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Chromatographic analysis of natural dyes in mediaeval Islamic paper

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Abstract

Numerous natural dyes were used to dye mediaeval Islamic paper from the tenth to the nineteenth century, using a variety of techniques. The objective of this research is to develop an analytical method using high performance liquid chromatography with diode array detection (HPLC–DAD) to identify natural dyes in forty historical Islamic paper manuscripts from two collections. In addition, novel information was obtained from original treatises containing recipes for dyeing paper and the chronological use of dyes in dyeing mediaeval Islamic paper between the tenth and seventeenth centuries. The results show that thirty-four of the forty manuscripts examined contained dyes. Six natural dyes were detected, including henna, madder, lac, safflower, turmeric, and weld. This is the first study aimed at developing a method for determining various natural dyes in Islamic paper from a wide historical and geographical range in the mediaeval time and to fill significant gaps in the technical and historical knowledge of papermaking.

Keywords Natural dyes, HPLC–DAD, Dyeing, Islamic paper, Quasi-Islamic paper

Introduction

Islamic paper, manufactured in the Islamic cultural realm from the western borders of China to Islamic Spain from the eighth century AD to the seventeenth century AD or perhaps later [1], was produced in a range of natural colours from grey to cream to dark cream, depending on the raw materials and manufacturing process [2, 3]. Due to trade and the decline of the paper industry in the Middle East from the sixteenth century thereafter [4], "quasi-Islamic paper" started being produced, that is a hybrid paper in which the substrate is European but the finish such as colouring, sizing and polishing is Islamic. Both Islamic and quasi-Islamic paper were dyed with various natural dyes for many reasons such as aesthetic [5, 6], legibility [7], symbolic [8] or even preservation [9] (Fig. 1).

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It is often assumed that the methods for dyeing Islamic paper developed from techniques for dyeing textiles [1, 10, 11], until it was actually found that the dyeing process was applied to ready-made paper dipped directly into a dye bath, indeed similar to the techniques for dyeing textiles [9], and to date there is no record of dyes being intentionally added to the paper pulp during the papermaking process. While there are numerous historical recipes for dyeing paper in Persian literature, most of which date from post-mediaeval time [11–13], there is still a lack of research on what materials were used to dye mediaeval Islamic paper, particularly in Arabic literature and in the region where the main centres such as Baghdad, Damascus, Tripoli, and Cairo were located for the manufacture of this paper from the eighth century onwards [14].

Natural dyes from plant or animal sources have been used since historical times to dye textiles, especially common fibres such as linen, wool, cotton, and silk, but also some other materials such as food and leather [15–17]. These dyes were extracted from various parts of raw materials such as fruits, seeds, bark, flowers, roots, and the extraction methods for plenty of them were studied,

Fig. 1 Coloured half folios from the Historic Reference Material Collection of the Heritage Science Laboratory Ljubljana: **a** AP130, **b** AP5, **c** AP125-1, and **d** AP145. (Credit: Ibrahim Elrefaey)

and dyes of various hues were obtained [18, 19]. Their presence in historical objects can thus provide valuable information about the history and culture of a particular time and place, reflecting the characteristics of local crafts and the existence of trade routes in different societies [20].

Identification of these dyes in historical objects has long been a challenge. The main obstacles include contamination originating from the environment in which the object was discovered or stored, the small quantities and limited availability of historical samples, and, most importantly, the low concentrations of dyes [21, 22]. In addition, several external factors can cause natural dyes to degrade and convert to degradation products that are not always known, making these dyes less detectable. These factors include exposure to light, temperature, pH, and storage time [23–25]. The investigation of degradation processes and products is another future perspective.

