Forensic dye analysis in cultural heritage: Unraveling the authenticity of the earliest Persian knotted-pile silk carpet

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A B S T R A C T

The use of forensic dye analysis in the field of cultural heritage is introduced, and a case study is presented determining the dating of a potentially important textile fragment from the Cleveland Museum of Art. The fragment, attributed on stylistic grounds to the 15th century, is purportedly the oldest surviving example of a Persian knotted-pile silk carpet. Raman spectroscopy combined with liquid chromatography − mass spectrometry determined the dyes used in the fragment include Metanil yellow, Congo red, and indigo, possibly in its synthetic form. Based on the dates of introduction for these dyes (1879, 1884, and 1897, respectively) and the first appearance of the textile fragment in 1928, the object is shown to be almost certainly a late 19th or early 20th century creation. Furthermore, impurities found in the red dye are suggested as potential markers of a pre-1970s synthetic route for manufacturing Congo red or possibly degraded Congo red due to environmental pollutants.

1. Introduction

Dye analysis is a common aspect of forensic investigations involving crime scene evidence such as textile fibers [1], hairs [2], plastics [3], and inks [4]. These investigations employ a variety of analytical approaches including UV−visible, Fourier transform infrared (FTIR), Raman, and mass spectroscopies (MS), as well as separation techniques such as thin layer chromatography (TLC) and liquid chromatography (LC). In most instances involving textiles, the analyst seeks to differentiate a range of dyes to show similarity or dissimilarity between a piece of evidence and comparable items found on a suspect or within their possession. This approach can sometimes involve chemometric methods that help discriminate dyes based on subtle differences in their analytical data [5]. Absolute identification of the dye molecules is not always necessary.

Similar material analyses take place in museums, where technical examination of cultural heritage objects—including dye analysis—is routine [6]. In this instance, however, the goals can be more diverse, and sometimes more demanding in terms of the specificity required. For instance, precise identification of dyes is

necessary to inform decisions made by art conservators, who care for museum collections, such as defining display parameters to safeguard colorants with known light sensitivities [7]. Dye identification can also allow curators, who interpret museum collections, to suggest a particular cultural association or a specific geographic region for an artifact [8], or to establish potential trade routes connecting groups of people [9]. These investigations share many of the same practical considerations as those in crime scene evidence analyses - complex samples in minute quantities that are often irreplaceable - making the fields of forensic and cultural heritage dye analysis similar.

One "forensic" application of dye analysis to museum collections is the unmasking of forgeries or reproductions and other innocent creations that have worked their way into the art market under false pretenses. Such objects are a constant concern for museums and collectors as they represent large financial investments, pollute the art historical record, and deceive the visiting public. As a result, museum professionals have sought to identify and remove such objects from their collections, and scientific approaches to the study of questioned artifacts in combination with connoisseurship have long been useful tools for those efforts [10,11].

Throughout history, societies have used organic colorants to dye the fibers used to make textiles. Initially, these colorants were

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natural extracts from plants, fungi, and animal dyestuffs [12,13]. Examples include carmine from the cochineal insect (*Dactylopius coccus*) [14] or indigoids from the *Indigofera* genus of plants [15]. Identification of these natural dyes provides little information about the date of an object, as they have been available since antiquity and are still available today. In 1856 with the discovery of mauvine by the English scientist William Perkin, chemists began producing synthetic dyes, initially from starting materials derived from coal tar [16]. Since then, the chemical industry has generated many economically important synthetic dyes and organic pigments. Through the creation and use of synthetic dyes, a collection of temporal waypoints has been created that can link the presence of a synthetic color to specific dates of introduction [17–19]. In cultural heritage, this is referred to by the Latin phrase *terminus post quem*, or the "limit (date) after which" an object was made.

Terminus post quem dating can only provide the earliest date of manufacture. For instance, Chen and coworkers identified the synthetic dye Direct Red 23 (C.I. 29160) from red embroidery on a man's ceremonial coat (*khalat*) from Uzbekistan (2012.85) in the collection of the Indianapolis Museum of Art at Newfields (IMA) [20]; that dye was introduced in 1900 by W A. Israel & R. Kothe [17], establishing the coat as a 20th century artifact. This identification provided curators with an objective measure of the object's age that supported dating based on the garment's style and craftsmanship. When a dye is identified whose creation post-dates the purported date of the object, then the artifact's date must be reconsidered. The presence of anachronistic materials, other than those due to a repair or later addition, can be evidence of accidental misattribution or intentional misrepresentation. Examples of this approach to unmasking forgeries using a variety of analytical techniques abound in published analyses of paintings [21], postage stamps [22], and enamels [23], for instance. Many additional examples of using pigment anachronisms to identify fakes are collected in published books on forger's techniques [10,11].

Although the presence of synthetic colorants can indicate the earliest possible date of production, the latest possible date usually cannot be determined without other information, such as the object's provenance (history of ownership), since dyes theoretically remain available forever after their discovery. A relatively small number of colorants, however, saw only short periods of use that might help bookend the date; for instance, the Naphthol AS pigment PR11 (C.I.12,430) was introduced in 1911 [17], and discontinued in the mid-1990s [24]. Even in such cases, one cannot rule out the use of old caches of a defunct colorant [25], the intentional re-creation of an obsolete colorant [26], or the clever ruse of a forger to acquire period artists' materials to mislead buyers or curators [27]. Regardless, the *terminus post quem* date alone is often enough to unmask inauthentic objects, whether made to deceive or not; it is otherwise difficult to explain an object whose imagery and other traits suggest manufacture before its colorants were available.

