia, and of the possible differences in the two cultures' metal threads.

Conclusion: In addition to knowledge gathered from investigation of weave structure and from historical and iconographic studies, analysis of dyes and metal threads will contribute to a clearer differentiation of those two cultural groups of textiles.

Keywords: Persian/Safavid, Indian/Mughal, 16th -18th c, Velvet, Natural dyes, Metal threads, HPLC-PDA, SEM-EDS

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Background/Introduction

Textile productions such as velvets, printed and painted textiles, brocade, carpets and shawls from Safavid/Persian culture and from Mughal/Indian culture have specifically had problems with attribution based on historical and iconographical studies [1]. Attributing historic objects is crucial to understanding them. It was considered that more definite attribution of textile productions from two cultures may be achieved by investigating the materials and techniques of weaving and dyeing used on the textiles, in conjunction with historical and iconographical studies. It is apparent that the approach to attribution of an oriental carpet has changed from using designs only, to technical features, because the latter are more related to the places of manufacturers [2].

The Safavid Empire was established in 1501 in the geographical area of contemporary Iran, which was, ruled by powerful sovereigns, the Safavid shahs. The 2nd Safavid shah, Tahmasp, was once known to be an inspiring patron of poets, musicians, and painters [3]. Textile productions from the Safavid court are known to be supreme [4]. The Mughal Empire originated in India with the invasion of northern India in 1526 by a Muslim prince, Babur, from Central Asia. Starting from the visit by the Mughal Emperor to the Safavid court in 1544, the two courts had political and cultural exchanges. The Mughal School of Art was established by the Mughal Emperor as an expression of his appreciation of the magnificent achievements of Safavid shah's artists. Those artists were invited to join the Mughal emperor's entourage at a time when the Safavid court had become puritanical because of political changes. The problem of attributing some of these textiles comes from the constant cultural exchanges between the two imperial courts for at least two centuries [5].

In terms of scientific analysis of dyes used in early Persian and Indian textile productions, little research has been done, in particular, little comparative study of productions from the two cultures. Only one comparative study of dyes on carpets from those cultures is mentioned in an exhibition catalogue, *Flower Underfoot*, at the Metropolitan Museum of Art (MMA) [6,7], although the part of scientific studies is not published. The study reports that lac insect dye was thought by some to indicate Indian carpets as opposed to Persian. However, lac appeared in many Persian carpets, and its use would not be seen as a valid indicator of origin. For yellow dyes, it reported that not much can be concluded at this point from the limited results. Other related analyses are of a group of early Indian silk textiles [8] and Persian carpets [9-11]. Some of those analytical results do not include scientific data. In addition, each of these studies presents an analysis of dyes of textiles from only one culture or one object. In order to attribute textiles from those two cultures, it would clearly be necessary to study larger groups of textiles from the two cultures.

A number of technical studies have found that scanning electron microscopy with compositional analysis by energy dispersive X-ray spectrometry (SEM-EDS) is a productive method for investigating of metal wrapped threads from different periods and cultures, and has been used to measure the dimensions of the metal wrapping, to characterize the substrate metal, and any surface layer such as gilding. Some studies concentrated on qualitative compositional characterization of the metal strips, typically silver-gilt [12-14]. Other studies have also used SEM-EDS for quantitative compositional analyses and characterization of the layer structures of gilt-silver as well as silvered copper, and more modern metal wrappings made with brass coated copper or aluminum foil [15,16]. While most compositional analysis of metal wrappings has been done with SEM-EDS, some have also supplemented this with wavelength dispersive X-ray spectrometry (WDS) quantitative analysis of the interiors of the metal strips to get better results on the minor elements which may be below the minimum detection limits of SEM-EDS [17]. While most metal wrapped threads use thin metal strips wrapped around a fiber core, research has also been done to characterize threads produced with strips of metal coated organic material, either cellulosic or proteinaceous based [18,19]. While some studies have concentrated on textiles with different types of metal wrapped threads from India and Persia [12,20,21], the present work is the first comparative study of Indian and Persian textiles to also combine the study of the metal threads from the two cultures with dye analysis.

In this project, velvets are the subject of studies among those textile productions. Velvet is woven as supplemental warp loops on the foundation and the loops are usually later cut, resulting in the raised surface pile [22] page 80. It has a complex weaving structure and is woven by highly skilled weavers [23]. High quality velvets indicate that the culture has a high level of textile manufacture [24]. Weave structure, dyes and metal from metal threads were analyzed and compared from fifteen Persian velvets and six Indian velvets in MMA collections. Dyes were analyzed by high performance liquid chromatography with photo diode array detector. Analysis of metal of the metal-wrapped threads was performed using scanning electron microscopy with energy dispersive X-ray spectrometry. This was done in order to investigate whether the velvets from the two cultures could be attributed with certainty using these results along with historical and iconographical studies. In this paper, a part of such analysis of dyes and metal of metal threads is reported. The study involving more integrated

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results from weave structure and historical and iconographical studies is forthcoming.

Results and discussion

Natural dyes used on the velvets

Table 1 summarizes natural dyes which were suggested to have been used in Persian or Indian velvets. In the Additional file 1, suggested dyes used in individual velvets are shown.

Samples for analysis were mainly collected from piles. When pile samples were difficult to collect, samples of the foundation threads were collected instead. The fiber materials were all silk. Examples of Persian and Mughal velvet are shown in Figures 1 and 2.

[RED] The chromatograms of some of the red pile samples are shown in Figure 3 as examples. Red pile samples from the Persian velvets appeared to be dyed mainly with cochineal. Red pile samples from Indian velvets were dyed mainly with lac, although there were exceptions. One of the Indian velvets was dyed with cochineal, and one of the Persian velvets was dyed with a combination of cochineal and lac.

Carminic acid was detected from the red piles of those Persian velvets as the main colorant. Natural dyes whose major colorant is carminic acid are known to be American cochineal (*Dactylopius coccus* Costa), Polish cochineal (*Porphyrophora polonica* Linnaeus), and Armenian cochineal (*Porphyrophora hamelii* Brandt) and possibly cochineals of other species of *Dactylopius* and *Porphyrophora* genus. The composition of colorants in those cochineals is similar [25-27]. Therefore, those red piles appeared to be dyed with one of those cochineals. Wouters and Verhecken [25,26] also found that a minor component, dcII, is generally found more in American cochineal than in Armenian or Polish cochineals, and so a system using the dcII to differentiate yarn samples dyed with those insects was developed. The structure of the dcII was identified as 7-*C*-glycoside of flavokermesic acid [28]. Further, Serrano et al. [27] developed the system using multivariate data analysis to differentiate those different species of cochineals. In this paper, the system had not yet been applied to differentiate them, and the species of cochineals used on those red thread samples was not determined. Because the system evaluates minor components, it was considered essential to carefully repeat the test with the experimental conditions used in our lab in order to evaluate the ratio of color composition.

Ellagic acid was always detected from the samples in which carminic acid was detected, but not the samples dyed with lac. The ellagic acid detected from those samples was most likely derived from hydrolysable tannins [29] pages 286, 298. Those silks might have been weighted with tannins [29] page 287, [30]. It is reported that in Persia, tannins were also applied with metal salts such as alum to assist as fixers [31].

Laccaic acids were detected from the red piles from a majority of those Indian velvets. The examples are shown in Figure 3. The peak at 17 minutes is likely laccaic acid A which was found as a main red colorant in lac dye [25]. There are different species of genus *Kerria* which produce laccaic acids, though the most common lac insect is (*Kerria lacca* Kerr), and *Kerria lacca* is harvested in India, Southeast Asia, and Southern China [32] page 656.

Armenian cochineal is currently found near Mount Ararat, although it appeared to have been harvested in other regions of the Caucasus, Turkey and Iran [32] page 648, where the Safavid Empire existed. Armenian cochineal is reported to have been used in textiles found in Syria, Khotan, and Egypt from the 1st to 5th centuries [29] pages 73–75: in a caftan of 7th-century Sassanid Persia and in a hat given by Henry VIII in the first half of the 16th century [32] pages 650–652. The production center of Polish cochineal appears to have been in Central and Eastern Europe: Germany, Poland, Romania or Ukraine [32] pages 638–640. It is reported that textiles dyed with polish cochineal were also found near these regions: France, Belgium, Romania, and Hungary [32] pages 645–646, also in Italy [29] pages 67–69. It may be possible that Polish cochineal was exported to Persia via Venice in 16th – 18th centuries because American cochineal is reported to have been exported via Venice to Persia by the end of the 16th century [32] pages 630–631, 645, indicating presence of a trade route. In terms of the historical record of use of American cochineal in the Middle East, the investigation by Phipps reported that in the 16th -18th centuries, cochineal from America was exported to Spain and from there to the Middle East to supply the Ottoman emperor. It was also exported from America to the Philippines, and then using sea routes, to China, and finally to the Middle East via the Silk Road [33] page 27. Cardon and Böhmer reported that by the end of the 16th century, cochineal from America was re-exported via Venice to Persia and Central Asia [32] pages 630–631, [34]. Thus the dyes used on the red pile of those velvets could be cochineal from either America or from the Old World.

