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Twentieth century Iranian carpets: investigation of red dye molecules and study of traditional madder dyeing techniques

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Abstract

Red is undoubtedly one of the principal colors in Iranian carpets. During the twentieth century, a golden era for Iranian carpet production and export industry, madder was still one of the primary constituents of the red dyestuff, used according to various dyeing methods which is specific for Iran. Compared to the earlier periods, the said period witnessed a clear increase in the hues of the color red and in the alternation of physical and visual properties. We, therefore, aim to get a better insight into the chemical and physical properties of the component which made it all possible—dyes. To this effect, eighteen red wool samples with various hues were collected from seven Iranian carpets belonging to the aforementioned period (from Ali Mirzaei's private collection) and analyzed using three techniques: reversed-phase-high-performance liquid chromatography (RP-HPLC-DAD), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM–EDX) and colorimetry. We also studied traditional dying recipes to underpin the scientific process involved. We focused on recipes based on madder, which are mordanted with organic additives such as *qarehqurut* (a kind of Iranian dairy product; also known as *Gharehghorut*). These substances, additionally, helped control the acidity of the dyebath; a common technique from the period. The effect of these substances on the hue, the associated red dye chemistry, various visual and physical properties, including color fastness, are reported. Our study revealed, among other facts, that the additive *qarehqurut* is highly efficient at improving color absorption and at increasing lightfastness. Another salient finding was that, besides madder, various synthetic dye sources were used by the twentieth century "traditional" Iranian red dyeing industry.

Keywords: Iranian carpet, Madder, Red color, Dyeing, Synthetic dyes

Introduction

Iran has always been known for its majestic carpets, and artistic rugs but what made Iran so successful at producing them? One of the crucial factors was the dyeing technique. Most classical Persian carpets are a blend of red which dominates the central field and blue or green are used for the border [1]. These colorful dyes were extracted from natural sources until the development of synthetic dyes which occurred in the mid-nineteenth century [2]. In particular, the mauve dye by Perkin in 1856 and several coal-tar-based dyes, were adopted in Iran to produce bright and vivid colors [3].

The twentieth century was a turning point for traditional Iranian carpet production. After a period of stagnation, Persian carpets regained their popularity world-wide. The workshops started flourishing and the new invented synthetic dyes, especially red, came to the fore, leading to the appearance of richer hues [4, 5]. Consequently, various scientific studies have been carried out on textiles from Central Asia [6, 7], and Iran [8], belonging to the period between the late nineteenth to the early twentieth century.

For the study of cultural heritage collections and for the science of conservation, a knowledge of the chemistry underlying the dyeing process is indispensable. In particular, such an understanding has been used to learn the history and creation of cultural-heritage objects [3]. Comparing the ancient and modern processes will enable

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to estimate if the tradition survived the industrial revolution [9]. However, our current scientific understanding of the aforesaid dying process is very limited. For instance, it is known from Iranian traditional documents on the subject that some of the organic additives, such as *doogh* and *qarehqurut* were used to keep the pH of the dyeing bath low (i.e. keep the bath acidic) [4, 5, 10]. It is also known that *qarehqurut* was the most popular material in Iranian traditional dyeing technique which uses madder. On the other hand, aluminum sulfate was the most used mordant in the dying recipes of madder [4, 5]. Through this study, we significantly improve the state of the art.

Our study sheds valuable light on the process of fading, a major concern to museum personnel who are responsible for preservation of textiles for future generations, as well as on the science of traditional dyeing technique in Iran [11]. Light radiation is one of the most important contributors to fading.

Iranian carpets, in most of the museums and the hundred cases that we can see nowadays in museums worldwide [12], it is necessary to investigate the Iranian dyeing techniques, to shed light on their impact on color fastness, different physical and chemical properties as well as their influence on the final reddish hues. In the case of cultural heritage, dyes have different destruction speeds, and it appears in various range of fragility. In addition, various requirements for restoration and conservation actions are needed. Apart from identification and determination mordant ions in synthetic or natural dyes and dyeing condition it is necessary to know, which kinds of dyestuff were used (synthetic or natural).

In the present study we started with the identifying the colorants of the case studies samples and found out that apart from madder, also synthetic dyes were applied in the twentieth century Iranian carpet samples.

In addition, this study is focused on the effect of *qarehqurut* in mordanting and dying on color, fastness, and properties of woolen yarn dyed with madder roots. This will help to understanding of the impact of organic additives to the mordanting and dyeing of wool with madder roots. *Qarehqurut* is a natural product common in Iranian traditional dyeing as well as lactic acid, citric acid, yogurt, and lemon. According to different studies, the best color depth will be achieved in pH around 4–5 and the best material-to-liquor ratio that was recommended in Iranian traditional recipes was 1:30 [4, 5, 10]. According to our aims about dye standards and dyeing process, we had a lot of possibilities to combine and create proper recipes. Two different methods, twentieth-century 'traditional' Iranian red dyeing techniques and modern laboratory dyeing techniques, were considered to create two sets of standard samples, and to see the characterization of both methods.

Experimental

Samples

Persian carpets from twentieth century (historical samples)

All of the eighteen samples collected, were obtained from rugs and carpets pieces that dated back to the twentieth century. They were knots made of wool with different red hues (Table 1).

Modern samples

Prepared samples focused on the Iranian traditional dyeing recipes with madder and *qarehqurut* as organic additives, a prevalent technique in the twentieth century.

Materials and reagents

The dye experiments were done on untreated woolen three-ply yarns using additive *qarehqurut* and cultivated madder (*Rubia tinctorum* L.) purchased from Esfahan, Iran. Additionally, aluminum sulfate (analytical grade) from Sigma-Aldrich (Milwaukee, WI, USA) was applied as mordant. The said solutions were dissolved in distilled water.

Mordanting

Mordanting experiments were performed by pre-mordanting method (MD procedure). Upon dissolving aluminum sulfate in water, it completely dissociates into its constituent ions i.e. Al^{3+}, K^{+} and SO_4^{2-}. Among all constituents, aluminum ion is believed to have the crucial role in mordanting fiber [9]. Different amounts of aluminum sulfate ($Al_2(SO_4)_3$) (20–6–5% o.w.f. (on weight of the fiber) were utilized. The used material-to-liquor ratios were 1:30, 1:40 and 1:50 and each amount of aluminum sulfate was added to water in separate mordant baths. The substrates were placed in mordanting baths, thoroughly wetted out in order to ensure any trapped air is removed from the substance. The water-soaked wool yarns were consequently introduced to mordant solutions with initial temperature set at 45 °C. Temperature level was then raised to 85 °C for 60 min. At the end of the 1-h process, mordanted wool samples were washed with cold distilled water.

Wool dyeing

Two different dyeing methods based on (i) European standard protocol (code: M-STD), and (ii) the Iranian traditional dyeing system database were applied.

Dyeing group one (DG1)

Experiment procedures were performed according to standard protocol, (code: M-STD). Briefly, 1 g coarsely ground madder in a polyester netting bag was placed into a beaker with 50 mL of water while keeping material-to-liquor ratio (M:L) of 1:50. Meanwhile, in order

Table 1 Historical samples A (Design: Adobe, Region: Bakhtiari-Esfahan, Sample ID: A1, A2, A3, Type of sample: Knot); B (Design: Border, Region: Esfahan, Sample ID: B1, B2, B3, Type of sample: Knot); C (Design: Toranj (medallion), Region: Qashghai-Fars, Sample ID: C1, C2, Type of sample: Knot); D (Design: Vagireh, Region: Arak, Sample ID: D1, D2, Type of sample: Knot); E (Design: Mahi dar ham (fish), Region: Malayer-Hamedan, Sample ID: E1, E2, Type of sample: Knot); F (Design: Shekasteh-Khur, Region: Bakhtiari-Esfahan, Sample ID: F1, F2, F3, F4, Type of sample: Knot); G (Design: Lachak va Toranj, Region: Saneh-Kurdestan, Sample ID: G1, G2, Type of sample: Knot)