This paper describes the application of forensic dye analysis to cultural heritage as part of a technical study of an intriguing and potentially important Persian carpet fragment (1988.243) in the collections of the Cleveland Museum of Art (CMA). The scientific analysis of museum artworks does not appear to be common in the forensic science literature; to the authors' knowledge, in the past forty years *Forensic Science International* has published only four articles based on cultural heritage [28–31], and none of them dealt with dye analysis. Partnerships between cultural heritage chemists, also known as conservation scientists, and forensic analytical chemists have in the past resulted in exciting synergy. For instance, author Smith collaborated with forensic analytical chemists at Curtin University to repurpose an ancient Egyptian pigment as a modern luminescent fingerprint dusting powder [32,33]. The authors hope that reports on the forensic analysis of cultural artifacts will be of interest to this specialist readership, especially considering art-based crimes ranked as the third largest source of criminal activity in 2014 according to the US Department of Justice and UNESCO [34].

1.1. The earliest Persian silk knotted-pile carpet fragment

In 1988 CMA acquired a fragment (1988.243) believed by some on stylistic and other grounds to represent the earliest known Persian silk knotted-pile carpet, possibly dating from the 15th century, Fig. 1. Others believe the fragment to be a fake. As detailed below, the fragment's provenance extends only as far back as 1928, when it was already in its present, fragmentary state. Despite questions raised about its authenticity, no technical or scientific analysis has been undertaken on the fragment since it entered the CMA's collection [35].

The fragment first appeared in about 1928 and was described in *Oriental Art: Ceramics, Fabrics, Carpets* by Raymond Koechlin and Gaston Migeon [36]. Migeon (1861–1930) was a French art historian and former curator at the Louvre Museum, Paris; Koechlin (1860–1931) was president of the French Council of National Museums. In their introductory essay on carpets, they state:

"We have however the good fortune to be able to illustrate here a piece of silk carpet decorated with conventionalized animals so unique in its archaic style (whether original or survival) that we feel justified in offering it as the oldest known example of a carpet containing living figures though we are unable to claim Persia or Egypt as its origin, rather than Sicily or Spain. Persia is however the most probable." [36, p. 17, pl. LXXXII].

A color photographic reproduction was included, and the text accompanying the image reads, "Piece of a silk carpet decorated with conventionalized animals and lettering decoratively distorsed [sic] … Islamic art before XV century. Belongs to Mr. George Hewitz [sic, Hewitt] Myers, Washington." The text continues, "Without doubt the oldest specimen of carpet known with the exception of the small piece with Cufic inscriptions from the excavations at
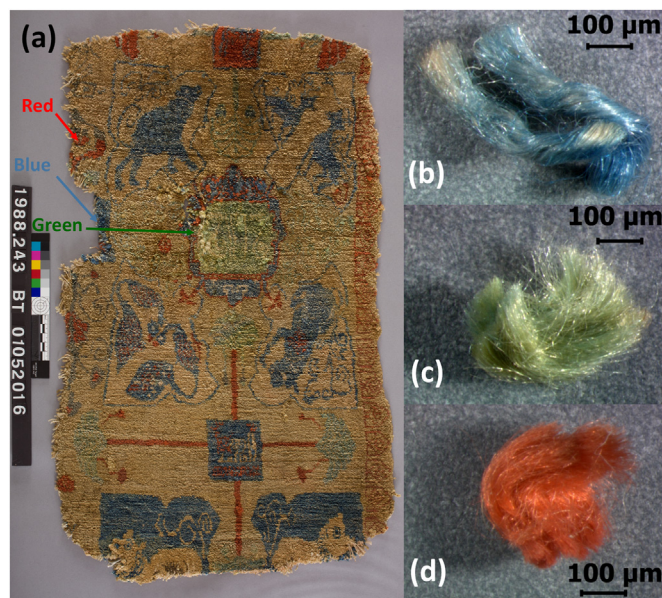
Fig. 1. Carpet fragment CMA 1988.243 (a) with samples of blue (b), green (c), and red (d) silk tufts for dye analysis. Sample locations are marked in (a). The fragment measures 60.6 × 37.5 cm. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fostat (Arabian Museum at Cairo—Ali Bey Bagtrat and Gabriel, pl. XXXI, Paris 1921)." As organic, perishable artifacts, carpets of significant age rarely survive, and silk objects are particularly prone to degradation, depolymerization, hydrolysis, and yellowing when exposed to light, heat, pollution, insects, and bio-organisms.

George Hewitt Myers (1875−1957), who owned the carpet fragment at the time of the Koechlin and Migeon publication, was a well-known carpet collector in the 1920s. He founded The Textile Museum in Washington, DC (now the George Washington University Museum and The Textile Museum) in 1925 and was its primary benefactor. By then his collection numbered some 275 carpets. In the 1930s, his attention turned to collecting other types of textiles and from that point onward his carpet collection grew only slowly [37]. Myers purchased the fragment in question from the noted Parisian dealer Paul Mallon by 1928 according to handwritten notes by Mallon's stepson in the CMA's files.

CMA records go on to say that in 1947, Maurice Sven Dimand, curator of Near Eastern Art at the Metropolitan Museum of Art, told Myers that the carpet fragment was a fake. As a result, Myers asked Mallon to refund the purchase price and presumably sent the fragment back to Paris. The fragment's whereabouts for the next four decades are unknown. Mallon died in Paris in December 1975; in 1988, his stepson, Milton Girod-Mallon, gave the fragment to the CMA [35].