A few red foundation threads were tested. They were mainly dyed with madder. The type of madder was possibly *Rubia tinctorum* L. because alizarin and purpurin were detected as main colorants in the extracts [35].

[YELLOW] Yellow samples from those Persian velvets are often dyed with yellow larkspur (*Delphinium semibarbatum* Bien. ex Boiss, *D. zalil* Aitch. & Hemsl.). Examples of the chromatograms of samples dyed with yellow larkspur are shown in Figure 4A. The main colorants of yellow larkspur are flavonoids; they were identified as quercetin 3-*O*-

Table 1 Suggested dyes used on samples of each color from the Persian and Indian velvets

Color	Type of thread	Persian velvets		Indian velvets	
		Suggested dyes		Suggested dyes	
		Single dye used on the sample	Dye mixed to the dye in the left column	Single dye used on the sample	Dye mixed to the dye in the left column
Red	**Pile**	*Cochineal* (7/7)	Cochineal only (6/7)	*Lac* (6/7)	Cochineal only (6/7)
			Lac (1/7)		Cochineal (1/7)
	Other types of threads				Madder (1/1)
Yellow	**Pile**	*Yellow larkspur* (10/12)	Yellow larkspur only (8/10)	*Turmeric* (4/5)	Turmeric only (2/4)
			Luteolin containing dye (2/10)		Unknown yellow dye B (1/4)
		Unknown yellow dye A (2/12)			Yellow larkspur (1/4)
				Unidentified (1/5)	
	Other types of threads	Yellow larkspur (2/5)		Turmeric (1/1)	(Soluble redwood?) (1/1)
		Unknown yellow dye A (3/5)			
Yellow-2	**Core yarn, metal thread**	*Yellow larkspur (3/5)*		Unidentified (2/2)	
		Unknown yellow dye A (1/5)	Turmeric (1/5)		
		Unidentified (1/5)			
Green and Bluish Green	**Pile**	*Yellow larkspur + Indigo dye (6/8)*		*Yellow larkspur + Indigo dye (7/9)*	
		Unknown yellow dye A + indigo dye (2/8)		Turmeric + indigo dye (2/9)	
	Other types of threads	Yellow larkspur + Indigo dye (2/2)		Turmeric + indigo dye (1/1)	
Pink and Orange	**Pile**	*Safflower (11/13)*	Safflower only (3/13)	*Safflower (6/6)*	Safflower only (2/6)
			Yellow larkspur (3/13)		Yellow larkspur (1/6)
			Unknown yellow dye A (4/13)		Turmeric (2/6)
			Turmeric + unknown yellow dye A (1/13)		Unknown yellow dye C + yellow larkspur (1/6)
		(Soluble redwood?) (1/13)			
		Unidentified (1/13)			
	Other types of threads			Madder + turmeric + (soluble redwood?) (1/1)	
PinK-2	**Core yarn, metal thread**	*Safflower + turmeric (2/2)*		*Safflower + turmeric (2/2)*	
Brown and Reddish Brown	**Pile**	*Soluble redwood (3/3)*	Soluble redwood only (2/3)		
			Safflower (1/3)		

Table 1 Suggested dyes used on samples of each color from the Persian and Indian velvets *(Continued)*

Purple	**Pile**	Safflower + indigo dye + yellow larkspur (1/3)		
		Safflower + indigo dye + unknown yellow dye A (1/3)		
		Safflower + indigo dye (1/3)		
Black	**Pile**	*Tannin dye (4/4)*	Tannin dye only (3/4)	*Tannin dye (1/1)*
			Soluble redwood (1/4)	
Blue	**Pile**	*Indigo dye (5/5)*		

The dyes shown in Italic are the main dyes used in each color. The numbers in parentheses are (the number of samples in which the dye was used/the total number of samples of the color). Indian velvet of acc. no. 27.115 showed two different weaving techniques within the same velvet based on our study: the center panel and one corner showed characteristics of an Indian weaving technique and the border showed the Persian weaving technique.

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Figure 1 Persian velvet tent panel with hunting scene, ca. 1540, detailed (acc. no. 1972.189).

hexoside, kaempferol 3-*O*-hexoside and isorhamnetin 3-*O*-hexoside [36]. The UV spectra of the retention time at 15.5 and 16.5 minutes in the chromatogram of the green pile of acc. no. 27.115 are shown in Figure 4B and C respectively, as an example (The green was achieved by a combination of yellow larkspur and indigo dye.). Those peaks of the reference yellow larkspur are shown in Figure 4D and E. Yellow larkspur grows in Central Asia, from Iran and Afghanistan to northern India [32] page 207, and cultivated in Baltistan and Persia [37] page 3229. Other common names are *isparak, esperek, asbarg,* and *zalili* [31,32] page 206, [37] page 3229. This dye was reported to be the main yellow dye used by the nomadic people of Persia; the Caucasus and Turkestan [32] page 208.

Some of those yellow pile samples used a combination of yellow larkspur and another flavonoid dye containing luteolin, luteolin 7-*O*-glucoside, and apigenin (Figure 4A, a chromatogram of acc. no. 14.67 is shown as an example). Those components were also detected from a 16-17th century Safavid carpet [9]. Luteolin is found in various dye plants [32] page 171.

Figure 2 Mughal velvet fragments, mid-17th century, detailed (acc. no. 30.18).

Weld (*Reseda luteola*, L.) which is a well-known dye to find luteolin. It was used in Europe and the Mediterranean area since antiquity [29] page 215, [32] page 169 and also reported to have been used in the Ottoman Empire which was geographically near to Persia [38,39], [40] page 145. The dye found in those Safavid velvets may be from weld, or it could be different plant dyes from which those flavonoids are also found. For example, from yellow leaves of the grapevine which was reported to be used in Persia [31], quercetin-3-glucuronoside, quercetin-3-glucoside, quercetin-3-rhamnoside, myricetin, apigenin-7-glucoside, luteolin-7-glucoside and quercetin-3-rhamnogalactoside were detected [41], although it was reported that quercetin 3-*O*-glucronide is a primary flavonoid [36].

There seems to be another yellow dye frequently used on yellow samples; in this paper it is indicated as unknown yellow dye A (UYD-A). The chromatograms at 350, 300, and 520 nm of some of the samples are shown in Figure 5.

Although the dye has not been identified, the UYD-A may be a dye related to safflower plant (*Carthamus tinctoria* L.) or may include the plant. The UV spectrum of the peak at 16.7 minutes of the UYD-A matches the spectrum of kaempferol 3-*O*-glucoside standard (Figure 5A) and the retention time is very close. Kaempferol 3-*O*-glucoside was found in safflower petals [42]. However, it could be other flavonol 3-*O*-glycosides. Among flavonoids, only flavonol 3-*O*-substituted compounds absorb in the range of 350–354 nm [36,43] page 36–39. A major peak at 14.7 minutes of the chromatogram at 350 nm of the safflower reference sample (λmax 399 nm), which appears to be quinochalcone found in safflower petals [42,44], was also found in those UYD-A (λmax 395 ± 5 nm), although they were not major peaks (Figure 5A). Ct components which were described as colorless markers of safflower red by Wouters et al. [44] were also observed in those chromatograms (Figure 5B). These Ct components were detected from aqueous and alkaline extracts of safflower petals, indicating that they originate from safflower petals [44]. They are representative of safflower red and found also in the sample completely faded by light-induced accelerated aging [44]. They were characterized by their retention time, UV–vis spectrum and mass spectrum but chemically unidentified [44]. A minute amount of carthamin was also observed in some extracts of the UYD-A (Figure 5C). UV spectra of those four components from the sample acc. no. 2002.494.667 (yellow foundation warp) are shown in Figure 5, as an example. Kaempferol which is also found in safflower [44] was detected in those UYD-A (Figure 5A). The λmax of kaempferol was 370 and 266 nm, and the λmax of the peaks at 21.7 minutes in the chromatograms of Figure 5A were 369 ± 4 and 266 ± 2 nm (The UV spectra are not shown).