Over the decades, numerous analytical techniques have been used to identify natural dyes in historic objects, but the choice of approach, whether destructive or non-destructive sampling, with more attention paid to manuscripts, often remains questionable [26]. There is no doubt that non-destructive techniques such as spectroscopic analysis are ethically preferable, but this has often led to inconclusive results for dyes in the past, with techniques such as Raman microscopy, surface-enhanced Raman spectroscopy (SERS), fibre-optic reflectance spectroscopy (FORS), UV–vis reflectance, emission spectroscopy, and fluorescence spectroscopy [27–34]. This might be due to the presence of other additives, such as mordants that also achieved different hues [18, 19]. In addition, interpretation of spectroscopic results is more challenging when various finishing materials such as sizing and polishing are used [35], and the potential presence of multiple dyes [13], in which case the use of a separation technique is required to identify these materials.

Higher accuracy in the identification of dyes in historical objects and manuscripts can instead be achieved using chromatography [26, 36, 37], however, this is destructive and requires sacrificial samples. However, the separation of the components in samples where more than one dye is present allows for a more accurate and reliable identification. In this work, the collections of Islamic manuscripts at the University of Ljubljana and Ain Shams University were used as sacrificial collections to develop and optimise analytical protocols

using destructive sampling to enable the development of non-destructive techniques in the future.

Various chromatographic techniques were used for the analysis of natural dyes in historical objects, especially textiles [16, 22]. High-performance liquid chromatography coupled to diode array detection (HPLC–DAD) has become standard as it can reliably, accurately, and inexpensively identify the plant or animal source of dyes based on retention times and spectra of selected marker compounds, and this method has been used to routinely identify numerous natural dyes on textiles [16, 22, 38–41]. On this basis, the identification of various dyes used in Islamic paper can be achieved with confidence using DAD as a detector if the retention times and UV–vis spectra can be reliably compared with the literature and/or standard and reference materials, as has been done in this research. In further work, liquid chromatography-mass spectrometry can be used to obtain more information about the structure of these compounds, based on their mass spectra [42].

Although coloured paper is a major area of interest within the field of manuscripts, very little is known about it, especially in Islamic paper, on which only two studies have been conducted in the last decade. First, weld (*Reseda luteola* L.) was identified in three historical yellow paper samples from the Mamluk era in Egypt (1250–1517 AD) using high performance liquid chromatography—electrospray ionisation—mass spectrometry (HPLC–ESI–MS) [9]. Second, safflower (*Carthamus tinctorius* L.) was identified in three historical orange paper interleave samples from a nineteenth century Moroccan manuscript using HPLC–DAD [43]. However, the orange colour in this quasi-Islamic paper is obtained via a mixture of a yellow dye and a red dye, and the red dye used alongside safflower was not identified. Moreover, these two works are only fragmentary single-case studies, and to date there is no study that aims to identify the natural dyes in mediaeval Islamic coloured paper in a broader geographical, historical, and analytical context. Third, henna (*Lawsonia inermis* L.) and madder (*Rubia tinctorum* L.) were identified in two Islamic papers from the sixteenth to the nineteenth century, collected from the Near East, Central Asia and North Africa [44].

In this work, an analytical method based on HPLC–DAD was developed to identify natural dyes in two collections used as sources of historical paper samples. The objective was also to establish a reference collection for natural dyes used in Islamic paper to enable the development and optimisation of the method with other destructive, micro-destructive, and non-destructive techniques in the future. This includes the use of paper dye recipes from seven unpublished original Arabic historical sources that have not yet been translated into English to understand the materials, techniques, and chronological use of dyes used in dyeing mediaeval Islamic paper between the tenth and seventeenth centuries.

Materials and methods

Chemicals and materials

The main components of the selected dyes were purchased: lawsone (Merck, 97%), alizarin (Merck), laccaic acid (TCI America), luteolin (HWI group, 94%), apigenin (Merck), curcumin (Carl Roth, ≥ 90%), and hydroxysafflor yellow A (PhytoLab). The solid compounds were used to prepare solutions at 10 ppm in a 85:15 mixture of 0.1% trifluoracetic acid (TFA—Fisher, HPLC grade, > 99%) in water, and acetonitrile (LabExpert, HPLC grade, > 99.9%). The seven dyes used to prepare reference materials were obtained from Kremer Pigmente: Henna (*Lawsonia inermis* L.), madder (*Rubia tinctorum* L.), lac (*Kerria lacca* kerr), weld (*Reseda luteola* L.), turmeric (*Curcuma longa* L.), saffron (*Crocus sativus* L.), and safflower (*Carthamus tinctorius* L.). Whatman filter paper No. 1, which is chemically similar to traditional Islamic paper [45], was used as the substrate for the reference materials. Soda was purchased from Poch (99.5%); alum and natron were purchased from local stores. The chemicals used for the extraction of dyes were: (HCl) (Gram Mol 37%); disodium ethylenediaminetetraacetate (Na_2EDTA) (Kemika, > 99%); methanol (Honeywell, LC–MS grade, 99%).