In the fall of 2018, a London carpet expert and dealer asked that the fragment be radiocarbon (^{14}C) dated to lay to rest questions about its age. Radiocarbon dating is seen by some as the gold standard for ancient rug authentication and dating [38], and its use has helped uncover fake textiles, such as some of the purportedly medieval 'Buyid Silks' held in several collections, including the CMA's [39]. This request prompted author Hanson, CMA's textile conservator, to consider more conservative initial steps, and she recommended that dye analysis precede radiocarbon dating because it is less invasive. While both techniques require sample(s) to be removed, dye analysis would allow less than 1 mg of a pile knot to be taken from an unobtrusive area. In contrast, radiocarbon dating would require a much larger sample of the undyed foundation warp yarn, which would compromise the stability of the knotted-pile structure in the area sampled. One caveat to this procedure was that if only natural dyes were identified, the fragment's date would still be in question, although additional important technical information would be added to our understanding of the fragment.

2. Materials & methods

2.1. Samples

Sampling was preceded by examination using stereo, brightfield, fluorescence, and polarized light microscopy, which indicated the sampled pile was natural silk from an unrestored area of the fragment. Three small samples (bundles), one each of the red, green, and blue dyed silk were taken from the locations indicated in Fig. 1(a) without compromising the structure of the fragment. The samples were sent to the IMA for chemical analysis. Each bundle was divided into two roughly equal parts. One was used for non-destructive spectroscopic analysis followed by dye extraction and chromatographic analysis while the other was retained for future study. Authentic reference dye samples were acquired from various suppliers as detailed in Table 1.

2.2. X-ray fluorescence spectroscopy (XRF)

A Bruker Tracer III-V handheld XRF with rhodium tube, silicon-pin detector, and polymer window (~3 × 5 mm oval spot) was used

to identify any inorganic salts, i.e. mordants, applied to the silk fibers during the dyeing process. Experimental parameters included 40 keV tube voltage, 6.5 μA current, and 180 s live time acquisitions with no filtering of the excitation beam. A vacuum attachment allowed for light element detection. Elemental survey spectra were collected in the region from 0 to 40 keV.

2.3. Raman microspectroscopy

Raman spectra were acquired using a Bruker Senterra microspectrometer on a Z-axis gantry. The analysis utilized a 785 nm laser to overcome innate fluorescence in the fibers. Laser power at the sample was 7.67 mW. The spectra are the result of 3 s integrations with 120 co-additions. A 50× ultra-long working distance objective was used to focus on a single fiber. The analysis spot size was on the order of 1 μm, and the spectral resolution was in the range of 9−18 cm^{-1}. OPUS software allowed for automated cosmic spike removal, peak shape correction, and spectral calibration.

2.4. Liquid chromatography − diode array detector - mass spectrometry (LC-DAD-MS)

Analysis of dyes by LC-DAD-MS was performed as described in detail by the authors elsewhere [20]. Because sample sizes were necessarily limited and the nature of the colorants were unknown, the method described was intentionally generic, capable of identifying a wide array of natural and synthetic colorants. LC-DAD-MS was performed on dye extracts of each sample using a Thermo Accela LC system coupled to both a DAD and an LTQ electrospray ionization MS detector in sequence. The entire system was under the control of Thermo Xcalibur ver 2.2 software. LC analysis was performed using a Restek Ultra C18 reverse phase column (150 mm × 4.6 mm, 5 μm particle). The column was eluted at 0.5 mL/min using a water-acetonitrile gradient system containing 0.1% formic acid. After equilibration at 3% acetonitrile, separation was affected by a linear gradient of acetonitrile increasing from 3 to 93% in 60 min. The DAD detector was set to record spectra in the range 200−800 nm at 20 Hz. The MS collected a full-scan mass spectrum (FSMS) in the m/z range 50−2000 followed by two MS/MS spectra of fragment ions resulting from helium collision-induced dissociation (CID) respectively of the highest and second highest ion detected in the FSMS. The sequence alternated rapidly between positive and negative ionization modes.

The weights of fiber extracted for dye analysis were 396 μg for blue, 458 μg for red, and 524 μg for green. Each fiber sample was extracted in 200 μL of a 1:1 pyridine:water solution containing 50 mM oxalic acid (OAPW) at 80 °C for 60 min. Dye extraction efficiency has been studied thoroughly in the forensic science community. Wiggens has reviewed the extraction of synthetic dyes from crime scene fibers [40]; however, natural dyes from historic samples require special considerations in the cultural heritage field. Wiggens only cursorily mentions the largest class of natural, historic dyes, the mordant dyes, which he calls metallized dyes. Acidic solutions are required to hydrolyze dye molecules from their inorganic mordants, although strong mineral acids like HCl are prone to also degrading important glycosyl conjugates of natural dyes that can provide indications of plant species and other botanical and biological information. OAPW was originally developed to effectively liberate dyes from the mordant and fiber while maintaining glycosidic linkages [41], and it has since been found to recover synthetic dyes from historic textile fibers [42]. Indigoid compounds are not completely extracted using OAPW, and so a 60 min extraction in dimethylsulfoxide (DMSO) at 80 °C is used when indigoids were suspected or traces of indigotin were detected in OAPW extracts. Indigoids are vat dyes and are not bound to the

Table 1

Compounds in CMA 1988.243 as determined by LC-DAD-MS, as well as data from relevant standards. The samples are color coded for clarity according to their visual appearance.