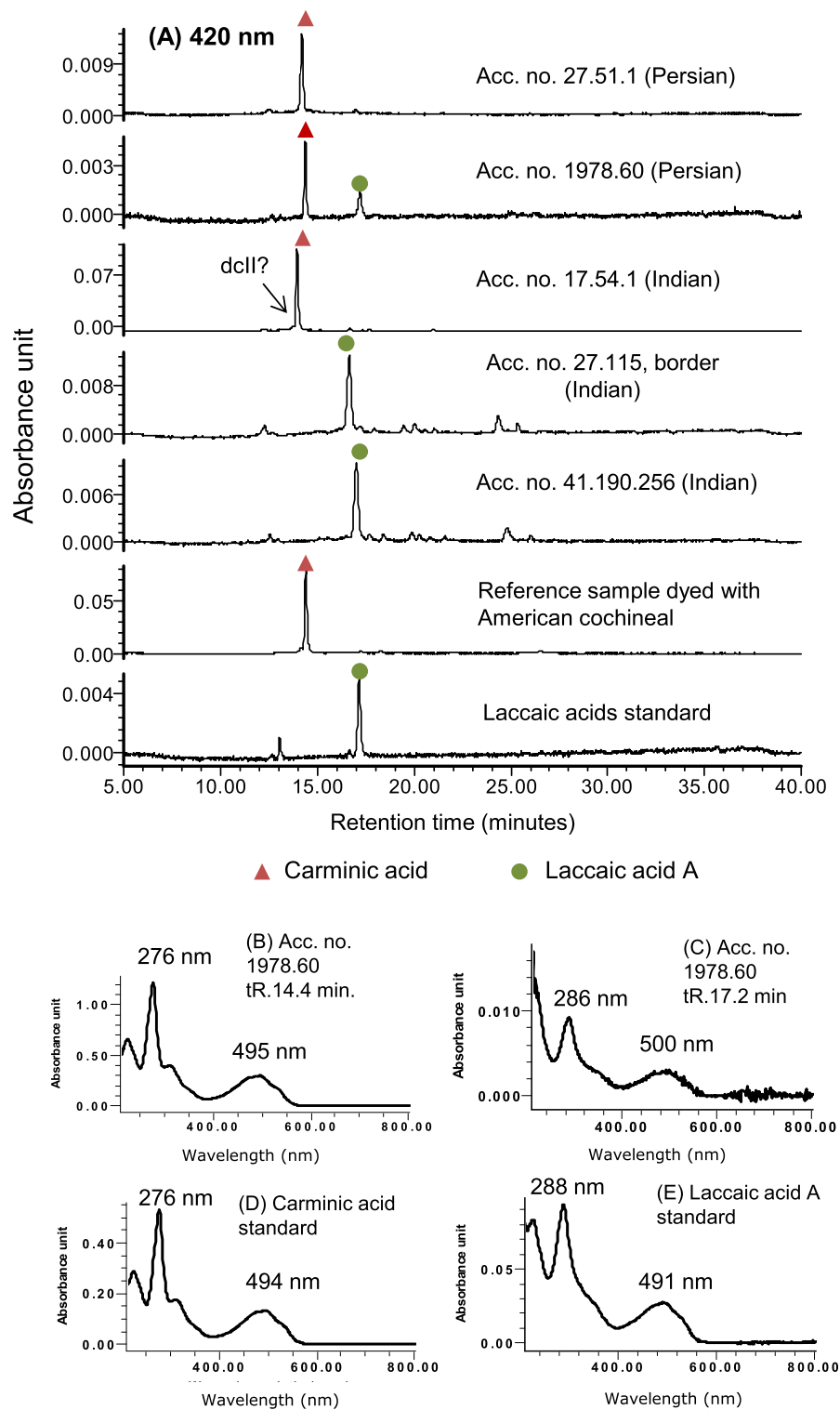Shibayama *et al. Heritage Science* (2015) 3:12

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Figure 3 Chromatograms and UV-visible spectra of selected red pile samples. Chromatograms at 420 nm of HCl extracts from red samples, from a reference sample dyed with American cochineal, and of laccaic acids standard. 420 nm was used to construct the chromatograms to indicate the peak of dcII component of cochineal **(A)**. UV-visible spectra of the peak at 14.4 minutes **(B)** and 17.2 minutes **(C)** of the chromatogram of the velvet acc. no. 1978.60 as an example, and UV-visible spectra of carminic acid standard **(D)** and laccaic acid A standard **(E)**.

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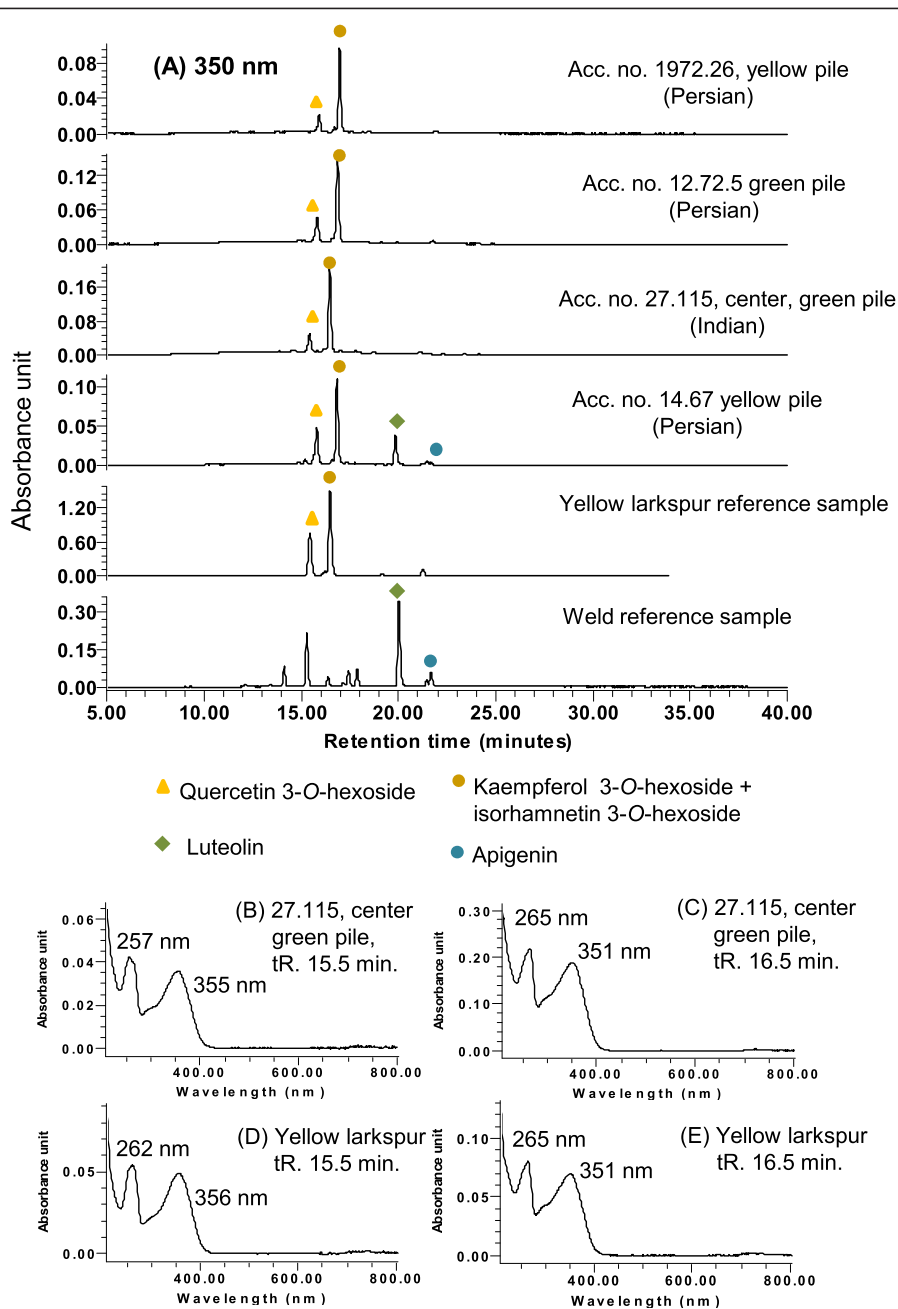
Figure 4 Chromatograms and UV-visible spectra of selected yellow and green samples dyed with yellow larkspur. Chromatograms at 350 nm of EDTA extracts from yellow and green samples and from reference samples dyed with yellow larkspur and weld **(A)**. UV-visible spectra of the peaks at 15.5 minutes **(B and D)** and 16.5 minutes **(C and E)** of the chromatograms of a green pile sample from velvet acc. no. 27.115 as an example, and of a reference sample dyed with yellow larkspur.