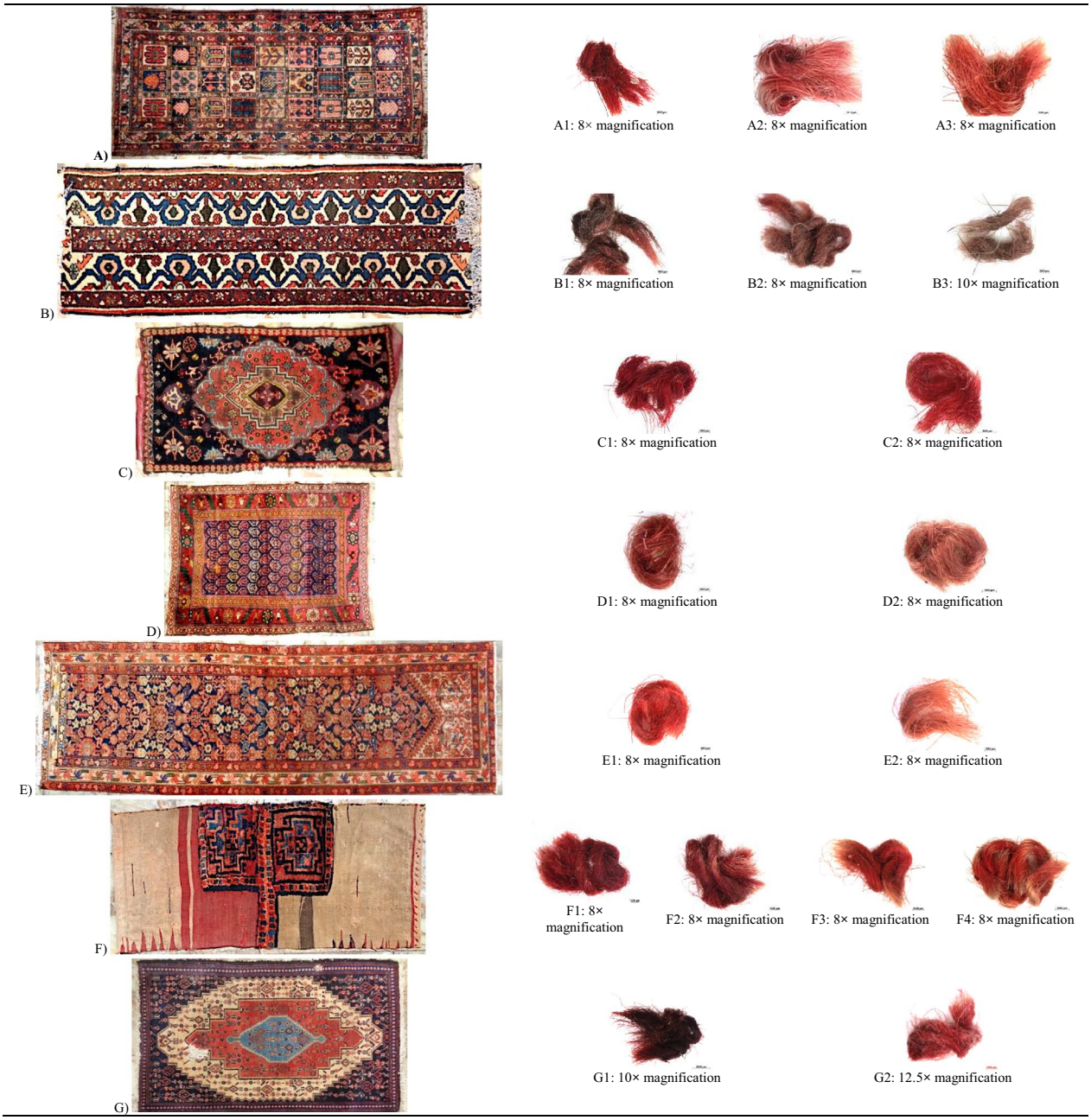


Table 1 (continued)

A1: L*: 25.97, a*: 23.26, b*: 8.55; A2: L*: 39.84, a*: 25.77, b*: 11.53; A3: L*: 34.89, a*: 28.15, b*: 18.29

B1: L*: 27.06, a*: 11.34, b*: 6.41; B2: L*: 37.22, a*: 18.09, b*: 10.44; B3; L*: 39.84, a*: 25.77, b*: 11.53

C1: L*: 25.06, a*: 24.50, b*: 9.01; C2: L*: 24.50, a*: 17.02, b*: 6.95

D1: L*: 41.04, a*: 25.87, b*: 12.99; D2: L*: 28.20, a*: 6.53, b*: 4.47

E1: L*: 35.31, a*: 29.30, b*: 17.80; E2: L*: 43.01, a*: 23.32, b*: 21.94

F1: L*: 21.56, a*: 10.52, b*: 12.42; F2: L*: 36.52, a*: 23.27, b*: 10.53; F3: L*: 24.65, a*: 21.23, b*: 7.46; F4: L*: 27.32, a*: 22.88, b*: 9.45

G1: L*: 33.79, a*: 25.70, b*: 17.40; G2: L*: 37.31, a*: 30.70, b*: 22.19

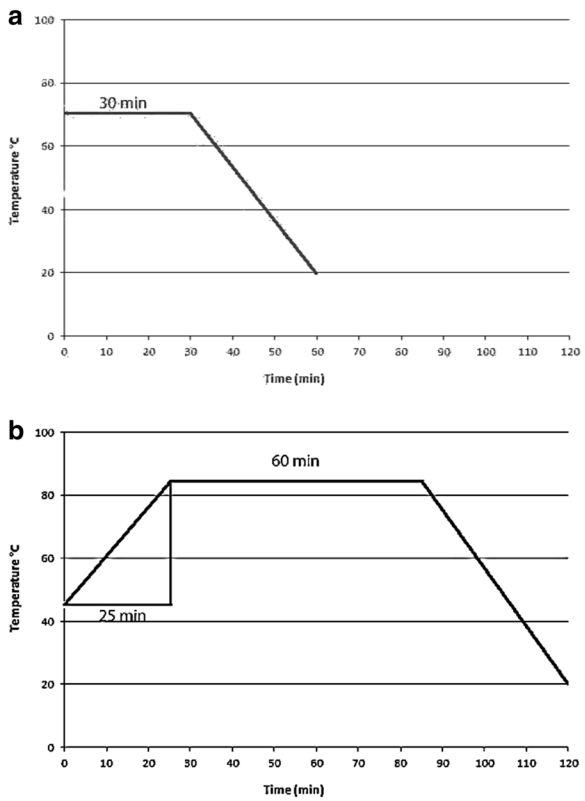


Fig. 1 The diagram of dying **a** dyeing with standard portocol (code: M-STD), **b** Iranian traditional dyeing system database

to get maximum yield, madder root powder was kept in aqueous solution overnight. The mixture was heated at 70 °C for 60 min prior to removing the netting bag in order to prepare the solution for dyeing. Once the polyester netting bag was removed and the temperature was stabilized at 70 °C, 0.5 g of mordanted wool was placed in the dyeing bath to absorb dye for 30 min at the 70 °C (Fig. 1). Throughout the 30-min procedure, the bath was constantly stirred to achieve homogeneous results. After dyeing, samples were divided into two equal parts one of which was removed from the bath. The removed half was thoroughly rinsed with distilled water (DG1-A) while the second half was left to rest in the dyeing bath for another 14 h in order to be able to measure the difference in colorant absorption (DG1-B).

Dyeing group two (DG2)

According to traditional Iranian dyeing documents, the material to liquor ratio of the dye bath was kept at 1:40 with water pH 6.43. Furthermore, the wool fibers were dyed using exhaustion method in acidic medium by using 5% *qarehqurut*. After adding *qarehqurut*, the pH would be decreased to 4.03. Finally, the madder powder was directly added to the dye bath at which point the pH would reach 5.58.

The temperature program for the dyeing, in the Iranian tradition, was as follows: initial temperature was set at 45 °C (when fibers were placed in the bath), it was gradually increased up to 85 °C over 30 min. The dyeing procedure lasted 60 min (Fig. 1) at the end of which, dyed wool yarns were divided into halves. One half was washed with distilled water and subsequently shade dried (DG2-A) while the other half was left in the bath to reach room temperature and incubate overnight (DG2-B). Finally, samples were washed with distilled water and shadow dried.

Chromophore studies

Chromophore extraction procedure

After pre-examination under microscope, the dyes were recovered from the sample fibers by using 0.5 mg of sample for extraction. Subsequently, each sample was treated in 250 µL of a methanol/acetone/water/2.1 M oxalic acid solution (30:30:40:1, v/v/v/v) for 15 min at 80 °C in a heating bloc under constant stirring [13]. Acid preparation was initially directly filtered through a porous polyethylene frit for extract-clean (of 1.5 mL). Afterward, the solution was placed in an extract-clean reservoir (of 1.5 mL). The clear filtrate was finally dried in a vacuum evaporator. The dried material was re-dissolved in 30/30 µL methanol/water (1/1, v/v) from which 20 µL was extracted for injection.

RP-HPLC-DAD analysis

The equipment consisted of a quaternary high-pressure pump (Alliance. Waters, USA), a photo diode array detector (Model 996, Waters, USA) and a system for data storage, manipulation and retrieval (Empower, Waters, USA). Assessment was done through comparing retention

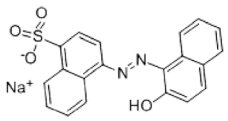
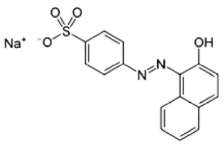
time (Rt) and UV–Visible absorbance spectra recorded between 240 and 800 nm of each detected chromophore with the retention times and spectra from reference molecules from an in-house, non-commercial database of natural and synthetic dye molecules. This database was built up by the data (spectra and retention time) obtained from analysis of pure dye molecules and from analysis of extracted dyes from yarns dyed with natural or synthetic dye sources. A more detailed description of the analytical protocol and reference database was earlier published [14].

The relative ratios of the peak areas of each molecule were recorded in Tables 2 and 3 at 255 nm and 430 nm wavelength in order to obtain an indication of the relative amounts of all the compounds present in one analysis at a particular wavelength.