Historic sources

Seven Arabic primary texts that contain numerous recipes for colouring paper and explain the materials and traditional techniques used in the Arab world during the Islamic mediaeval era were used as original sources for the study. These primary sources cover the historical boundaries from the tenth to the seventeenth century AD and the Arab world during the mediaeval Islamic era as geographical boundaries. In this work, three red and four yellow dyes were selected because visual assessment of paper in the two historical collections revealed the pre-dominance of these two colours, and the historical primary source recipes also suggest these dyes as sources for obtaining the red and yellow colour in Islamic paper and are listed in the Supplementary Information (Additional file 1: Tables S1, S2, and S3).

Model samples

The model samples were reconstructed according to the recipes given in the historic sources (Additional file 1: Table S1). In the next step, these samples were artificially aged for 70 days in a climate test chamber (Vötschtechnik—ClimeEvent) at a temperature of 50 °C and relative humidity of 70% [46].

Historical samples

Two collections were used as sources of historical paper samples for the study: the Historical Reference Material Collection of the Heritage Science Laboratory Ljubljana, which contains 260 samples of Islamic papers from the sixteenth to nineteenth centuries (of which 20 yellow and red samples were selected for analysis) from the Near East, Central Asia, and North Africa; and the collection of Ain Shams University in Egypt, with 90 Islamic manuscripts from the fifteenth to nineteenth centuries (of which nineteenth yellow and red samples were selected for analysis) from Egypt, Syria, and Turkey. "AP" indicates the manuscripts from the Ljubljana collection, while "AS" is used for the manuscripts from the Ain Shams collection. The full list of historical samples and their weights processed for HPLC–DAD analysis are listed in Additional file 1: Table S4. At the moment, both collections are under suitable environmental conditions in which the reference collections used for dye analysis were stored.

Extraction protocol

Two extraction protocols based on the methods described in the literature [47, 48] were tested on lac and saffron-dyed model samples using: (i) ACN/EDTA extraction; (ii) MeOH/HCl extraction. For both methods, samples of about 50 mm^2 in size and 3–5 mg in weight were cut from the original paper sheet, weighed, and placed in glass vials. For the ACN/EDTA extraction, 500 µL of 1:1 v/v mixture of 0.1% EDTA in H_2O and acetonitrile (ACN) were added to each sample. ACN was tested as organic solvent instead of DMF, as traditional in dye extraction methods, to minimise the use of hazardous solvents. For artificially aged model samples dyed with henna and safflower and for all the samples removed from historical manuscripts, the volume of extracting solution added to the samples in the ACN/EDTA protocol was reduced to 150 µL. The vials were then sonicated for 60 min at 60 °C. After filtration with 0.45 µm PTFE syringe filters, the solution was injected directly into the HPLC–DAD.

For the MeOH/HCl protocol, 620 µL of 30:1 v/v mixture of methanol (MeOH) and hydrochloric acid (HCl) 37% were added to the samples in glass vials, which were then sonicated for 60 min at 60 °C. Once reached room temperature, the solution was transferred to a second glass vial and brought to dryness under nitrogen flow. The precipitate was recovered with 500 µL of MilliQ water. The aqueous solution was filtered with 0.45 µm PTFE syringe filters and injected into the HPLC–DAD.