Safflower yellow, which is extracted from dried safflower flower petals with water before carthamin (a main red colorant of safflower) is extracted in alkaline aqueous solution to achieve bright pink [32] page 55, [44,45] page 40, may be used on those samples. Safflower yellow is reported to have been found in two 8th- or 9th-century pieces of samite from Persia, made into a chasuble [46]. However, a sample made with reference safflower yellow did not reproduce a similar

chromatogram as shown in the Figure 5A in a preliminary experiment (unpublished observations). UYD-A may be consisted of safflower yellow and other dyes, or may contain a degraded stage of safflower red dye. Further study is necessary to characterize those components to clearly identify the UYD-A.

A main dye used on yellow samples of those Indian velvets was turmeric. Examples are shown in Figure 6A.
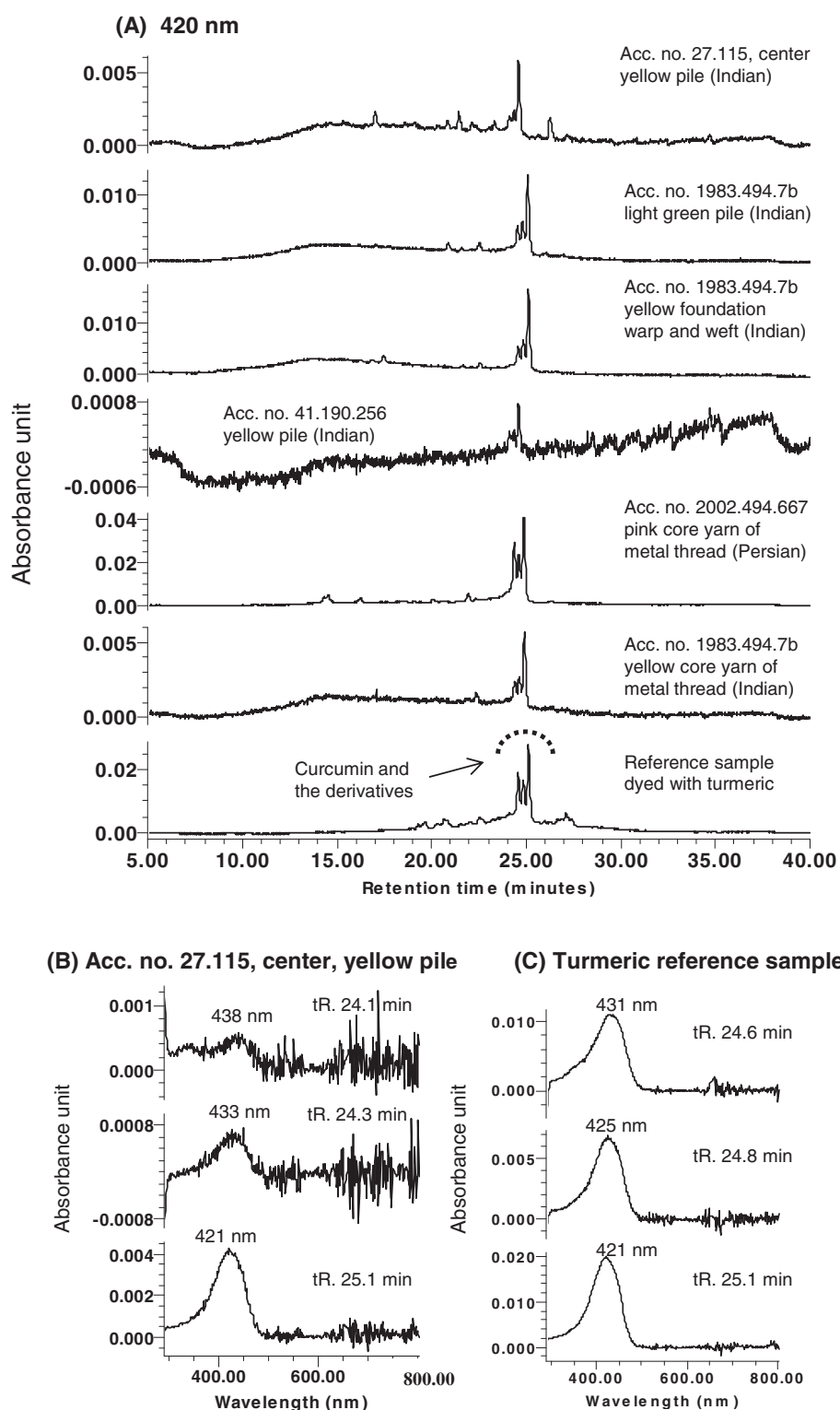
Figure 5 Chromatograms and UV-visible spectra of selected samples dyed with unknown yellow dye A (UYD-A). Chromatograms at 350 nm **(A)**, 300 nm **(B)**, and 520 nm **(C)** of EDTA extracts from samples dyed with UYD-A and from a reference sample dyed with safflower, and UV-visible spectra of selected peaks.

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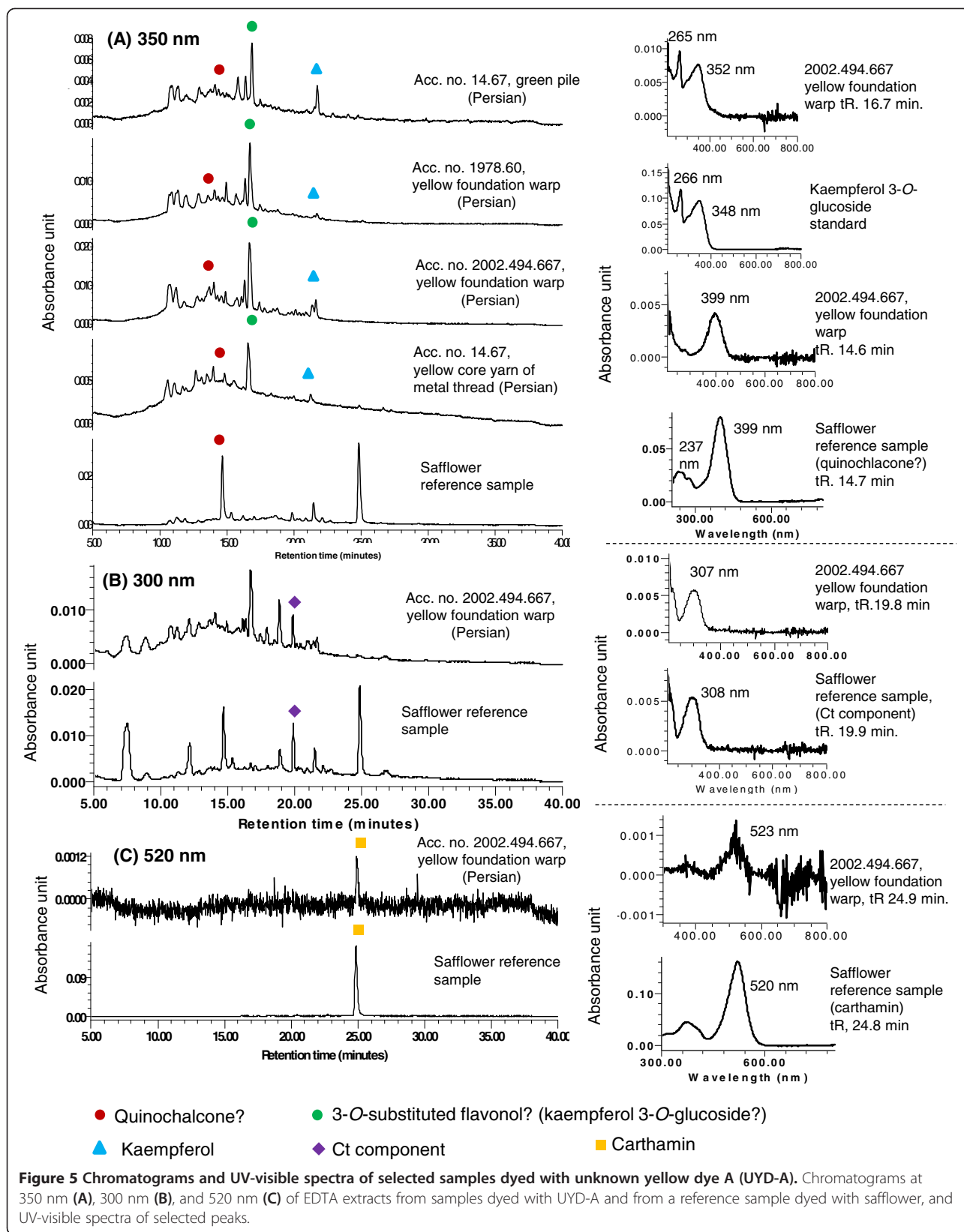
Figure 6 Chromatograms and the UV-visible spectra of selected samples dyed with turmeric. Chromatograms at 420 nm of EDTA extracts from samples dyed with turmeric and from a reference sample dyed with turmeric **(A)**. The UV-visible spectra of the three peaks of 24–25 minutes in the chromatograms of the extracts from the yellow pile of velvet acc. no. 27.115 (center part) **(B)** as an example and from a reference sample dyed with turmeric **(C)**.