SEM–EDX studies

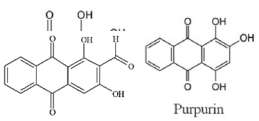
Samples were mounted in aluminum sample holders with double-sided adhesive carbon tape attached to a graphite disc and coated with an Au–Pd layer. Analyses were carried out in a Carl Zeiss EVO 15 LS variable pressure scanning electron microscope coupled with a Bruker X-ray energy dispersion spectrometer, used for morphological characterization and point chemical analysis both at the surface as well as in fractured zones

Table 2 Historical samples—synthetic dye

Sample code	Dye compounds: (M: major compound) (m: minor compound)	Relative ratio of peak areas of detected spectra at 255 nm	Chemical structure
A1	S1 (Rt:22.1 min)	100% S1	 Acid Red 88 Fast Red AV, CI 15620
A2	S1 (Rt:22.1 min)	100% S1	
A3	S2 (Rt:16.9 min) (M)–S1 (Rt:22.1 min) (m)	66% S2, 4% S2′, 30% S1	
C1	S1 double peak (Rt:21.6 min–Rt:22.1 min)	67–33% S1–S1	
C2	S1 double peak (Rt:21.6 min–Rt:22.1 min) (M) S2 (Rt:16.9 min) (m)	12% S2, 64–24% S1–S1	
D1	S2 (Rt:16.9 min)	100% S2	 Acid Orange 7 Orange II, CI 15510
E1	S1 (Rt:21.5 min)	100% S1	
E2	S2 (Rt:16.9 min)	100% S2	
F1	S1 double peak (Rt:21.4 min–Rt:21.9 min) (M), S1′ (Rt:21–Rt:22.8 min) (m), S2 (Rt:16.9 min) (m)	4% S2, 5% S1′, 64–27% S1–S1, 1% S1′	
F2	S1 double peak (Rt:21.4 min–Rt:21.9 min) (M), S1′ (Rt:21–Rt:22.8 min) (m), S2 (Rt:16.9 min) (m)	4% S2, 5% S1′, 57–30% S1–S1, 3% S1′	
F3	S2 (Rt:16.9) (M), S2′ (Rt:18.6 min) (m), S1 double peak (Rt:21.4 min–Rt:21.9 min) (m), S1′ (Rt:21–Rt:22.8 min) (m)	69% S2, 6% S2′, 1% S1′, 16–8% S1–S1	
F4	S2 (16.9 min) (M), S2′ (Rt:18.6 min) (m), S1 double peak (Rt:21.4 min–Rt:21.9 min) (m)	82% S2, 6% S2′, 9–2% S1–S1	
G1	S1 double peak (Rt:21.4–Rt:21.9 min)	80–20% S1–S1	
G2	S1 double peak (Rt:21.4–Rt:21.9 min)	74–26% S1–S1	

S1 absorbance spectrum maxima at 217–288–314–324–514 nm, *S2* absorbance spectrum maxima at 229–310–487 nm, *S1′* similar absorbance spectra as S1, *S2′* similar absorbance spectra as S2, *S1–S1* S1 double peak, *relative ratio (%)* individual peak area divided by sum of peak areas multiplied by 100

Table 3 Historical samples—natural dye

Sample code	Dye compounds: (M: major compound) (m: minor compound)	Relative ratio of peak areas of detected spectra at 255 nm	Chemical structure
B1	Alizarin (M), purpurin (m), nordamnacanthal (m)	3% luteolin-7-*O*-glucoside, 92% alizarin, 3% purpurin, 2% nordamnacanthal	 Nordamnacanthal Purpurin
	Luteolin-7-*O*-glucoside (m)		
B2	Alizarin (M), purpurin (m), nordamnacanthal (m)	87% alizarin, 10% purpurin, 2% nordamnacanthal	
B3	Alizarin (M), purpurin (m)	91% alizarin, 9% purpurin	
D2	Alizarin (M), purpurin (m)	85% alizarin, 15% purpurin	

Relative ratio (%) individual peak area divided by sum of peak areas multiplied by 100

of the wool dyed fibers for mordant assessment. Acceleration voltages of 15.0 kV and 20.0 kV were used for SEM and EDX analyses, respectively.

Colorimetric studies

All analyses were undertaken with a colorimeter BYK-Gardner GmbH using combination of Illuminate CIE D65, 10° of observation angle and specular component excluded for the light (illuminate/observer conditions).

To this end, measurement of reflectance was performed at maximum absorption wavelength (ƛmax 450 nm). Analyses were performed in four different points of each wool sample; namely, 2 in the horizontal plane and 2 in the vertical one with average value used for data interpretation.

Accelerated ageing studies

An ATLAS sun test CPS+/XLS+ equipped with 1 air-cooled 1500 W xenon lamp was utilized, with 28 × 20 cm (560 cm^2) exposure area. The ageing conditions were as follows: temperature set at 35 °C while irradiance was stabilized at 45 W/m^2. Samples were collected after 168 and 504 h of light exposure. The change which could have occurred in a test may be due to inconsistencies in lightness, chroma or hue, or any combination of these. Regardless of the character of the change, the assessment is based upon the magnitude of the visual contrast between the specimen after the test and a specimen of the original material.

Results and discussion

Characterization of old samples

Historical samples group A

Three red samples were collected from Persian Carpet A, and all of them were examined via colorimetric analysis. A1 ($L^*=25.97$; $a^*=23.26$; $b^*=8.55$), A2 ($L^*=39.84$; $a^*=25.77$; $b^*=11.53$), and A3 ($L^*=34.89$; $a^*=28.15$; $b^*=18.29$). From a visual and colorimetric point of view, samples demonstrated distinct red hues. A1 had the lowest b* value compared to A2 and A3. A2 had the higher value of L* than the other samples and A3 had the highest a* value.

By RP-HPLC-DAD analysis, two compounds named S1 (compound with absorbance spectrum maxima at 217–288–314–324–514 nm eluting between Rt 21.1–21.5 min) and S2 (compound with absorbance spectrum maxima at 229–310–487 nm eluting at Rt16.9 min) were found. Compound S1 (Rt 21.1 min) was detected in samples A1 and A2, while in A3, compound S1 and S2 (Rt16.9 min) were found (Table 2). Presumably, compound S2 was formed due to degradation of compound S1, which might explain the variation in ratios encountered in references as well as in the historical samples [15].

The identified dyes in the group A samples refer to the synthetic diazo acid dyes Acid Red 88 (AR88) and/or Acid Orange 7 (AO7).

Through performing SEM–EDX analysis, morphological characterization had shown that the fiber surfaces had the typical scale structure of wool's cuticle cells, as well as scale loss and roughened surfaces [2]. The distribution of different elements on the fibers—supposed to be deposited material—degraded product and/or intentionally added elements.

Elemental analysis performed by EDX, revealed S and Ca as the main elements (±), and Si as accessory element and Na, Al, Mg, Cl and K acted as trace elements.

Historical samples group B

Microscopic and visual observations revealed that samples were fragile with a high amount of deposited materials on the fibers. Furthermore, in the sample B1 and B3, some naturally black-brownish fiber was detected.

Three red samples were collected from Persian Carpet B, B1 ($L^*=27.06$; $a^*=11.34$; $b^*=16.41$), B2 ($L^*=37.22$; $a^*=18.09$; $b^*=10.44$), and B3 ($L^*=39.84$; $a^*=25.77$; $b^*=11.53$). Colorimetric examinations revealed that all the samples were found in the red–yellow zone, while B1 had the lowest b* value. B3 had the highest L* and a* values among the three samples; i.e. it was lighter and contained more yellow-reddish hue.

Samples were run through Point micro chemical analysis by EDX. Results demonstrated that metal ions were not evenly distributed [16]. Samples B1 and B3 had the same profile, the recognized elements also had the same quantity. The main elements (±) were S, Ca and Si; the accessory elements (+) were Al, Mg, K, Fe and P, and finally Cl and Na were trace elements (−). In addition, in sample B2, the amount of S, as the main element (±), was much higher than B1 and B3. In the case of accessory elements (+), Si and Al were detected. Additionally, trace elements Na, Mg and K were found. While it is possible that the said elements came from the environment; their presence could also be explained due to existence of mordant which could be the case for aluminum sulfate [17].

The RP-HPLC-DAD results of the samples group B (1,2,3) were shown in Table 3. The main peak at Rt 18.5 min belongs to alizarin and the second peak at Rt 22.1 min points at purpurin. In all three samples, the relative ratio (%) of the alizarin was much higher than the relative ratio of purpurin (at 255 nm) [15].

A glucoside of luteolin (luteolin-7-*O*-glucoside) was detected together with the anthraquinone compounds in sample B1. It is a marker for the use of a natural

luteolin-rich yellow dye source from vegetal origin. Luteolin is the major dye in a growing number of dye plants from different botanical families and used in a broad geographical and historical context, which makes the identification towards a particular plant source impossible. Among the most likely sources are weld (*Reseda luteola* L.), sawwort (*Serratula tinctoria* L.), dyer's greenweed (*Genista tinctoria* L.) or chamomile species such as yellow or dyer's chamomile (*Anthemis tinctoria* L.) or true chamomile (*Matricaria chamomilla* L.) [18–20]. Other luteolin yellow plants reported by Bohmer to be present in Turkey and surrounding areas are three-leafed sage (*Salvia triloba* L.), Monk's pepper tree (*Vitex agnus castu* L.) among others [20].