HPLC–DAD method

Based on literature methods [49, 50], we tested three chromatographic methods with different gradients of two eluents: acetonitrile (eluent A) and 0.1% w/w TFA in water (eluent B). The three gradients are listed in Additional file 1: Table S5 and are referred to as Methods 1–3. The final method is given in the table as "Method—Final" where the two eluents were used to create a gradient for the mobile phase that started at 95% of eluent B and was maintained for one minute; eluent B was then reduced to 70% in 14 min, then to 40% in another 5 min; eluent B was maintained at 40% for 10 min, then reduced to 5% in 5 min, and maintained at 5% for another 10 min. The gradient was then returned to the initial conditions (Eluent A: 5%; Eluent B: 95%) within 5 min.

All other parameters were the same for all three methods: injection volume: 20 µL; flow: 0.8 mL/min; DAD acquisition range: 190–800 nm; reference wavelength: 700 nm. Chromatograms were recorded at five wavelengths: 250, 280, 350, 450, and 500 nm. For the aged model samples dyed with henna and safflower and for all the samples from the historical manuscripts, the injection volume was increased from 20 to 60 µL.

Instruments

HPLC

HPLC–DAD analysis was performed using an Agilent 1100 series equipped with quaternary pump, degasser, autosampler and diode array detector. The column used was a Kinetex® 5-µm C18 (150×4.6 mm ID). The spectra were recorded in the wavelength range 190–800 nm.

Colorimetry

The colorimetry data were acquired using a Gretagmacbeth Spectrolino. All data were recorded using the "No" filter, that is with no modification to the emitted radiation of the light source. The D50 light source was used for all measurements, and all data were recorded in reflectance mode. The reflected radiation was collected in the wavelength range 380–730 nm. The colour of the samples was studied by recording the CIE-L*a*b* values.

Results and discussion

HPLC–DAD

Protocol optimisation

Two extraction methods were tested using an organic solvent and either a strong acid (HCl) or a chelating agent (EDTA). The methods were tested on two dyes: lac and saffron. Comparable results were obtained for both methods, regardless of whether alum was used as a mordant in dyeing the paper or not. The method with EDTA was evaluated as the best for both dyes due to the higher intensity of the signals in the chromatograms (evaluated at 250 nm, Additional file 1: Figures S4, S7, and S8). In addition, this method has practical advantages over the HCl method because it is less time consuming and poses