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In those chromatograms at 420 nm, the UV-visible spectrum of the peak at 25 minutes matched the spectrum of standard curcumin and eluted at the same time as the standard curcumin. Curcumin is a main colorant of turmeric (*Curcuma longa* L.); the two other peaks are likely curcumin derivatives, demethoxycurcumin and bisdemethoxycurcumin, reported to be the two other curcuminoids in turmeric [47,48]. The UV spectra of the peaks at 24–25 minutes of acc. no. 27.115 (center, yellow pile) are shown in Figure 6B, as an example, and those of turmeric reference sample are shown in Figure 6C. Turmeric is thought to be originally from southern Asia, most probably from India, and from there introduced into most tropical countries [32] page 319.

Some samples were mixed with another dye such as yellow larkspur or an unidentified plant dye. From one sample of Indian velvet, emodin was detected with flavonoids. The dye is indicated as unknown yellow dye B in Table 1. Emodin is often found in *Rhamnus, Ventilago or Rheum* species [49]. Some plants of those species used in areas of India and Persia are *Rhamnus infectorius* L., *Ventilago madraspatna* Gaertn. or *Rheum emodi* Wall. (Himalayan rhubarb) [8,31,50].

Yellow core yarns of metal threads of those Persian velvets were mainly dyed with yellow larkspur, except for one sample dyed with a combination of UYD-A and probably turmeric. This results show a tendency similar to that of yellow thread samples.

[GREEN] Green or bluish green thread samples from both the Persian and Indian velvets were dyed with a combination of indigo dye and a yellow dye. Indigotin was detected from all the green samples analyzed in this study. Indigo precursors from which indigotin is produced, are found in various types of plants such as *Indigofera* species or *Isatis* species [32] page 337.

In this paper, a dye from which indigotin was detected is indicated as indigo dye; the type of plant source is not intended to be specified with the term.

In the 16th -18th centuries in India and Persia, *Indigofera tinctoria* L. appears to be an important plant source for indigo dye [31,51]. *Indigofera tinctoria* is thought to have spread with dyeing technology from India to the Middle East [51]. The dye was introduced into Mesopotamia during the 7th century and the plant grows in Huzistan (Southwestern Iran) [31].

The majority of yellow dye used on the green samples from both Persian and Indian velvets was yellow larkspur (Figure 4). The UYD-A was also used on a few Persian velvets (Figure 5A). Turmeric was used on green samples of some of those Indian velvets (Figure 6). This summary is different from the yellow samples of those Indian velvets where yellow larkspur was not used as often.

This color was not indicative enough to distinguish the two productions. It may rather be an evidence of the relationship between the two cultures. At the same time, those Indian velvets using the green threads dyed with a combination of indigo dye and turmeric may strongly represent an Indian production in particular, at the time when Persian dyeing and weaving techniques were known to be the best in the world [31,52] page 27–28.

Carthamin, a main colorant of safflower, was detected from a green pile sample from the velvet of acc. no. 1972.189 with indigo dye (Figures 1 and 7A). A hypothesis could be that the sample may have originally been purple, which color was produced by a mixture of pink safflower and blue indigo dye. Subsequently, then, the safflower was faded or discolored to yellow and currently appears to be green. Ct components which are markers of safflower [44] also appeared to be observed in the chromatogram (Figure 7B). The UV spectra of those components of the sample, acc. no. 1972.189 (green pile) are shown in Figure 7. There was a purple pile sample from one of the Persian velvets in which safflower, indigo dye, and yellow larkspur were all detected.

There were confusing cases of suggested dyes based on detected components from thread samples. Type C component which was first mentioned by Nowik [53] was detected from a light green sample of the velvet of acc. no. 1983.494.7b (Figure 8B) with colorants of turmeric and indigo dye (Figure 6A) (The data to show the presence of indigotin is not shown). Type C component is probably a degradation product of brazilein, a main color component of soluble redwood [54]. Type C component was also detected in the sample of a mixture of foundation warp and weft of the same velvet (Figure 8B). The foundation warp and weft currently appeared to be yellow overall and colorants of turmeric (yellow dye) were detected (Figure 6A), but some parts show reddish tone. Detecting type C component from the foundation threads suggests that it was dyed with a combination of turmeric and soluble redwood. Because the Type C component was not a major component in the light green thread sample (Figure 8B), it was speculated that the light green thread sample may have been contaminated with type C component from the foundation warp and weft. Also, indigotin was detected from the foundation thread sample of the same velvet and the indigotin may have contaminated the foundation threads from the green and light green piles. Those warp and wefts are tightly packed in the velvets. Minute pieces of fiber from the different colored threads may have been attached to the threads. Thread samples were examined under an optical microscope of low magnification to remove contaminated fibers before extracting dyes; however, the level of magnification was not enough to observe those contaminations. This type of contamination was often observed in those samples, as noted in the Additional file 1.
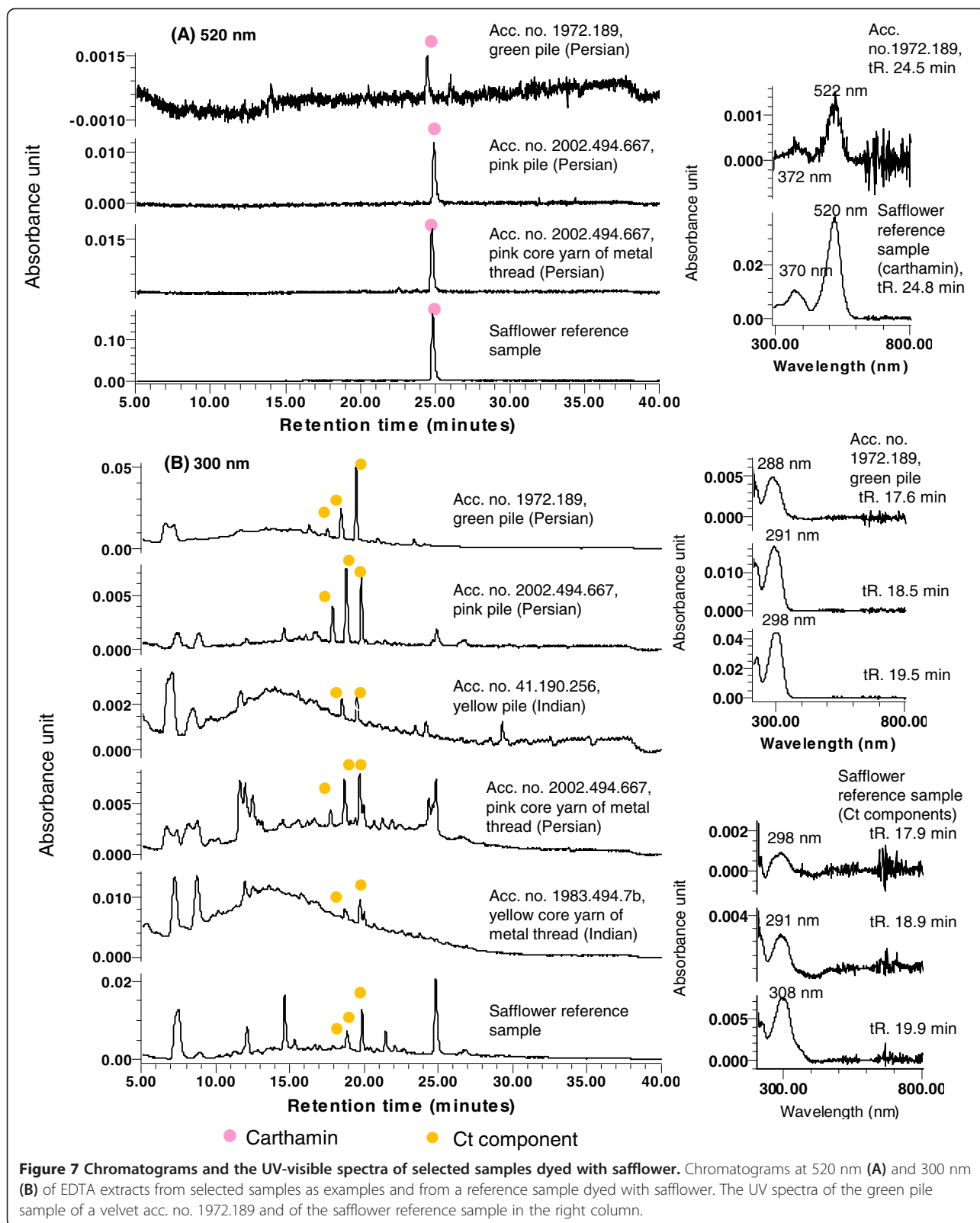
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Figure 7 Chromatograms and the UV-visible spectra of selected samples dyed with safflower. Chromatograms at 520 nm **(A)** and 300 nm **(B)** of EDTA extracts from selected samples as examples and from a reference sample dyed with safflower. The UV spectra of the green pile sample of a velvet acc. no. 1972.189 and of the safflower reference sample in the right column.
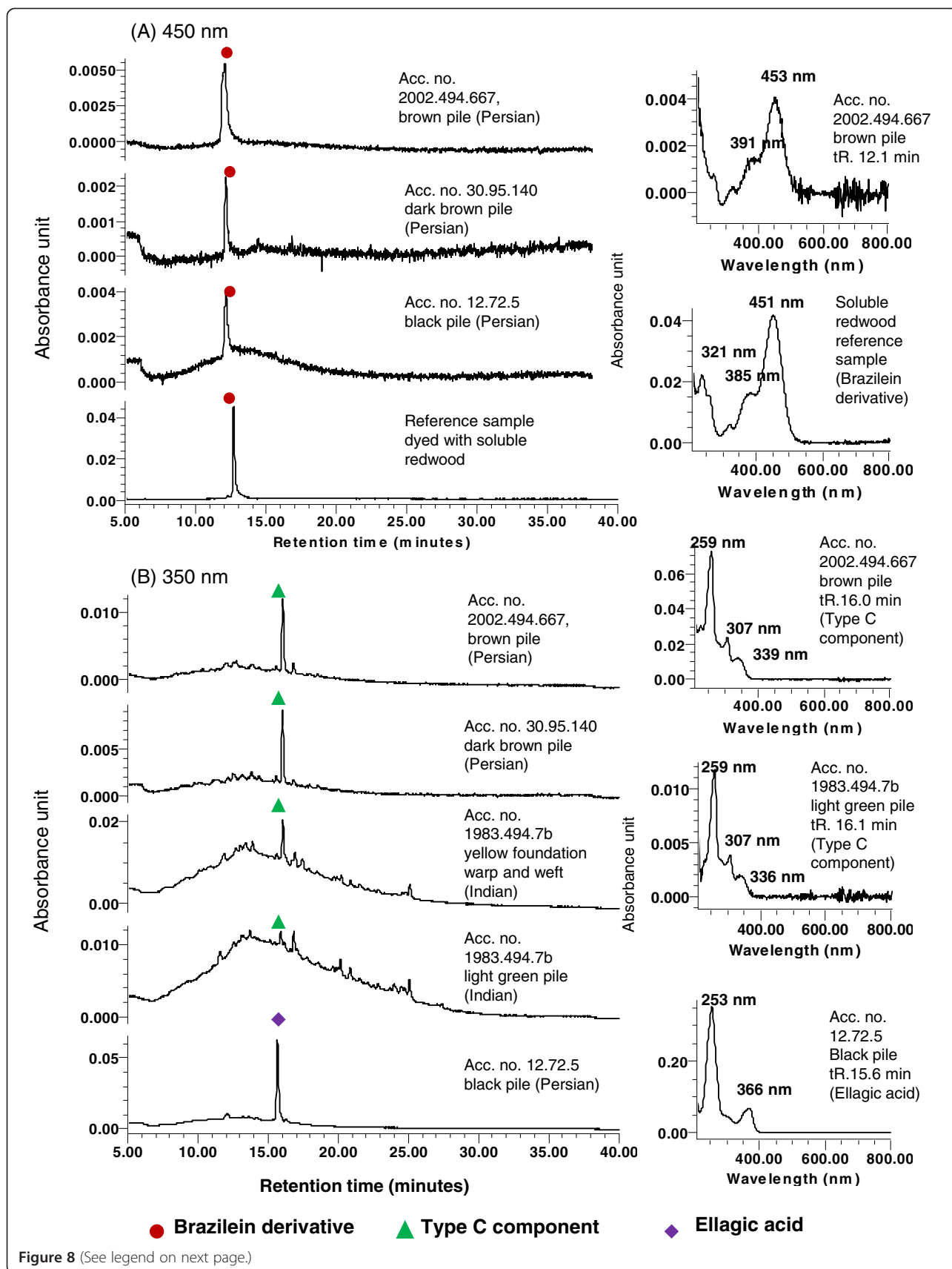
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Figure 8 (See legend on next page.)