Sample	Compound	RT (min)	λ_{max} (nm)	MS Polarity	Parent ion (m/z)	m/z of daughter ion generated from parent ion (relative abundance)
				Carpet Samples		
blue fiber	indigotin	46.0	609	neg	293	273 (6), 249 (5), 236 (100), 221 (39)
				pos	263	245 (6), 239 (15),238 (18), 235 (59), 220 (10), 219 (100)
	isatin	24.3	417	neg	n/a	n/a
				pos	n/a	n/a
green fiber	Metanil yellow (major)	43.1	418	neg	352	325 (4), 324 (19), 260 (14), 157 (6), 156 (100)
				pos	354	244 (5), 185 (5), 175 (35), 171 (5), 170 (64), 169 (100), 168 (11), 157 (77), 109 (16)
	indigotin (minor)	46.1	609	neg	293	273 (1), 249 (1), 237 (1), 236 (100), 221 (37)
				pos	263	245 (8), 239 (15), 238 (16), 235 (73), 220 (11), 219 (100)
	isatin	24.4	310, 425	neg	n/a	n/a
				pos	n/a	n/a
red fiber	ellagic acid	25.5	367	neg	301	284 (19), 258 (15), 257 (100), 229 (54), 185 (32)
				pos	n/a	n/a
	unknown	28.5	281	neg	675	595 (3), 427 (100), 363 (1), 247 (4)
				pos	677	677 (30), 660 (23), 657 (26), 650 (48), 615 (20), 597 (72), 593 (29), 587 (51), 571 (41), 563 (100), 533 (28), 501 (67), 429 (48)
	unknown	32.3	327, 478	neg	663	584 (8), 583 (35), 416 (7), 415 (100), 386 (25)
				pos	665	417 (22), 353 (100), 325 (21), 249 (12)
	Congo red	36.1	337, 505	neg	651	572 (32), 571 (100), 543 (10), 417 (6), 416 (7), 235 (7), 234 (7), 233 (11)
				pos	653	636 (6), 573 (22), 418 (100), 390 (18), 389 (79), 388 (9), 353 (85), 325 (34), 232 (6)
	pseudo-purpurin	38.0	493	neg	299	255 (100)
				pos	n/a	n/a
	munjistin	38.2	484	neg	283	265 (4), 239 (100)
				pos	n/a	n/a
	alizarin	42.2	429	neg	239	229 (35), 219 (44), 211 (100), 210 (9), 179 (19), 167 (14)
				pos	241	n/a
	Metanil yellow	43.1	417	neg	352	325 (3), 324 (17), 260 (12), 157 (5), 156 (100)

				pos	354	244 (4), 185 (4), 175 (34), 171 (4), 170 (60), 169 (100), 168 (10), 157 (74), 109 (14)
	purpurin	46.0	482	neg	255	228 (11), 227 (100), 183 (7)
				pos	257	n/a
Reference Compounds						
alizarin Fisher #A-425	alizarin	42.5	431	neg	239	239 (100), 219 (25), 212 (16), 211 (81), 195 (18), 167 (10)
				pos	n/a	n/a
Congo red Sigma #C-6767	Congo red	36.8	336, 505	neg	651	572 (39), 571 (100), 543 (9), 417 (6), 416 (7), 235 (8), 234 (8), 233 (11)
				pos	653	n/a
ellagic acid Sigma #E2250	ellagic acid	25.9	367	neg	301	301 (35), 284 (21), 258 (12), 257 (100), 229 (52), 185 (26)
				pos	n/a	n/a
indigo, syn Aldrich #229296 **indigo, gen** Kremer #36000	indigotin	46.0	609	neg	293	273 (1), 249 (1), 236 (100), 237 (1), 221 (38), 193 (1)
				pos	263	245 (6), 239 (9), 238 (14), 235 (56), 219 (100)
isatin Fluka #58240	isatin	24.4	300, 420	neg	146	118 (100)
				pos	148	130 (100), 120 (41), 92 (13)
Metanil yellow Alfa Aesar #A17527	Metanil yellow	43.3	419	neg	352	325 (3), 324 (17), 260 (13), 157 (6), 156 (100)
				pos	354	244 (4), 185 (5), 175 (32), 171 (4), 170 (59), 169 (100), 168 (10), 157 (74), 109 (14)
purpurin Fluka #82631	purpurin	46.5	480	neg	255	228 (11), 227 (100), 183 (7)
				pos	257	n/a

fiber with mordants, and therefore do not require an acidic solvent.

Following extraction, the OAPW solutions were evaporated using heat with a nitrogen purge, and the dried residues were redissolved in 100 μL of a 1:1 methanol:water solution and filtered through a 0.45 μm syringe filter to remove any insoluble materials prior to analysis by LC-DAD-MS. However, extracts in DMSO were filtered and analyzed directly. A blank chromatogram was run before each sample extract to verify that there was no carryover or contaminants from the previous injection.