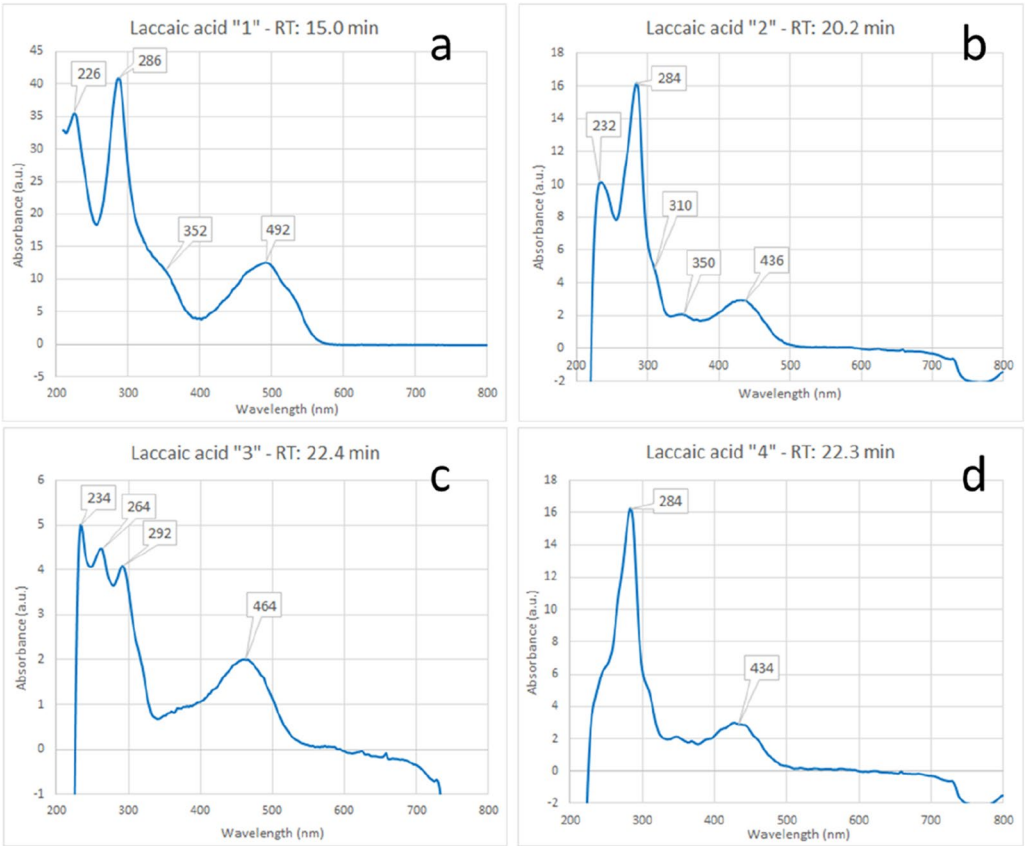

Fig. 2 UV–vis spectra associated with lac compounds, probably laccaic acids. The retention time for each spectrum is reported in the panels. **a** Laccaic acid "1", recorded in the analysis of laccaic acid standard; **b** laccaic acid "2", recorded in the analysis of lac dye bath; **c** laccaic acid "3", recorded in the analysis of lac dye bath; **d** laccaic acid "4", recorded in the analysis of unmordanted lac-dyed model paper

fewer health hazards. Extraction with EDTA also allows the detection of glycosides, which may be essential for the identification of flavonoid dyes such as weld [48] and which are converted to the corresponding aglycones during treatment with HCl. Therefore, the EDTA method was chosen to proceed with the analysis of the remaining model samples as well as samples from historical manuscripts.

Three HPLC–DAD elution methods were evaluated by injecting a mixture of the standards for each dye at a concentration of 10 ppm. The best separation of the standard compounds was obtained with the method starting at 95% of the aqueous phase and reaching 95% of the organic phase (Additional file 1: Table S5, Figure S1). This method was therefore used for all subsequent analyses.

Model samples

Unaged The identification of the dyes used to colour the model samples was successful for all the unaged models. Identification was based on detection of the compounds selected as markers for each dye by comparing both retention time and UV–vis spectrum with results obtained with standard pure compounds and dye baths analysed by the same method. For henna, madder and safflower, the identification is based on a single analyte: lawsone, alizarin and hydroxysafflor yellow A, respectively (Additional file 1: Figures S2, S3, and S5). In turmeric, three curcuminoids were detected and used as markers: curcumin, which was also analysed as a standard, and demethoxy- and bisdemethoxycurcumin, all of which have very similar spectra [51] (Additional file 1: Figures S9, S8). In the case of weld, lac, and saffron, identification of the compounds could not be based on retention times alone because several compounds with very similar spectra were detected. For example, standard luteolin elutes at about 19.3 min, but spectra similar to those of luteolin were found in weld-dyed paper between ~ 11 to ~ 19 min (Additional file 1: Figures S11, S12). The presence of multiple compounds with similar spectra may be due to the presence of other flavones (such as apigenin and chrysoeriol) as well as the presence of glycosides [52]. Although crocin and crocetin have not been analysed as standards for saffron, several compounds have been found in saffron-dyed paper with spectra corresponding to the two compounds described