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[PINK and ORANGE] Pink or orange pile samples from both velvets appear to be dyed with safflower (*Carthamus tinctorius* L.) or a combination of safflower and other dyes. The UV-visible spectra and the retention times of the main colorant of those samples were compared with the main colorant detected from a reference sample dyed with safflower, and the λmax of the main colorant (372, 522 nm) was compared with those of carthamin in literature as identified [55]. The chromatograms of the selected samples dyed with safflower are shown in Figure 7.

In Persian velvets, yellow larkspur and UYD-A were mainly added to safflower for color variations. In Indian velvets, yellow larkspur or turmeric were added to safflower. However, there were exceptions as shown in Table 1.

From the yellow pile sample of the Indian velvet of acc. no. 41.190.256, Ct components which indicate a use of safflower [44], were detected along with colorants of turmeric (Figures 6A and 7B). The pile is currently light yellow; however the yellow pile may have originally been orange or pink dyed with a combination of safflower and turmeric.

There were Persian velvets in which the metal threads had pink core yarns. Also there were two core yarn samples of an Indian velvet whose current colors are yellow but from which Ct components (markers of safflower) [44] were detected (Figure 7B, acc. no. 1983.494.7b yellow core yarn of metal thread, as an example). This may suggest that the original color of the core yarn of the metal thread might have been pink. They were all dyed with a combination of safflower and turmeric (Figures 6A and 7A, and B). Turmeric, a characteristic of Indian production, was used for the pink core yarn in both Persian and Indian velvets.

[BLACK] Black pile samples from both the Indian and Persian velvets appeared to be dyed with tannins. Ellagic acid, which is likely formed from hydrolysable tannin [56], was detected at 15.6 minutes from those black samples (Figure 8B). In one of the black thread samples of Persian velvet (acc. no. 12.72.5), a brazilein derivative formed by acid extraction of brazilein, the main colorant of soluble redwood [53], was detected in addition to ellagic acid, indicating the use of soluble redwood with tannins (Figure 8A and B). Those black pile samples appeared to be more brittle than other colored samples and those black piles missing from the velvets. This was likely caused by iron-mordant being used with tannins to achieve the black color [56,57] page 95–96.

Ellagic acid is produced from ellagitannins under hydrolytic conditions [58] page 91. Ellagitannins represent one of two subdivisions of hydrolysable tannins (the other is gallotannins) [58] page 91, [59]. Ellagitannins are found in *Terminalia* species, e.g. myrobalan (*Terminalia chebula* Retz.) [58] page 122, and also in *Quercus* species with gallotannins [60]. Walnut pellicle and seeds (*Juglans regia* L.) contains both ellagitannins and gallotannins [61,62]. Although catechu (*Acacia catechu* Willd.) is known to contain a large amount of condensed tannins [58] page 14, *Acacia* species are also known to contain both hydrolysable and condensed tannins [60].

Plant sources which are known to be used for brown or black in Persia include walnut (*Juglans regia* L.), Valonea oak (*Quercus aegilops* L.*)*, pomegranate (*Punica granatum* L.*)*, and oak gall (*Quercus* species) [31,52], [63] page 103. Plant sources for brown and black in India include catechu, myrobalan, *Quercus fenestrate* Roxb., leaves of teak (*Tectona grandis* L.f.*)*, pomegranate (*Punica granatum* L.) and *Soymida febrifuga* A.Juss. [8,64] page 64. When dyeing textiles with those tannin dyes for black or brown, the process often included the addition of iron-containing substances. Indigo dye was also known to be used to dye black in the both cultures [31,64] page 64.

[BROWN] Brown and reddish brown samples from the two Persian velvets were dyed with soluble redwood and a combination of soluble redwood and safflower respectively. A brazilein derivative was detected from those samples, indicating that those samples were dyed with soluble redwood (Figure 8A shows the chromatograms and the UV spectrum of some of the samples as examples). Type C components were detected from those samples as well (Figure 8B shows the chromatograms and the UV spectrum of some of the samples as examples).

[BLUE] Blue samples from Persian velvets were dyed with indigo dye. Indigotin was detected from all the blue samples. The chromatogram of the extract from the dark blue pile of the Persian velvet (acc.no. 09.50.1107) showed the presence of both carthamin and indigotin suggesting that safflower and indigo dye were used on the dark blue sample. Currently the color appeared to be dark blue to the naked eye, however originally it may have been more purplish.