3. Results & discussion

3.1. XRF

Many natural, historic dyes require the fiber to be pretreated with an inorganic salt (a mordant) prior to the dyebath to generate a washfast product [13]. The mordant binds to both the fiber and the dye molecule to create an insoluble complex. Mordants also affect the final color of the fiber: a limited number of dyes used with several mordants can subtly alter hues in a textile. The entire fiber bundle of each color was analyzed directly on the polymer window of the portable XRF prior to dividing the sample. All three fiber colors were found to contain aluminum, sulfur, calcium, potassium, and iron. This suggests the silk threads may have been treated with alum ($K_2SO_4Al(SO_4)_3 \cdot 24H_2O$), cream of tartar (potassium bitartrate, $KC_4H_5O_6$) and/or ferrous sulfate ($FeSO_4 \cdot 7H_2O$) as mordants, although greater specificity could not be determined. These results are qualitatively similar to a recent study of ancient Persian wool rugs from the Safavid Period (1499−1722) using particle induced x-ray emission (PIXE) that also identified the widespread use of Al and Fe mordants [43]. However, sulfur also exists in small amounts in the silk biopolymer fibroin, and it and the other elements detected could also occur naturally in the dust and debris that have accumulated in the fibers over time, in hard water used in the dying process, or in the previous use life of the object [44]. It is worth noting that the results of this potentially non-invasive analysis are entirely consistent with a 15th century silk textile.
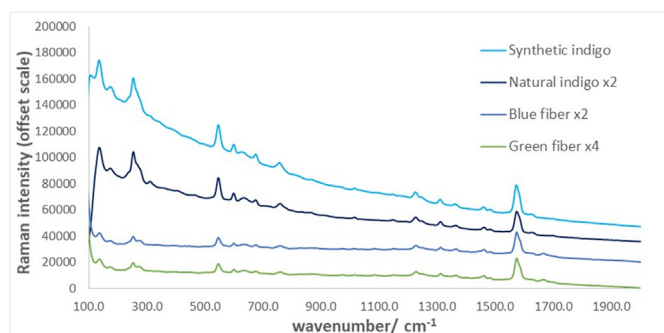
3.2. Raman spectroscopy

Raman microspectroscopy was used as a rapid, non-destructive approach to pre-screen the colored fibers for their dye content. The Raman scattering of the red fiber was extremely weak, yielding a poor quality, unidentifiable Raman spectrum. However, the Raman scattering of components in both the blue and green fibers was stronger, as shown in Fig. 2. These spectra are consistent with the Raman spectrum for both synthetic (C.I. 73000) and genuine natural indigo (C.I. 75780) as shown. The spectrum was weaker for the green fiber compared to the blue fiber, probably due to a lower concentration of indigo in the former where it is likely mixed with a yellow dye that did not yield a strong Raman spectral component.

Vandenabeele and Moens have shown that natural and synthetic indigo can be discriminated based on their dispersive Raman spectra [45]. In their study, 20 pure pigment samples, from both synthetic indigotin and natural extracts from the indigo and woad plants, were analyzed five times each to build a spectral library of known samples. Using chemometric techniques including principle component analysis, hierarchical cluster analysis, and linear discriminant analysis, the natural and synthetic samples could be separated. This approach was not applied to the data from the carpet fragment, however, because the authors did not have an appropriate number of authentic indigo standards, and the approach has not been proven on dyed fibers or extracts of historic fiber samples.
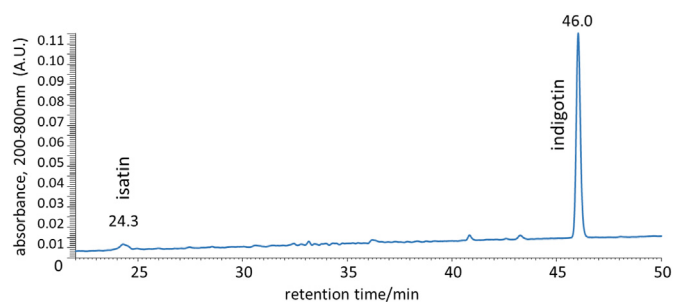
3.3. LC-DAD-MS analysis

The extracts of all three fiber colors were analyzed by LC-DAD-MS to identify principal colorant molecules, dye adjuvants, and serendipitously transferred color from the dyeing process or previous use of the textile. Fig. 3 shows the chromatogram from the blue fiber bundle extracted with DMSO. The main chromatographic peak at 46 min was identified as indigotin, the principle colorant of natural and synthetic indigo, based on its characteristic UV−vis and MS spectra [46]. Identification of each compound was based on the physical data described in Table 1, which includes chromatographic retention time, wavelength maxima in the UV−vis absorption spectrum, parent ion from the FSMS in both the positive and negative modes, and the MS/MS fragmentation data whenever possible. Additionally, comparisons were made with data from reference materials run under the same conditions and literature resources [47].

Indigo was found in both the blue and green thread samples

Fig. 3. Chromatogram of the DMSO extract of the blue fiber showing the main chromophoric peak assigned to indigotin and a minor peak for the degradation product isatin. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

(Table 1), although only a relatively small amount was seen in the green fiber. The presence of indigo in these samples, and the reduced signal of indigo in the green thread, are consistent with their Raman spectra (vide supra). The blue fiber may also contain a small amount of isatin; a minor component elutes at 24.3 min, which is similar to that of an isatin standard (Table 1). Because of the low amount of this component present in the blue fiber, the UV−vis and MS signals were both weak, making conclusive assignment difficult. However, since isatin is a known light-induced degradation product of indigo and is also used in its synthesis, its presence in the sample is not unexpected [46]. No other indigoids were found, including the red isomer of indigotin, i.e. indirubin, which could indicate that the indigo in the sample is synthetic. Textiles dyed with natural sources of plant-derived indigo commonly contain both indigo and indirubin, along with isatin, although an absolute criterion for determining if indigo is natural or synthetic based on LC-MS data remains elusive. Synthetic indigo was first produced by the German manufacturer BASF in 1897 [17]. The potential presence of synthetic indigo could indicate that the silk in the carpet fragment was dyed sometime between 1897 when the dye was first available and 1928 when the carpet was first documented.

In addition to indigo, the green fiber was also found to contain the synthetic dye Metanil yellow (C.I. 13065), also known as Acid Yellow 36. Based on the chromatographic data, the amount of Metanil yellow is much greater than that of indigo in the green fiber. As a poor dispersive Raman scatterer with near-infrared excitation, Metanil yellow was not detected in the initial spectroscopic survey. Metanil yellow was first synthesized by C. Rumpff in 1879 [17]. It has been found in other late 19th/early 20th century museum textiles using LC techniques including several Uzbek suzani [48], a sitara that hung on the Bab al-Tawba inside the Ka'ba in Mecca [49], and a Baluchi prayer rug and bag [50].