The combination of the yellow dye source together with madder suggest a more orange/red shade of the sample.

The detection of alizarin as major anthraquinone dye compound, in combination with purpurin and nordamnacanthal as minor anthraquinone dye compounds indicated the application of plant roots from the *Rubiaceae* family [15, 21].

Historical samples group C

From visual point of view, both samples had bright red color but sample C2 ($L^*=24.50$; $a^*=17.02$; $b^*=16.95$), was more fragile than C1 ($L^*=25.06$; $a^*=24.50$; $b^*=9.01$). By colorimetric examinations, all the two samples were found in the red–yellow zone, while C1 had the higher b* and a* values, and in the case of L* value, both had more or less the same profile.

The RP-HPLC-DAD results of the samples group C (1,2) checked at 255 nm, exhibited that samples C1 and C2 had the S1 peak at Rt 21.6 min as main peak. Due to the instable character of S1, a derivative was formed in both samples, eluting just after the initial peak (Rt 21.6 min). In addition to these two peaks, sample C2 also contained S2 at Rt 16.9 min. These compounds referred to the use of synthetic dyes Acid Red 88 and/or Acid Orange 7 (Table 2) [15].

In the case of elemental analysis, which was performed by EDX on the C1 sample, the main elements (±) were S and Si, and in the case of accessory elements (+) Ca, Al, Mg, Fe and Cl were found. Other elements like K, Na and P were recognized as trace elements (−). Moreover, in the sample C2, the main elements (±) were S and Ca, Al, Si and Cl were presented as accessory elements (+). In addition, Mg, K, Fe, P and Na were found as trace elements (−).

Historical samples group D

Two red samples were collected from Persian carpet D, D1 ($L^*=41.04$; $a^*=25.87$; $b^*=12.99$), and D2 ($L^*=28.20$; $a^*=6.53$; $b^*=4.47$). The RP-HPLC-DAD analyses of the samples of group D demonstrated that in sample D2, the main peak at Rt 18.5 min indicated alizarin as the major anthraquinone dye compound while the second peak at Rt 22.1 min showed purpurin as the minor anthraquinone dye compound. The characterized colorant was madder (Table 3). In sample D1, there was a double peak S1 at Rt 21.6–Rt 22.1 min, which again is linked with the use of Acid Orange 7 (AO7) and/or Acid Red 88 (AR88) [15] (Table 2). Thus, both synthetic and natural colorants were used in the carpet.

Morphological characterization of the fiber surfaces showed that sample D2—recognized as a natural dye (madder)—contained a substantial amount of particles that may have originated from degradation or intentionally added particles (Fig. 2). After having carried out EDX analysis on both samples, results proved that apart from S, and Ca Cl were also the main elements (±) in both samples. Meanwhile, presence of Cl could be linked to the method applied to wash the carpet after producing to make all colors more vivid [22]. On the other hand, Na and Mg in both samples and Al and Si in sample D2 were found as accessory elements (+). In the sample D1 only Si was recognized as trace element (−), while in D2, K and Fe were highlighted as trace elements (−).

Historical samples group E

Colorimetric examinations and visual assessment state that sample E1 ($L^*=35.31$; $a^*=29.30$; $b^*=17.80$) and E2 ($L^*=43.01$; $a^*=23.32$; $b^*=21.94$) had various hues of red; meanwhile, E2 had higher L* and b*value and lower a* value.

Via molecular analysis using RP-HPLC-DAD of group E samples, synthetic dyes were again detected. In sample E1, the peak S1 at Rt 21.5 min was detected and sample E2 contained the peak S2 at Rt 16.9 min, both linked again to the use of the same red dyestuff(s) Acid Red 88 (AR88) or acid orange 7 (AO7) [15].

SEM images showed the morphological characterization of the fiber surfaces in sample E1 and E2, while the distribution of deposited materials was not the same and amount of degradation in sample E2 was higher. By applying EDX analysis, it appeared that both samples had more or less the same amount of identical elements with. S and Ca were main elements (±), while Si, Mg, Na, Al, Cl, and Fe were identified as accessory elements (+), with K as trace element (−).

Historical samples group F

Four red samples were collected from Persian carpet F, F1 ($L^*=21.56$; $a^*=10.52$; $b^*=2.42$), F2 ($L^*=36.52$; $a^*=23.27$; $b^*=10.53$), F3 ($L^*=24.65$; $a^*=21.23$; $b^*=7.46$), and F4 ($L^*=27.32$; $a^*=22.88$; $b^*=9.45$).

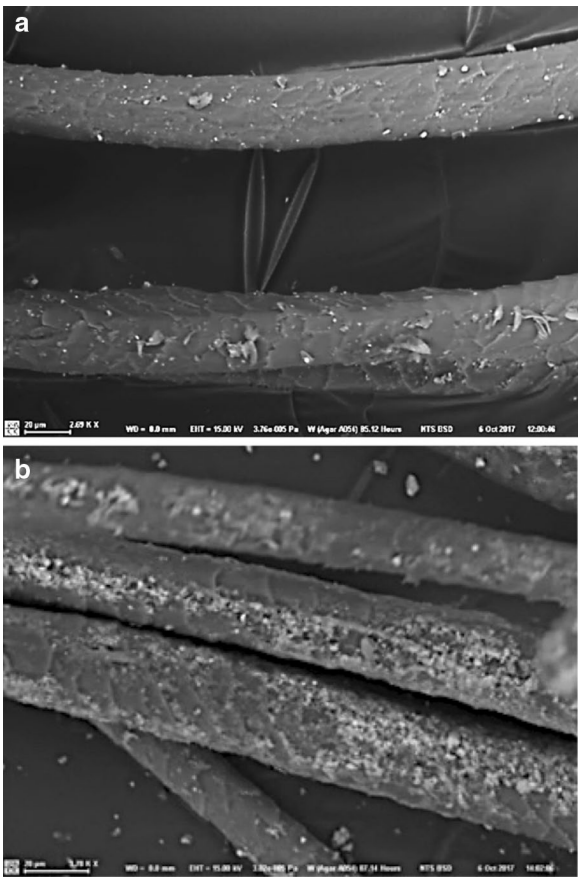


Fig. 2 Scanning electron microscopy, **a** sample D1 ~ 2700× magnification, **b** sample D2 ~ 3700× magnification

RP-HPLC-DAD analysis proved that, in samples F1 and F2, the double peak of S1 formed the major compound coupled with small amounts of other S1 derivatives (named S1') at Rt 21.0 min and Rt 22.8 min and S2 at Rt 16.9 min. In the case of samples F3 and F4, the main dye compound detected was S2. It was found in the presence of minor amounts of a S2 derivative at Rt 18.6 min and the S1 double peak and derivatives [15] (Table 2). All samples of group F were dyed with synthetic dye(s), Acid Orange 7 (AO7) and/or Acid Red 88.

Historical sample group G

According to visual and colorimetric assessments, sample G2 ($L^*=37.31$; $a^*=30.70$; $b^*=22.19$) was lighter than G1 ($L^*=33.79$; $a^*=25.70$; $b^*=14.70$) with a higher a^* and b^* value.

According to Table 2, samples G1 and G2 contained the double S1 peak (at Rt 21.4 min and Rt 21.9 min) with largely similar relative ratio (%) of the peak areas. Once more, Acid Red 88 (AR88) and/or Acid Orange 7 (AO7) were used [15]. RP-HPLC-DAD analysis indicated both G1 and G2 samples contained synthetic dyes.

Based on EDX results, in both samples S and Ca were the main elements (±) while Si and Cl were the accessory elements (+) with varying amounts. The aforementioned manifests itself in sample G2, for instance, in which the amount of Cl was three times higher than sample G1. In the case of trace elements, in sample G1, Al, Mg and Fe were the only elements found whereas in the sample G2, Na, P, Al, Mg and Fe were present.

Characterization of raw materials

Madder

The elemental analysis of Iranian madder carried out by SEM mapping indicated that apart from C and O as the most abundant elements, K, Ca, Cl, Mg, Na, Al, P, Si and S were also available in the madder in different quantities. The RP-HPLC-DAD analysis of Iranian madder powder extracted at 70 °C exhibited several absorbance spectra at 255 nm and 430 nm (Table 4 and Fig. 3).

Wool SEM–EDX analyses were carried out on the washed pure wool to characterize the elements attributed to the nature of fiber. To this effect, S, Na and Si were counted as the main elements.

Qarehqurut (black kashk)

Qarehqurut or black *kashk* is a special Iranian dairy product subtracted from yoghurt. It is derived from the liquid leftover after: (1) straining yogurt or (2) removing fat from liquid yogurt. This liquid is then reduced by boiling to a certain concentration. The ultimate product is a non-homogenous dark brown sour paste, soluble in water with a pH that stands at approximately 4, mainly used to flavor food traditional Iranian cuisine [23]. The microflora is yoghurt microorganisms; lactic acid and acetaldehyde are known to be the main products of the aforementioned bacteria [24].