Metal-wrapped threads

Samples of metal-wrapped threads from seventeen different textiles were analyzed to characterize the compositions of the metal strips used to cover the threads [15,18]. Twenty-

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one different threads from seventeen different pieces were analyzed, as four of the pieces contained two different types of metal-wrapped threads (see Table 2). The metal substrates were in all cases silver, ranging in composition from nearly pure silver to ninety-six percent silver. Copper was the only additive to the silvers detected by EDS. Gold was detected on the surfaces of sixteen of the twenty-one threads (due to corrosion and blackening of the silver substrates, gilding was not always evident by visual examination alone). In all four of the textiles with two different types of metal-wrapped threads, one was found to be gilt-silver, while the other was only silver. Only one of the textiles with a single type of metal-wrapped thread was found to be silver without gilding. The metal strips used are very fine, averaging only about 0.2 mm in width. The metals strips ranged in size from about 0.1 mm to 0.3 mm in width, with only one thread significantly wider, acc. no. 46.156.5, found to contain a metal strip nearly 0.5 mm in width.

Looking at the Persian and Indian textiles separately, it does appear that a difference is seen in the silver used in the metal wrappings. While the Persian metal thread wrappings ranged in composition from about 96 to 99 percent silver, the five wrappings examined here from the four Indian textiles (acc. nos. 27.115, 30.18, 1974.272.1 and 1983.494.7b) all consisted of nearly pure silver, with only about 0.2 percent copper detected in the metals. Indeed one of these textiles, acc. no 1974.272.1, had originally been classified as being Persian. However, even before the results of the metal analysis was known, re-examination of the textiles for the present study had reclassified this piece as being of Indian origin, rather than Persian as originally thought. This would appear to be consistent with the results of the metal wrapping analyses.

The three Persian velvets and two Indian velvets had core yarns of metal thread that appeared to be dyed with the same type of dye: a combination of safflower and turmeric. Although the dye used on both sets of metal thread is the same, the metal composition of the two cultural types follows a similar tendency as was observed by the metal thread analyses. The metal composition of the Indian velvet metal thread consisted of nearly pure silver, but that of the Persian velvet metal thread was slightly less pure, containing some additional copper.

Table 2 SEM-EDS analyses of metal wrappings

Identification		Weight %		Width	
MMA Acc. No:		Ag	Cu	(mm)	Gilding
27.51.2	Persian	98.8	1.2	0.34	G
27.51.1	Persian	96.8	3.2	0.32	G
1972.26	Persian	99.5	0.5	0.14	NG
52.20.13	Persian	98.3	1.7	0.20	G
52.20.11	Persian	99.0	1.0	0.27	G
1972.189	Persian	97.7	2.3	0.24	G
14.67	Persian	97.6	2.4	0.14	G
12.72.5	Persian	96.0	4.0	0.12	G
		98.6	1.4	0.14	NG
46.156.5	Persian	98.9	1.1	0.25	G
		99.3	0.7	0.46	NG
30.59	Persian	99.2	0.8	0.17	NG
		98.3	1.7	0.26	G
11.134.1	Persian	97.8	2.2	0.13	G
2002.494.667	Persian	97.8	2.2	0.25	G
30.95.140	Persian	97.5	2.5	0.20	G
27.115	Indian	99.8	0.2	0.28	NG
		99.7	0.3	0.27	G
30.18	Indian	99.8	0.2	0.23	G
1983.494.7b	Indian	99.8	0.2	0.19	G
1974.272.1	Indian	99.8	0.2	0.34	G

Weight percentages of silver and copper detected in each sample are provided, as well as the width of the metal wrappings in millimeters. The presence of a gilding layer is indicated by G, with NG for not gilded. The results are organized by the individual textiles, listed by the Metropolitan Museum of Art accession numbers.

Experimental
High performance liquid chromatography with photodiode array detector (HPLC-PDA)
Materials
Small pieces of pile, foundation warp and weft threads were taken from the velvets. Some of these samples had been previously collected when the velvets were treated for conservation and mounting and then kept in each object's file at the Department of Textile Conservation (DTC) of MMA.

Reference samples to be compared were prepared using the following natural dyes by conservators at the DTC or by a scientist of the Museum's Department of Scientific Research; American cochineal (*Dactylopius coccus* Costa), madder (*Rubia tinctorum* L.), turmeric (*Curcuma longa* L.), safflower (*Carthamus tinctoria* L.), indigo (*Indigofera tinctoria* L.), weld (*Reseda luteola* L.), and brazilwood (*Caesalpinia echinata* Lamarck). The dyeing method used in the study basically followed Schweppes's method [65] but with some minor differences. Aluminum mordant was used for cochineal, madder, weld and brazilwood. A reference sample dyed with yellow larkspur (*Delphinium semibarbatum* Bien. ex Boiss) was provided by Professor Richard Laursen of Boston University.

The following standard color compounds, carminic acid, ellagic acid, emodin, curcumin, indigotin, alizarin, purpurin, apigenin, and quercetin 3-*O*-glucoside were purchased from Sigma-Aldrich Corporation (St. Louis, MO), and luteolin,

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luteloin 7-*O*-glucoside, kaempferol 3-*O*-glucoside and iso-rhamnetin 3-*O*-glucoside were purchased from Chroma-Dex, Corp. (Irvine, CA). Laccaic acids were graciously provided from Gifu Shellac Manufacturing Co., Ltd. (Gifu, Japan).

Methanol, formic acid, hydrochloric acid (HCl), dimethyformamide (DMF), and disodium ethylenedi-aminetetraacetate dihydrate (Na_2EDTA) of analytical re-agent grade were purchased from Fisher Scientific (Pittsburg, PA).

Extraction method

Acid extraction is effective in releasing color compounds of mordant dyes by hydrolyzing metal-dyestuff complex [29] page 22, and a method developed by Wouters and Verhecken [25] using hydrochloric acid (HCl) (a mixture of 37% $HCl/methanol/H_2O$, 2:1:1 (v/v/v)) has been widely used [29] page 40, [66-68]. Different concentrations of HCl, such as 0.5 M HCl in methanol [69] and 3 M HCl in ethanol [70], also have been used. Additionally, in recent years, several studies or comparative tests of extraction method have been performed in order to improve yields and/or unwanted degradation or reactions of color compounds such as hydrolysis of *O*-glycoside, decarboxylation or methylation of colorants during extraction using acids [71-75]. In those studies, a different extraction method was selected as the more suitable method such as 2 M trifluoroacetic acid in water/methanol: water (1:1, v/v) [71], Na_2EDTA in water/DMF (1:1, v/v) [72], EDTA or formic acid method [73], a mixture of oxalic acid and pyridine [74], or a combination of mild oxalic acid with traditional HCl hydrolysis for textile samples [75], and also it was found that some results using the same method are not repeatable [72]. This may indicate that each method has pros and cons and what is the most suitable method varies depending on how results are evaluated.

The extraction method used in this study was one that has been gradually modified based on those studies of extraction, and by examining results obtained by different extraction methods tried over the years. When adapting the proposed methods mentioned above, practical aspects such as compatibility of the reagents to the HPLC column and system in our lab, repeatability, or speed of the extraction procedure were considered for the modification. Further improvement of extraction method has been carried out to increase the yield and to provide better information as to the dye source since the time when this study was carried out.

In this study, depending on the target color compounds predicted to have been used on the sample, three extraction methods were employed. For red, dark red, black, and brown thread samples, a method of 1 N HCl was used, modified from a method developed by Wouters

and Verhecken [25], in particular to detect brazilein derivative as a sharp peak in the chromatographic conditions of this study. And additionally to obtain better yield for carminic acid than that with a method of Na_2EDTA [73] and also generally a lower chromatographic background than that of the method using a mixture of 37% $HCl/methanol/H_2O$, which was probably as a result of less decomposed materials from samples by the weaker acid (unpublished observations). For yellow, green, orange, and pink thread samples, a method of Na_2EDTA was used which was slightly modified from a method developed by Zhang and Laursen [73]. With this mild extraction method, flavonoid *O*-glycosides, and also curcumin and carthamin were detectable. For blue and green thread samples, a method of DMF was used to make indigotin become soluble [72,76]. In the case of green samples, they were extracted first with the method of Na_2EDTA for yellow color components, and then the residual threads were extracted with a DMF method.

[Method of 1 N HCl] A dye was extracted from an each thread sample (0.1 – 1 mg, 0.4 - 2 cm) with 100 μL of 1 N HCl in de-ionized water/methanol (2/3, v/v) at 90-95°C for 15 minutes in a dry bath incubator; the extract was then evaporated in a vacuum desiccator. The residue was dissolved in 15 μL of 17.6% formic acid in de-ionized water/methanol (1/1, v/v) and all the solution was injected into the HPLC system.