The red fiber sample was found to contain predominantly synthetic dyes along with a smaller amount of several compounds from natural sources (Table 1). The natural materials detected include ellagic acid, a hydrolysis product of tannins from gallnuts, which is sometimes used to treat silk as a weighting agent. Because silk was sold based on its weight, the addition of metal salts or organic compounds to the silk fiber or fabric added weight and thus increased its price. Weighting silk was a common practice in the 19th century, and Hacke reports the use of tannic compounds for this purpose [51]. Unfortunately, weighting negatively affects the preservation of silk. Selected ion monitoring at ellagic acid's psuedomolecular negative ion mass of m/z 301 revealed a trace presence in the green fiber extract too, but no conclusive evidence was found for it in the blue sample.

In addition, several components consistent with the use of the

Fig. 2. Raman spectra of the green (bottom) and blue (lower middle) fibers from CMA 1988.243 compared to that of synthetic indigo (top) and natural indigo (upper middle). The offset intensity scale shows comparative signal strength, although some spectra were multiplied as indicated in the legend to increase their readability. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

natural plant-based dye madder were identified in the red dyed silk: munjistin, pseudopurpurin, purpurin, and a small amount of alizarin. Of the *Rubia* species used as dyestuffs previously examined by LC methods, only *Rubia tinctorum* is known to contain both alizarin and purpurin [52]. Their combined presence in the red fiber suggests this is the plant species used to generate the dye appearing as a minor color component in the carpet fragment.

In addition to the natural compounds found in the extract of the red fiber sample, the synthetic dye Metanil yellow was again identified in the chromatogram at 43.1 min in significant quantities, suggesting intentional use rather than transfer from other areas of the textile. Three other major components eluted at 28.5, 32.3, and 36.1 min. One of the primary coloring components observed at 36.1 min was identified as the synthetic disazo dye Congo red (C.I. 22120). Congo red, created by P. Bottinger in 1884 [17,53], was the first of the so-called "direct dyes," Direct Red 28, meaning that it is taken up directly by the fiber without the need of a mordant. Interestingly, in a recent LC-DAD analysis of red dyes in 20th century Iranian carpets, the azo dyes Acid Red 88 (C.I. 15620) and/or Acid Orange 7 (C.I. 15510) were found on 14 of 18 red fiber samples, sometimes also with natural madder [54]. The use of both natural and synthetic dyes in the same colored fiber was also observed by the authors in the study of a 20th century Uzbek garment [20].

The other two major components observed in the red fiber sample have not yet been positively identified, although they are similar in their MS behavior to Congo red and are shown by the evidence here to be structurally related. The FSMS of Congo red in negative ionization mode from the chromatogram in Fig. 4 is shown in Fig. 5(a). It contains the pseudomolecular ion $[M - H]^-$ peak at m/z 651 along with a peak of m/z 325 that is assignable to the doubly charged ion $[M - 2H]^{2-}$ [55]. Furthermore, cluster ions were identified at higher m/z including 978 and 1305, although these are highly dependent on the ESI conditions.

Fig. 5(b) shows the MS/MS spectrum of the Congo red anion of m/z 651 in the FSMS after CID. Fig. 6 illustrates the fragments formed in the MS/MS experiment. Cleavage between the nitrogens of the azo group yields an ion of m/z 416 along with smaller fragments at m/z 233, 234, or 235 [55]. Sequential neutral losses of two equivalents of SO3 from the parent ion forms ions at first m/z 571

Fig. 5. Negative ionization FSMS of Congo red eluting at 36.1 min in the red fiber from CMA 1988.243 (a), and MS/MS spectrum from CID of the anion at m/z 651 (b). These data are consistent with those from a Congo red standard (not shown).
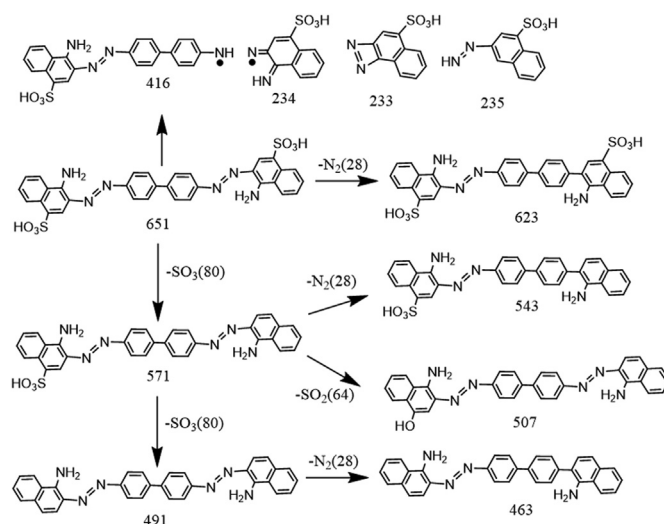
Fig. 6. MS/MS fragmentation scheme for Congo red. Molecules are shown as neutral species, but the molecular weights are for the singly charged negative ion.

and then 491. Neutral losses of N2 from the parent molecule and the mono- and di-de-sulfonated species generate ions at m/z 623, 543, and 463. The neutral loss of one SO3 and one SO2 from the parent molecule to leave a hydroxy-substituted analog accounts for the peak at m/z 507.