ATR-FTIR spectroscopy is performed on *qarehqurut* to have a more accurate image of its chemical composition (Fig. 4). Very strong peaks at 1504, 1342 and 1184, strong peaks at 1685, 1297, 1263, 969, 918, 873, 847, 805, 762 and 1456,1444 as double peaks were appeared, somehow 1373, 1105, 1056 were present as weak peaks.

To characterize elements of *qarehqurut*, both SEM–EDX mapping and EDX point analysis were applied. The results indicated that the said organic product consists of carbon (C) and oxygen (O) as well as other elements such as Ca, Na, P, S, Fe, K, Al, Cl and Mg (Fig. 5).

Mordanted wool fibers

Due to the presence of metal salt mordant, the basic chemical principle in the dyeing process is known to be

Table 4 Chromophores of Iranian madder detected by RP-HPLC–DAD at 255 nm

	Name	%	RT	Area_c
1	Ø	5.35	1.046	5.54
2	Ø	4.07	2.036	4.21
3	Unknown spectrum with max absorbance peaks 213–254–285–357	1.18	9.512	1.22
4	Unknown spectrum with max absorbance peaks 213–256–282–352	1.55	9.995	1.6
5	~Ruberythric acid (= very similar to rubetythric acid)	0.40	10.305	0.41
6	Ruberythric acid	1.80	11.732	1.86
7	Unknown spectrum with max absorbance peaks 251–278–344	0.47	13.012	0.49
8	Unknown spectrum with max absorbance peaks 219–258–272–339–410	0.65	15.211	0.67
9	Xanthopurpurin	0.70	15.988	0.72
10	Anthragallol	0.56	17.123	0.58
11	Pseudopurpurin + munjistin	11.28	17.772	11.67
12	Alizarin	39.54	18.873	40.92
13	Unknown spectrum with max absorbance peaks 223–252–284–436	0.87	19.905	0.9
14	Purpurin	1.22	22.46	1.26
15	~Rubiadin	0.68	25.291	0.7
16	Nordamnacanthal	29.36	26.84	30.38
17	Unknown spectrum with max absorbance peaks 214–245–270–280–391	0.19	28.756	0.2
18	~Xanthopurpurin	0.14	29.332	0.15

Area_c Sum of peak areas (only identified peaks), *RT* retention time, *Relative ratio (%)* individual peak area divided by sum of peak areas multiplied by 100

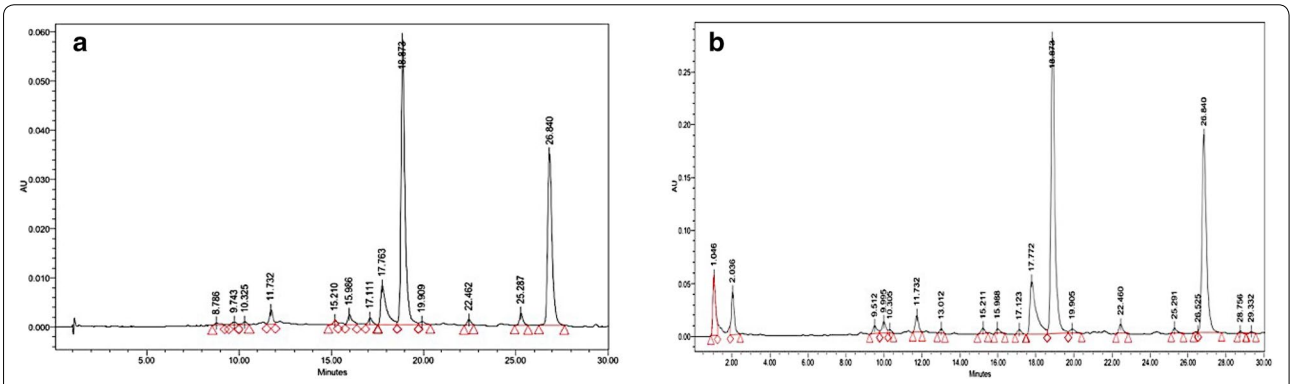


Fig. 3 Chromatogram of Iranian madder **a** at 430 nm, **b** at 255 nm

formation of colored metal complexes. In traditional dyeing, the complexes formed contained both aluminum and calcium. Color and shade of each complex is dependent on the metal ion involved [25].

Microscopic and visual assessment of mordanted wool fibers revealed that sample colors were mordanted with aluminum sulfate, look entirely white. Samples mordanted with both *qarehqurut* and aluminum sulfate, had more yellowish color, depending on the percentage of *qarehqurut* utilized; i.e. the higher the percentage of *qarehqurut* added, the higher the intensity of yellowish hue.

Regarding the pH of the baths and fibers mordanted with *qarehqurut* and aluminum sulfate, as mentioned earlier, pH of the *qarehqurut* solution was around 4–3.9. Post combining aluminum sulfate with *qarehqurut* solution, the pH of the baths slightly decreased and stood at 3.1–3.5. It was observed that the presence of higher percentages of aluminum sulfate, further decreased the pH of the *qarehqurut* solution. In brief, the pH of the mordanting solution with both aluminum sulfate and *qarehqurut* was lower than the pH of mordanting solutions with solely aluminum sulfate.

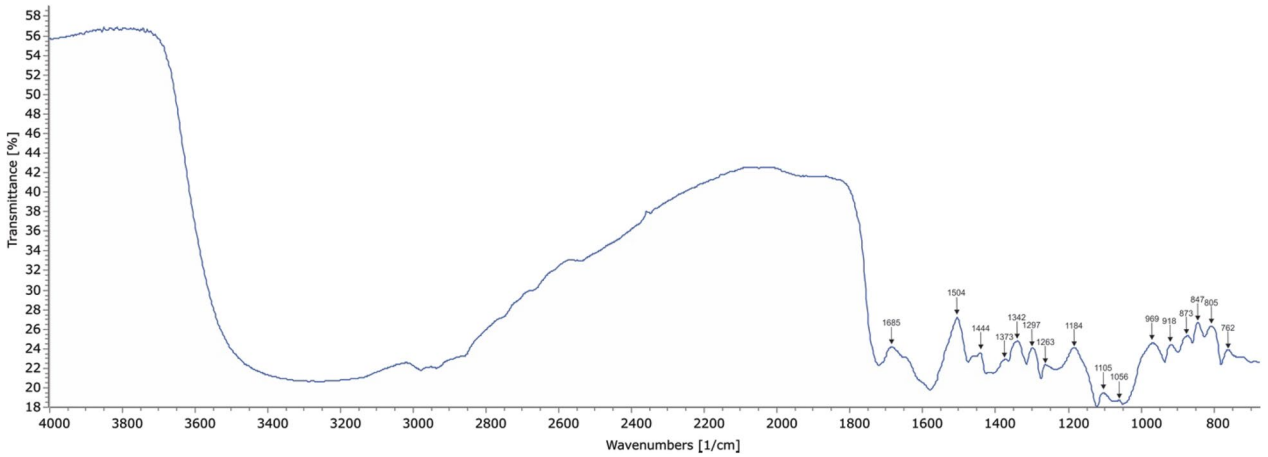


Fig. 4 FTIR-ATR spectra of qarehqurut. Recorded between 700 and 4000 cm^{-1}

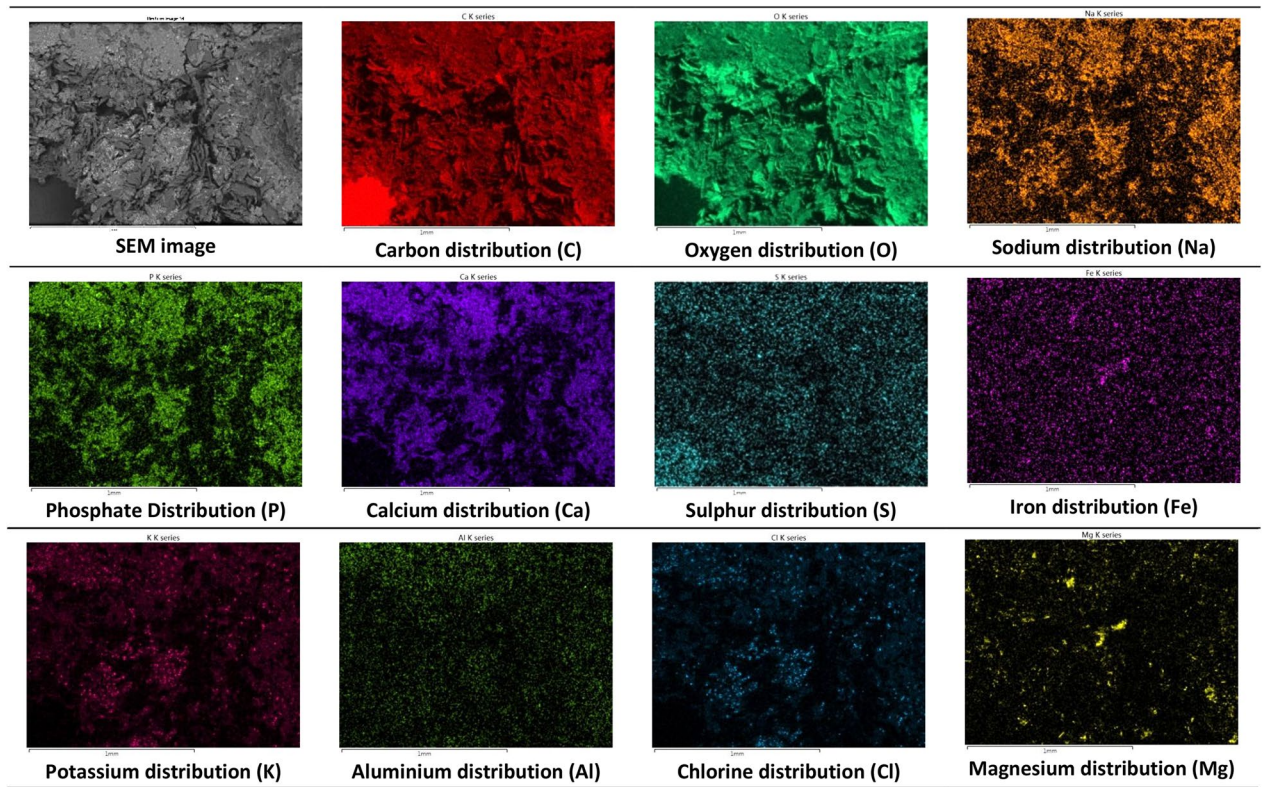


Fig. 5 SEM–EDX mapping of Qarehqurut with 4000× magnification. Distribution of existing elements in the Qarehqurut