[Method of Na_2EDTA] A dye was extracted from an each sample (0.1 – 1 mg, 0.4- 2 cm) with 100 μL of 0.001 M Na_2EDTA in de-ionized water/methanol (2/3, v/v) at 60-70°C for 20 minutes in a dry bath incubator after the sample was left for an hour at room temperature (RT) in the solution; the extract was then evaporated in a vacuum desiccator. The residue was dissolved in 15 μL of 17.6% formic acid in de-ionized water/methanol (1/1, v/v) and the entire solution was injected into the HPLC system.

[Method of DMF] A dye was extracted from an each sample (0.1 – 1 mg, 0.4- 2 cm) with 10–15 μL of DMF at 60-70°C for 20 minutes after the sample was left for an hour at RT in the solution. The extract was then evaporated in a vacuum desiccator. 7–8 μL of DMF was added if all the DMF of the extract was evaporated and then 7–8 μL of methanol was added, and the entire solution was injected into the HPLC system.

HPLC-PDA conditions

The analytical system used consisted of a 1525 μ binary HPLC pump, 2996 PDA detector, 1500 series column heater, and in-line degasser and a Rheodyne 7725i manual injector with 20-μl loop (Waters Corporation, Milford MA). An Xterra RP_{18} (3.5-μm pore size, 2.1 mm I.D. x 150.0 mm) reverse-phase column was used with a guard column (Xterra RP_{18} 3.5-μm pore size, 2.0 mm I.D. x10.0 mm) (Waters Corporation, Milford MA) with a flow rate of 0.2 ml/min. The column prefilter (2-μm pore size,

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Direct-Connect Universal Column Prefilter, Alltech Associates, Inc., Columbia MD) was attached in front of the guard column. The column temperature was 40°C.

The mobile phase was eluted in a gradient mode of methanol (A) and 0.88% formic acid in de-ionized water (v/v) (pH 2.3) (B). The gradient system was 90% (B) for 3 minutes → to 60% (B) in 7 minutes in a linear slope → to 0% (B) in 25 minutes in a linear slope and held at 0% (B) for 5 minutes. The operation and data processing software was Empower Pro. (2002).

Scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDS)

Small samples of metal-wrapped threads were taken from the textiles and the metal wrappings examined using an Oxford Instruments INCA Energy 300 Microanalysis system energy dispersive X-ray spectrometer with a LEO 1455 variable pressure scanning electron microscope, operated at an accelerating voltage of 20.0 kV. The metal strips were separated from the threads and attached to pure carbon sample mounts for examination in the SEM. The samples were flattened and arranged on the mounts so that both the inner and exterior surfaces could be viewed. Part of the each sample was mechanically cleaned with a steel scalpel before analysis to more accurately measure the metal compositions underneath any gilding or surface corrosion. The metal samples were examined uncoated in the SEM under high-vacuum conditions. Compositional results were quantified using the INCA EDS standardless analysis software.

Conclusions

To differentiate textile productions from those two cultures has been an issue. It was reported in only one previous study that dye analysis did not yet help to differentiate them because lac and cochineal which was thought to be used only in one or the other production, were found in both productions. Additionally, sufficient identification of dyes was not accomplished, in particular of yellow dyes [6]. However, in this study, identification and characterization of dyes from a major part of the yellow thread samples (and green ones, created by mixing yellow and blue dyes) were achieved, along with dyes of other colors. The result has shown that a range of dyes used on velvets of the two groups has overall shown a difference, despite there being no type of major dye used exclusively with either the Safavid or Mughal velvets.

There were types of dyes characteristic of either Persian velvets or Indian velvets, although there were some exceptions, and some dyes commonly used in both productions. The characteristic dyes used for Persian velvets were cochineal for red pile samples, yellow larkspur and

UYD-A for yellow samples. The cochineal species used on those samples were not determined in this study. For Indian velvets, lac was used for red pile samples and turmeric for yellow samples. A combination of yellow larkspur and indigo dye used to dye green samples was relatively common to the both productions. Safflower, soluble redwood such as sappanwood and indigo and tannin dyes were used for both productions. A combination of two or three dyes was often used to create one color in both productions. Those velvets which did not show this tendency are remarked in the Additional file 1. Those velvets were confusing to differentiate as either Persian or Indian velvet, based on dyes used on the velvets, because both productions used dyes more characteristic of the other's culture.

At times, it was difficult to determine the dyes used on some of the samples from the detected components because some dyes (e.g. safflower, soluble redwood) are very light sensitive and had faded significantly. There was also probable contamination of dyes from adjacent threads in the tightly packed weave structure of the velvets.

A previous study reported that use of lac red dye would not be a valid indicator of Indian origin as opposed to Persian origin, and lac appeared in many Persian as well as Indian carpets [6]. In this study, however, there did appear to be a strong indication that cochineal was used for Persian velvets and lac for Indian velvets. One possible reason may be that the all fiber materials in this study were silk. In the earlier study, lac was detected from the red pile of three 16th – 17th century Persian carpets which were wool [7]. Lac may have been mainly used for wool and cochineal for silk in Persian/Safavid textile productions, though there were exceptions (Indian velvet, acc. no. 17.54.1 used cochineal, and Persian velvet, acc. no. 1978.60 used a mixture of cochineal and lac for the red pile). Finding cochineal in silk may be a good indication for Persian origin, and lac may be found in wool of both Indian and Persian textiles. The statement of the earlier study [6] appears to be correct for woolen fibers, but maybe less so for silk fibers. More samples need to be analyzed. Combining information of dyes, fiber materials, and possibly other factors might contribute clearer differentiation of textile productions from the two cultures.

The use of yellow larkspur in Persia was often reported in literature [31,34], however, there had been no report in which yellow larkspur was found from historic Persian textiles. The first historic textile from which yellow larkspur was found by analysis is from an Uzbekistan textile (The identification is included in the paper by Laursen R, Zhang X, Osipova S: **Analysis of Dyes in Some Nineteenth Century Uzbek Suzanis,** presented at *The 25th Meeting of Dyes and History and*

Archaeology, 2006 in Suceava, Romania, submitted to the journal of Dyes and History and Archaeology). However, this study is the first in which yellow larkspur was detected from a group of precious Persian velvets having demonstrated that yellow larkspur is a representative yellow dye of Persia. Another yellow dye, indicated here as UYD-A, appeared to be more representative of Safavid productions than of Mughal productions, also the first time to be reported. Although the dye could not be identified, it showed a characteristic chromatogram recognizable for that dye.

Whereas there had been no comparative study of metal threads from velvets of the two cultures, this study showed possible differences between metal threads of the two cultures. While all metal threads from these textiles were found to be silver or gilt-silver, there did seem to be a small difference between Indian and Persian threads. All the Indian metal wrappings consisted of nearly pure silver, while on average, the Persian threads contained nearly two percent copper. Despite this, it should be noted that several of the Persian threads did use silver of greater than ninety-nine percent purity, so that there is actually only a very small difference between the compositions of these wrappings and those found in the Indian textiles. For this study, only a small number of Indian metal-wrapped threads could be analyzed. Analysis of more of these threads would need to be completed before a firm conclusion can be made about the apparent difference between the silver used in the metal wrappings. There are studies to have reported ratios of copper and silver in the metal threads [19,20]. However, this study is the first to have suggested a possible tendency of a different ratio of copper to silver between the two productions.

Although more analysis of dyes and metal threads from velvets of the both cultures is needed, the information on dyes and metal threads combined with knowledge gained from investigation of weaving techniques and historical and iconographic studies might offer some better ideas about the origin and basic makeup of each production.

Additional file

Additional file 1: Suggested natural dyes used in each Persian and Indian velvet. Note: Two of the velvets, acc. nos. 1974.272.1 and 2002.494.667, were recorded to be Persian and Indian respectively in the Museum cataloguing system, however, they are categorized as Indian and Persian respectively in this paper based on our updated research of weave structure and historical background.

Abbreviations

HPLC-PDA: High performance liquid chromatography with photodiode array detector; SEM-EDS: Scanning electron microscopy-energy dispersive X-ray spectrometry; WDS: Wavelength Dispersive X-ray spectrometry; DTC: Department of Textile Conservation; MMA: Metropolitan Museum of Art; HCl: Hydrochloric acid; DMF: Dimethylformamide; Na_2EDTA: Disodium ethylenediaminetetraacetate dehydrate; UYD-A: Unknown yellow dye A.

Authors' contributions
NS performed the dye analysis. MW performed metal thread analysis. EGM conceived the project. All authors read and approved the final manuscript.

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