The two unidentified compounds observed in the chromatogram of the red fiber extract have similar mass spectra to Congo red with respect to the presence of $[M - H]^-$ and $[M - 2H]^{2-}$, although their psuedomolecular ions are larger in mass by 24 (- m/z 675) and 12 units (- m/z 663), respectively (Table 1). Like Congo red, the fragmentation of their $[M - H]^-$ ion in negative ionization MS/MS includes loss of SO3 (−80) to give daughter ions (of relative abundance) m/z 595 (3%) and 583 (35%), respectively, indicating they are sulfonates. While the daughter ion m/z 595 is too small to attempt further CID fragmentation (MS/MS/MS), the daughter ion at m/z 583 was further fragmented to produce a series of MS/MS/MS subfragments, among which were ions of m/z value 555 (21%), 519 (8%), 503 (100%), and 475 (20%). When these ions are mapped in the
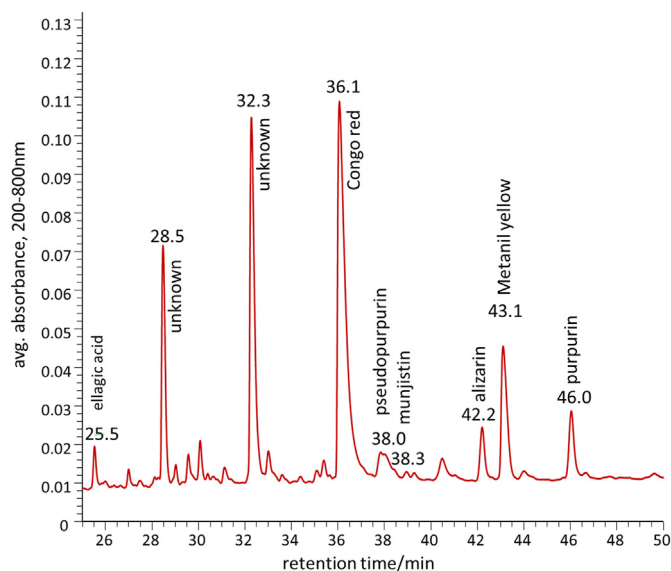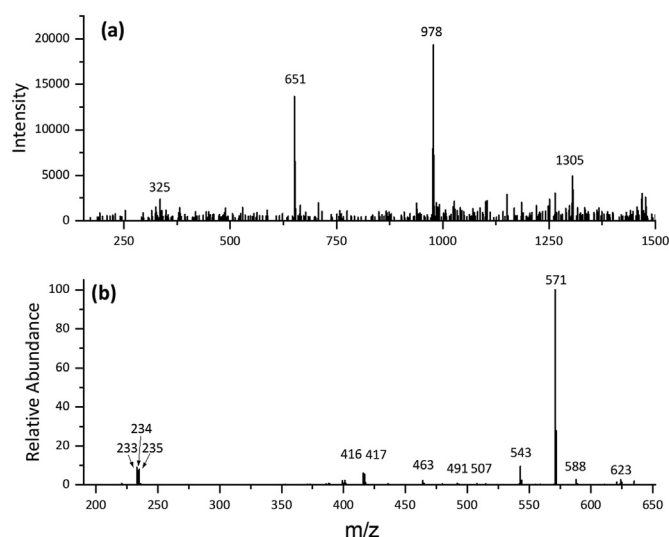

Fig. 4. Chromatogram of the red fiber from CMA 1988.243 recorded at 200–800 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

scheme shown in Fig. 7, fragmentation for the unknown compound of *m/z* 663 shows an analogous pattern to Congo red. These similarities in the MS data suggest the unknowns are related to Congo red, either as synthetic byproducts of its manufacture or from subsequent reactions or degradations.

LC-DAD-MS analysis of modern Congo red stains from three different suppliers (Sigma, Damon Educational Division, and Fisher Scientific) exhibited high purity and did not show the additional unknown compounds. Importantly, light aging experiments conducted with the pure reference samples of Congo red from Sigma and Damon did not create the two unknown compounds as photoproducts of Congo red degradation (not shown). The early synthesis of Congo red used benzidine as starting material, but it was abandoned in the 1970s due to its carcinogenic nature (47, 53). The Congo red in the carpet fragment may have been made using this earlier synthetic procedure, potentially resulting in synthetic byproducts not seen in modern manufacture of the dye. Indeed, other studies of Congo red have noted major impurities [56,57], and one of those studies separated the compounds using normal phase TLC with an elution order consistent with that found here using reverse phase LC [56]. The contaminants, however, were never identified.

A much older sample of Congo red was located in the form of pH test strips that were found in a university chemical stock room, inset of Fig. 8. Although the exact age of the sample is unknown, the
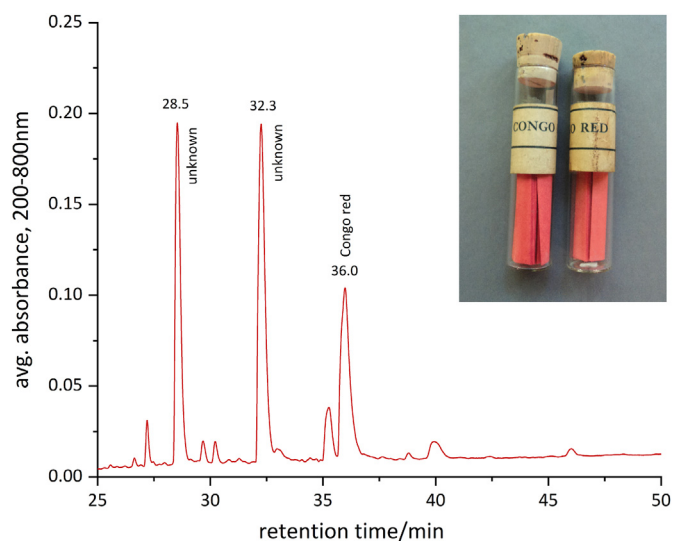