Color characteristics of all mordanted samples were assessed in terms of L*, a*, b*. It was clear that brightness (L* value) in all the mordanted samples with aluminum sulfate was higher; i.e. the said samples were evidently brighter. b* value which implies yellowish hue, was higher in the mordanted samples with *qarehqurut* and aluminum sulfate solution.

According to SEM–EDX analysis (elemental), S and Al were the elements detected in mordanted samples with aluminum sulfate. Meanwhile, abundance of Al in these samples were more than samples mordanted with aluminum sulfate and *qarehqurut*. In samples mordanted with aluminum sulfate and *qarehqurut*, S and Al were present as the main elements (±) and P was detected as

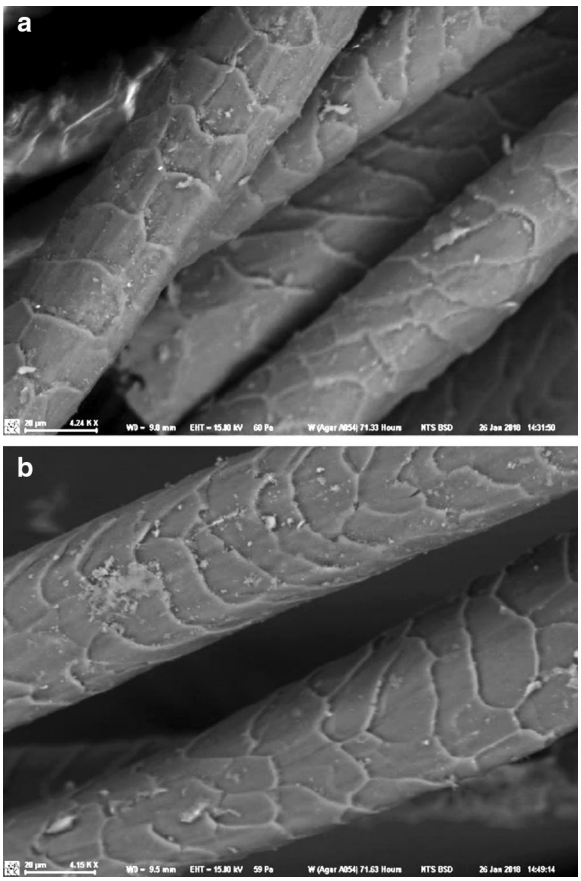


Fig. 6 Scanning electron microscopy with 4000×. **a** Mordanted sample M14 with 5% aluminum sulfate, **b** Mordanted sample M15 with 20% qarehqurut and 5% aluminum sulfate

accessory element (+). Furthermore, Na, Cl, K and Ca were found to be trace elements (−). All the mordanted samples analyzed by SEM, had the same morphology (Fig. 6).

Dyed wool fibers group one (DG1)

So far, the microscopic and visual assessment of dyed fibers group one (DG1) showed, the most saturated red color belonged to samples mordanted with 6% aluminum sulfate, with and without the company of *qarehqurut*. The red color in the mordanted samples with aluminum sulfate and *qarehqurut* was more saturated. Mordanted samples in which aluminum sulfate was utilized had a district red-orangish hue; meanwhile, samples mordanted with aluminum sulfate and *qarehqurut* were more saturated and appeared to be rather scarlet. Furthermore, in the case of mordanting with the various material-to-liquor ratio, samples dyed with 30:1 ratio resulted in a more saturated red color compared with other material-to-liquor ratios (40:1–50:1).

Leaving the samples for longer duration of time in the dyeing bath, resulted in slightly more saturated colors saturated. It also had an impact on homogeneity of dyed samples. However, by naked eyes, this difference was difficult to distinguish; colorimetric analysis was therefore required to better justify the outcome.

From the pH point of view, heating produced an increase in pH of the solution. All dyed samples exhibited an increase in pH once dyeing process was finalized. Post-dye pH value of all dyed samples in their respective solutions was more or less equal.

The red color of samples in which both aluminum sulfate and *qarehqurut* solutions were applied in mordanting process, seemed to appear more saturated. With reference to colorimetric results, once can state that, the said samples had lower L* value (darker hue) and lower b* value (less yellowish hue) in comparison with their match samples which did not contain *qarehqurut* in their mordanting process. On the other hand, mordanted samples with aluminum sulfate, had a red-orangish hue while, the a* value for both counterpart samples were more or less the same.

More specifically, to prove the visual and microscopic assessments of the experiment with regards to mordanting with various material-to-liquor ratios, results indicated 30:1 ratio had lower L* and b* values and the a* value was more or less the same. To this effect, it resulted in a more saturated red color compared with other material-to-liquor ratios (40:1–50:1). As a consequence of leaving samples to soak in the dyeing bath for longer duration, L* (luminance parameter) and b* values demonstrated quite a slight decrease; however, final colors appeared more saturated.

To carry out SEM–EDX assessment of dyed group one (DG1), nine samples were selected based on color variety. Elemental analysis of dyed samples via EDX analysis, found S, Al, P, Na, Cl, K, Ca, Mg and Si. The same element, though with different ratio, were also found in madder as well as *qarehqurut*. Samples mordanted with aluminum sulfate showcased a higher the amount of Al and P than other samples mordanted with combination of aluminum sulfate and *qarehqurut*. Moreover, in samples mordanted with aluminum sulfate and *qarehqurut* the amount of Cl was found to be higher than their peer samples mordanted solely with aluminum sulfate.

RP-HPLC-DAD analysis was performed on the nine selected samples out of 32 dyed samples group one (DG1). The results of the chromatographic analysis of the madder dyeing experiments is presented in Table 5, by giving an overview of the peak area values of the detected dye compounds, calculated at 255 nm and recalculated for 1 mg of

Table 5 Detected compounds in modern samples

Area_C values of the compounds at 255 nm/mg fibre									
Retention time (minutes):	**11.8**	**12.3**	**17.2**	**18.6**	**19.4**	**22.3**	**25.3**	**26.7**	**Total absorbed compounds**
Dye compounds:	**Ruberythic acid**	**Rubiadin-3-β-glucoside**	**Anthragallol**	**Alizarin**	**Pseudopurpurin + munjistin**	**Purpurin**	**Rubiadin**	**Nordamnacanthal**	
DG1_B02				5.53		2.07		0.23	7.83
ADG1_B02				0.83		0.23			1.07
DG1_B04				2.57		1.07		0.07	3.70
ADG1_B04				1.37		0.47			1.83
DG1_B05				5.93		2.83		0.57	9.33
ADG1_B05				0.70		0.30			1.00
DG1_B06				3.53		1.23		0.07	4.83
ADG1_B06				1.13		0.37			1.50
DG1_B09				4.77		2.10		0.23	7.10
ADG1_B09				1.37		0.43			1.80
DG1_B14				3.70		1.60		0.50	5.80
ADG1_B14				0.97		0.30			1.27
DG1_B15				3.47		0.63		0.07	4.17
ADG1_B15				6.13	0.23	1.97		0.87	9.20
DG1_B20				9.63		2.87		0.40	12.90
ADG1_B20				5.77	0.30	1.37		0.67	8.10
DG1_B21			1.33	19.27		7.53		1.37	29.50
ADG1_B21			0.10	6.17	0.63	1.60		0.40	8.90
DG2_B02	1.53	1.23		6.43		7.03		0.90	17.13
ADG2_B02	1.73	1.07	0.27	9.83	0.83	7.03	0.13	0.53	21.43
DG2_B04	1.30	0.97		3.10		3.97		0.33	9.67
ADG2_B04	0.97	0.43	0.20	4.80	0.73	4.53	0.03	0.27	11.97
DG2_B05	0.57	0.30		3.27		2.40		0.30	6.83
ADG2_B05	0.37	0.10	0.07	7.10	1.57	3.17	0.03	0.47	12.87
DG2_B06	0.63	0.47		2.13		2.40		0.27	5.90
ADG2_B06	1.53	0.83	0.27	9.33	0.93	7.07	0.13	0.70	20.80
DG2_B09	0.00	0.00		6.27		3.07		1.17	10.50
ADG2_B09	0.03		0.07	8.13	0.90	4.00	0.07	0.77	13.97
DG2_B14	0.20	0.07		2.00		1.30		0.23	3.80
ADG2_B14	0.10	0.03	0.03	2.03	0.07	0.90		0.30	3.47
DG2_B15	0.20	0.07		2.27		2.50		0.53	5.57
ADG2_B15	0.20		0.10	4.80	0.43	2.50	0.03	0.40	8.47
DG2_B20	0.40	0.20		5.27		4.40		0.83	11.10
ADG2_B20	0.23	0.07	0.10	5.47	0.43	2.33	0.03	0.43	9.10
DG2_B21	0.53	0.33		3.17		2.67		0.33	7.03
ADG2_B21	0.40	0.13	0.10	5.23	0.37	3.00	0.03	0.33	9.60

Area_c sum of peak areas (only identified peaks)

analysed fibre. The last column gives the total amount of absorbed compounds.

According to the detected results (Table 5) alizarin was detected as the major dye molecule, in combination with purpurin and nordamnacanthal as minor anthraquinone dye compounds (Fig. 7). The total absorbed dye compounds were the highest in sample DG1-221.

Dyed wool fibers group two (DG2)

Sample dyed group two (DG2) underwent microscopic and visual analysis. Dyed samples with madder roots resulted in

red–orange to scarlet shades. It could be stated that colors, in comparison with the dyed group one (DG1), were more saturated and more homogeneous. Nonetheless, their color values were quite close to each other. Samples in which aluminum sulfate and *qarehqurut s*olution was utilized, contained a more saturated color red. Mordanted samples with aluminum sulfate had an evidently red-orangish appearance. While, samples mordanted with both aluminum sulfate and *qarehqurut* displayed more bright and scarlet colors.

In the case of samples mordanted with 20% aluminum sulfate results were different. The said sampled exhibited quite similar red color values, very saturated and slightly red-orangish hue. Since one sample was washed immediately after the dyeing process (DG2-A) while the rest remained soaking dye baths in baths overnight (DG2-B) divergent results were logically expected.

Based on the observations in this study, material-to-liquor ratio had a direct impact on the color saturation; specifically, mordanted samples with lower material-to-liquor ratio (30:1) had more saturated colors. The material-to-liquor ratio of the dye bath in dyed group two (DG2) was 1:40 with a water pH of 6. By using *qarehqurut* 5%, its pH reached 4.03. Upon directly adding madder powder to the dye bath, pH reached to 5.58. By the same token, post-dyeing pH in all sample solutions showed an increase compared with pre-dyeing pH. Whereas, mordanted samples indicated a pH decrease subsequent to increase of aluminum sulfate percentage. Moreover, in samples mordanted with *qarehqurut*, post-dyeing pH value was rather lower than those samples that were processed without *qarehqurut*. In all samples, the pH of dyed samples showed an increase in comparison with mordanted samples.

The a*–b* plot of madder dyed samples indicated that all the samples dyed with madder roots were found in the red–yellow zone [26].

Distinguishing the difference between samples mordanted with 20% aluminum sulfate with *qarehqurut* and those that were mordanted with 20% aluminum sulfate with *qarehqurut* was quite impossible by naked eyes. Indeed, number registered through colorimetric analysis in different values were also very close. It could be claimed that, the aforementioned samples which did not contain *qarehqurut*, had lower L* value (darker hue) and lower b* value (less yellowish hue) than their counterpart samples with *qarehqurut* in their mordanting recipe. In fact, these differences were insignificant to the point that in some case both samples showed equal profiles.

In the case of samples mordanted with 5% and 6% aluminum sulfate, it was easier to notice the differences of red hue. The samples in which both aluminum sulfate and *qarehqurut* was used during mordanting process, seemed to exhibit a saturated red color. According to colorimetric results, they had lower L* values (darker hue), lower b* values (less yellowish hue) and the a* values were lower or equal in comparison with their counterpart samples without *qarehqurut* in their mordanting recipes. Mordanted samples just with aluminum sulfate possessed a red-orangish appearance.

As claimed in results of dyed group one, in the case of mordanting with the various material-to-liquor ratio, 30:1 ratio resulted in a lower L* and b* values while a* value was more or less the same. Thus, it produced more saturated red color than the other material-to-liquor ratios (40:1–50:1). Furthermore, based on the comparison between the other material-to-liquor ratios (40:1–50:1), it could generally be stated that lower material-to-liquor ratio caused lower L* and b* values while a* value was the same as before light exposure. By comparing dyed samples part A (DG2-A) and part B (DG2-B), it became clear that in samples that were left for a longer time in the dyeing bath, L* and b* values decreased very slightly, which could be mentioned as the reason behind the more saturated red.

SEM–EDX analysis of dyed group two (DG2) found elements such as S, Al, P, Na, Cl, K, Ca, Mg and Si. The same elements, thought with different amounts, were also found in madder as well as *qarehqurut*. In samples mordanted with only aluminum sulfate, the amount of absorbed Al was higher than other samples. Nonetheless, in terms of the rest of elements, all other samples had more or less the same profile.

The RP-HPLC-DAD outcomes of all dyed samples from group two (DG2-B) proved that more different dye components were detected after RP-HPLC-DAD analysis of the dyed samples from group two (DG2-B), compared to those from the DG1 group of dyeings (Table 5). Apart from alizarin, purpurin and nordamnacanthal, a minor amount of ruberythic acid and rubiadine-3-β-primveroside are systematically detected in various proportions.

Artificial aged dyed samples

After a 504-h light exposure, in order to gain better results of all the analysis and save time, 18 samples out of 84 aged dyed samples were selected to undergo SEM–EDX and RP-HPLC-DAD analyses as it was likewise carried out for mordanted and dyed samples. Furthermore, all the 18 aged dyed samples were divided into two groups, aged dyed group 1 part B (ADG1-B) and aged dyed group 2 part B (ADG2-B). To assessment the change by all the utilized analytical instruments, the samples were compared to their counterpart samples.

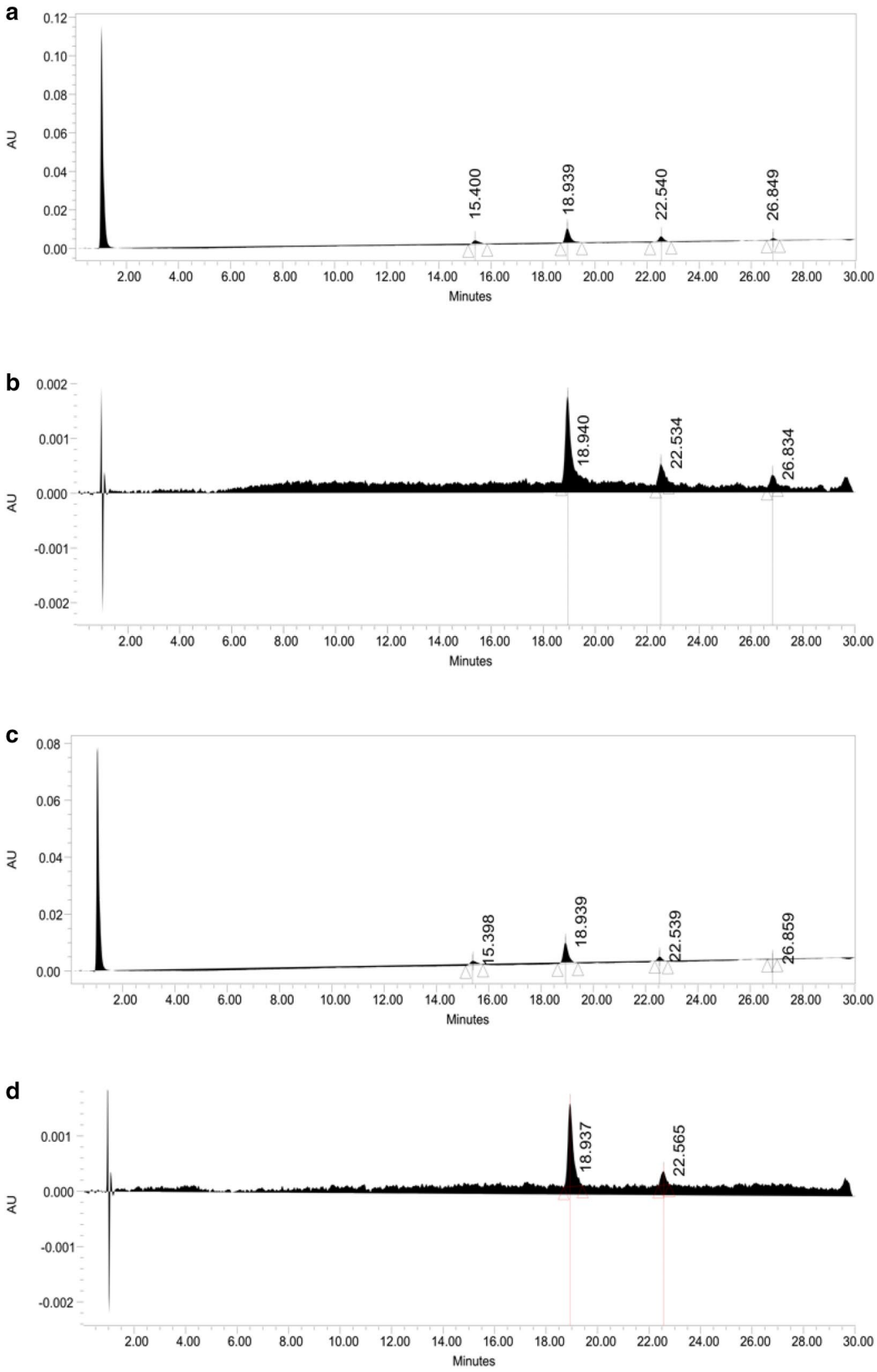


Fig. 7 Chromatogram of Dyed group one part B—**a** DG1-B14 at 255 nm, **b** DG1-B14 at 430 nm, **c** DG1-B15 at 255 nm, **d** DG1-B15 at 430 nm