Fig. 8. Chromatogram of the 1:1 methanol/water extract from Congo red pH paper (inset) showing two unknown compounds along with Congo red. Retention times are shifted by 0.26 min to correct for faster elution in a replacement LC column. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 7. Proposed negative ionization fragmentation pathway for unknown compounds in the red fiber sample for the species eluting at 32.3 min. All ions except *m/z* 635 are observed in MS/MS and MS/MS/MS experiments. The pattern mimics that of Congo red, suggesting a structural relationship between the unknowns and Congo red.

product packaging - a cork stoppered glass tube with a brittle, discolored brown paper printed commercial label - suggests that it is of considerable age, perhaps even the first half of the 20th century. When the dye was extracted from these test strips and analyzed using the LC-DAD-MS method, the same two major unknown bands at 28.5 and 32.3 min were seen in significant relative concentrations to Congo red as observed in the carpet fragment sample, Fig. 8. Although the exact chemical identification of these impurities remains elusive, their presence offers the tantalizing possibility that these unknown compounds could be markers for the earlier (pre-1970s) synthesis of Congo red. However, the authors cannot at this time rule out degradation reactions that could have generated the unknown compounds in the carpet sample and pH test papers over long periods of time. Additional efforts are currently underway to test these hypotheses and identify the unknowns' chemical structures.

4. Conclusions

Dye analysis of the CMA textile 1988.243 confirms that it is not a 15th century Persian carpet, but rather of more recent manufacture. This analysis was undertaken prior to radiocarbon dating in part because it is a less invasive analytical technique; the current understanding of the textile now obviates the need for further sampling or testing. Analysis of silk fiber samples from the carpet fragment using both spectroscopic and chromatographic techniques revealed that the blue fibers contained indigo, free of its companion isomer indirubin that commonly occurs in many natural indigo dyes. As noted, differentiation of natural versus synthetic indigo is difficult to achieve with confidence, but if the blue colorant is in fact synthetic indigo, that dye was first available in 1897. The green fiber contains a combination of indigo and Metanil yellow; the latter was first synthesized in 1879. The red dye used on the silk is largely Congo red, created in 1884, but also with significant Metanil yellow present. That sample also contains significant relative quantities of unknown, but related, disazo compounds that perhaps result from early synthetic routes to Congo red or from degradation reactions other than photooxidation by light exposure.

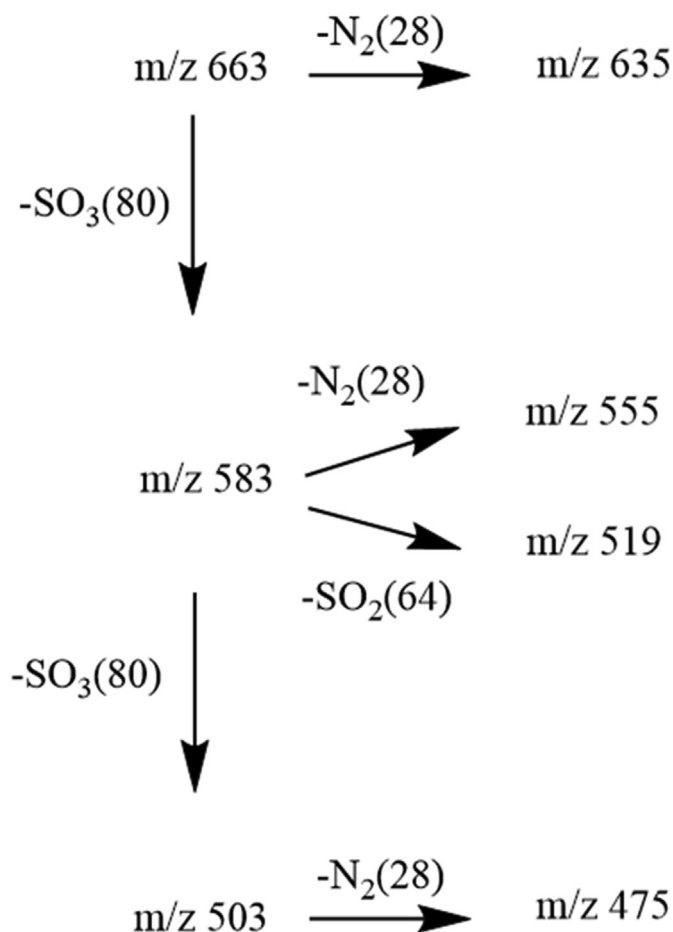From these analyses it is apparent that two of the three carpet

samples—the red and the yellow—are dyed using synthetic colorants not available until the last quarter of the 19th century. The third silk color, blue, may also be a synthetic dyestuff, advancing the *terminus post quem* to 1897 with the discovery of synthetic indigo, just 30 years prior to the first appearance of the fragment in the hands of a prominent collector in 1928. These results put to rest questions of the object's antiquity and the carpet's importance in the art historical record − it is a modern creation. Based on these findings, radiocarbon dating would add nothing further to the understanding of the object since the date range provided by dye analysis is narrower than that typical of radiocarbon dating [38]. If nothing else, the analysis presented here redirects future art historical research on the carpet fragment to the first three decades of the 20th century, enabling the CMA to concentrate its provenance research on this time period to untangle the story of the carpet's manufacture and introduction to the market.

Declaration of competing interest

The authors have no competing interests

Acknowledgments

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