Aged dyed samples group one (ADG1)

Microscopic and visual analysis showed, before aging samples mordanted with *qarehqurut* and aluminum sulfate, were more saturated and possessed a less orangish hue than samples mordanted with just aluminum sulfate. After 504 h of light exposure, although both faded, samples mordanted with *qarehqurut* and aluminum sulfate were faded less than other samples.

Color measurement assessment of aged fibers group one (ADG1) indicated an increase in the L* value in all samples. Since the L* values gauges fading its increase suggests that all samples became brighter. Samples mordanted with aluminum sulfate demonstrated a higher L* value (lighter) than their match samples which were mordanted with *qarehqurut* and aluminum sulfate. On the other hand, in all samples a* value decreased and b* value in most of samples remained unchanged.

Results from SEM–EDX analysis of aged fibers group one after 504 h of light exposure (ADG1-B) indicated that samples mordanted with aluminum sulfate showed a higher amount of P, Mg and Si than match samples mordanted with both *qarehqurut* and aluminum sulfate.

The RP-HPLC-DAD results revealed that the samples mordanted with *qarehqurut* and aluminum sulfate had alizarin as their main anthraquinone dye compound, present in combination with purpurin as minor anthraquinone dye compound.

Meanwhile, in samples ADG1-B15 and ADG1-B20, alizarin, purpurin, nordamnacanthal, pseudopurpurin and munjistin were found. As the two last compounds are not completely separated by the applied chromatographic extraction and analysis protocol, the sum of the peak areas of both are calculated in the Table 5. Most dye compounds were detected in sample ADG1-B21, more in particular alizarin, purpurin, nordamnacanthal, pseudopurpurin, munjisitin and anthragallol.

In all aged samples, the RP-HPLC-DAD results show that in samples mordanted with the combination of *qarehqurut* and aluminum sulfate, the amount of absorbed chromophore was higher than samples mordanted only with aluminum sulfate.

Aged dyed samples group two (ADG2)

Microscopic and visual assessment of aged fibers group two (ADG2) after 504 h of light exposure exhibited that all of these samples, before and after light exposure, had very clearly close red hues. Samples ADG2-B05 (20% aluminum sulfate) and ADG2-B09 (20% *qarehqurut* with 20% aluminum sulfate) were both pure red and visually the same before aging; however, after aging they became quite slightly lighter than before; sample ADG1-B09 slightly turned to red-orangish hue.

Before aging, sample ADG2-B15 (20% *qarehqurut* with 5% aluminum sulfate), and sample ADG2-B14 (5% aluminum sulfate) were visually very close red colors but sample ADG2-B14 had a slightly red-orangish hue. After 504 h of light exposure, their differences became more visible; i.e. sample ADG1-B15 was less faded than sample ADG2-B14. Hereafter, both samples showed a more red-orangish hue which was more apparent in sample ADG2-B14.

Visually, before aging, sample ADG2-B20 (6% aluminum sulfate) and sample ADG2-B21 (20% *qarehqurut* with 6% aluminum sulfate) had very close red hues. After the same amount of light exposure, both samples turned to an orangish hue as their colors faded; however, ADG2-B20 faded and yellowed more than its counterpart.

According to results coming from colorimetric analysis of aged fibers group two (ADG2) the luminance parameter (L*) had increased in all samples. Nonetheless, in samples mordanted with aluminum sulfate without *qarehqurut* the amount of increase in the differences of L* value was less than other samples. Samples mordanted with both aluminum sulfate and *qarehqurut* proved a better resistance to lightfastness. In samples mordanted with different percentages of aluminum sulfate and 20% *qarehqurut*, the a* value was constant and b* values increased. Using a higher amount of aluminum sulfate (20% w/w%) in mordanting process caused a scarlet hue and more resistance against light exposure.

After aging an increase in lightness (L*) and a decrease in redness (a*) was detected; whereas, yellowness (b* value) remained almost unaltered.

SEM–EDX assessment of aged fibers group two (ADG2-B) revealed that samples mordanted with *qarehqurut* and aluminum sulfate had a higher amount of Al, Cl and Mg than mordanted match samples with aluminum sulfate. Whereas, mordanted samples with aluminum sulfate had a higher amount of Si and P than their peer mordanted samples in which *qarehqurut* and aluminum sulfate were utilized.

Conclusion

Investigation of red dye molecules in twentieth-century Iranian carpets

The detection of alizarin as major anthraquinone dye compound, in combination with purpurin and nordamnacanthal as minor anthraquinone dye compounds indicates the use of plant roots from the *Rubiaceae* family. The given relative ratio between the compounds highlights the application of cultivated madder (*R. tinctorum* L.) species. Madder has been used for dyeing of samples B1, B2, B3 and D2. In 14 out of the 18 analyzed red samples synthetic dye molecules were found, linked with the same synthetic dyestuff(s) Acid Red 88 and/or Acid

Orange 7. These chemically quite related dyestuffs are characterized by the presence of marker molecules compounds S1 and/or S2 and derivatives.

The variation in the ratio of these two molecules and the presence to a greater or lesser extent of their derivatives in several samples is a sign of instability of dyes; on the other hand, it might also provide information on the degradation state of the analyzed historical yarns. Further study on the instability and degradation pathway of these synthetic dyes were not carried out in the scope of this study; nonetheless, it remains as a most interesting future research question.

Study of traditional madder dyeing techniques

In all the samples examined by SEM, before and after the 504-h light exposure, there was no morphological modifications. The major elemental finding from aged dyed samples which mordanted with aluminum sulfate had higher amount of Si and P than their peer samples mordanted with *qarehqurut* and aluminum sulfate.

As it was observed, color of samples mordanted with aluminum sulfate seemed to show a red-orangish hue. While in peer samples, the color of samples with mordanted *qarehqurut* and aluminum sulfate tended to be more of a scarlet hue.

Mordanting had a significant effect on the lightness of shades; i.e. dyed samples mordanted with *qarehqurut* and aluminum sulfate had better colorfastness in comparison with their peer mordanted with only aluminum sulfate. Dyed group two (DG2) which was based on Iranian traditional dyeing technique with madder, the L*a*b* differences were less than dyed group one.

Furthermore, the material-to-liquor ratio proved to have a direct impact on color absorption of fibers. Close study of lightness (L*) values reveals that darker shades were obtained with high dye concentration (1:30) while shades' lightness decreases as dye concentration goes up. Additionally, it was found that mordanting pH leaves a considerable effect on the shades of madder. Samples mordanted with the combination of *qarehqurut* and aluminum sulfate had lower pH values compared with their peer samples mordanted with aluminum sulfate.

To sum up, the study concludes that using organic products in mordanting and/or in dyeing with madder roots had a multidimensional positive effect on color absorption and lightfastness. In historical and prepared samples, the study found the same elements which could be due to having used the same material. Simultaneously, the elements found in madder roots were the same as those elements present in *qarehqurut*. Additionally, following RP-HPLC-DAD analysis, the study found that the detected chromophores-alizarin, purpurin and nordamnacanthal—stayed present after ageing although the peak areas of these main anthraquinone compounds varied post-aging.

Abbreviations

DAD: diode array detection; FTIR: Fourier transform infrared spectrometry; HPLC: high performance liquid chromatography; m/z: mass to charge ratio; MS: mass spectrometry; RP: reversed-phase; SEM: scanning electron microscopy; EDX: energy dispersive X-ray spectroscopy; M:L: material-to-liquor ratio; L*: lightness; a*: redness; b*: yellowness; DG1: dyed samples group one; DG2: dyed samples group two; ADG1: aged dyed samples group one; ADG2: aged dyed samples group two; ATR: attenuated total reflection spectrometry.

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Authors' contributions

ZC processed the experimental data, performed the analysis, drafted the manuscript and designed the figures and tables, IVB aided in interpreting the results and worked on the manuscript and supervised the work in Belgium, RM was involved in planning and supervised the work in Italy. All authors discussed the results and commented on the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

Data are available from the corresponding authors by request.

Competing interests

The authors declare that they have no competing interests.

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