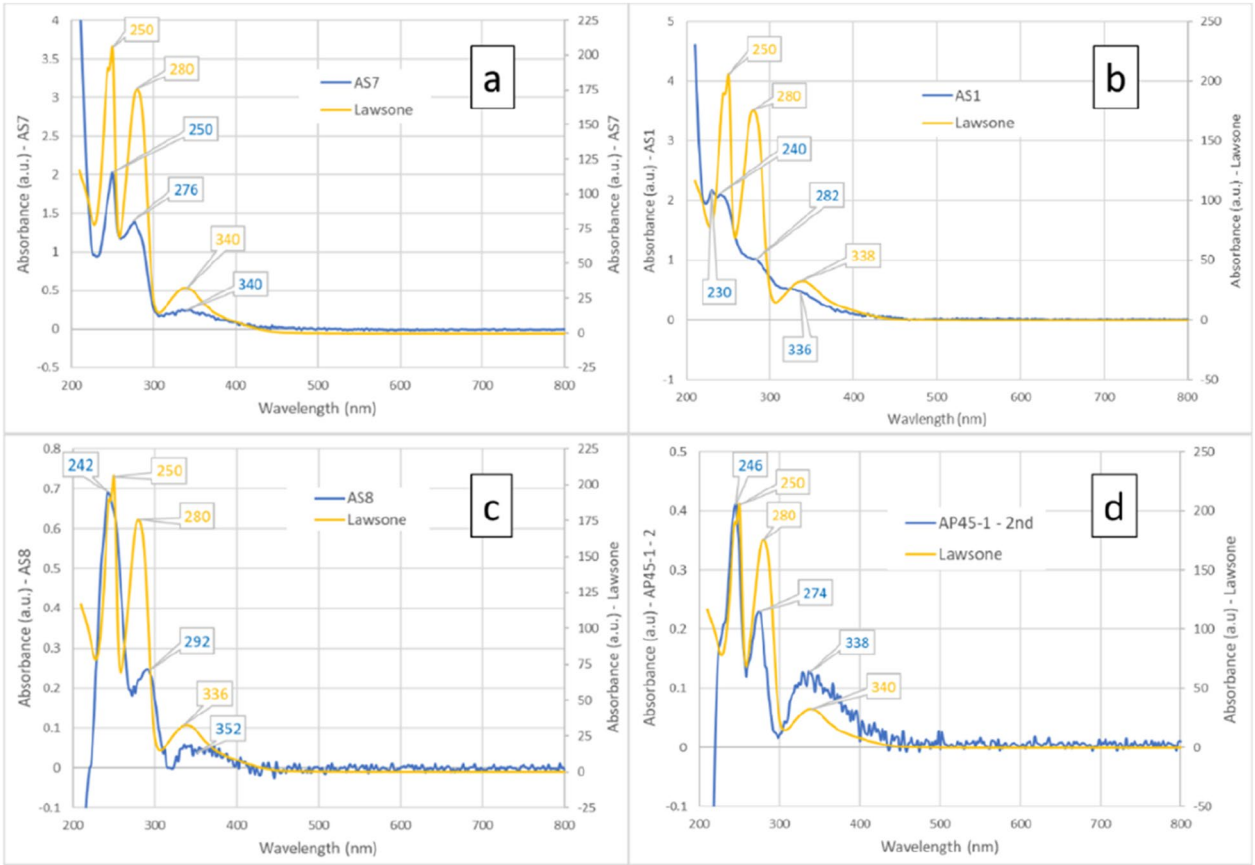

Fig. 3 UV–vis spectra associated with henna, recorded during HPLC–DAD analysis of: **a** sample AS7 (retention time: 16.7 min); **b** sample AS1 (retention time: 16.7 min); **c** sample AS8 (retention time: 16.6 min); **d** sample AP45-1–2 (retention time: 14.5 min)

in the literature [53] (Additional file 1: Figure S7). Lac dye is known to contain several laccaic acids [54], so it was not surprising that many signals (from 11 to 22 min) were associated with such compounds. Based on the comparison between the spectra of standard laccaic acid, lac bath, and un-mordanted and mordanted lac-dyed paper, four spectra were laccaic acids (Fig. 2). Three of the spectra, labelled laccaic acid "1", laccaic acid "2", and laccaic acid "4" in the figure, have a very similar profile to the spectra of laccaic acids in the literature [54, 55]. The spectrum labelled laccaic acid "3" in the figure does not resemble the spectra found in the literature, but it was found in the dye bath and in un-mordanted and mordanted lac-dyed paper and in no other model sample. Therefore, we assign this spectrum to one of the components of the lac dye (Fig. 3).

Aged The model samples were also analysed after artificial ageing. In general, the protocol identified most of the dyes in the samples: lac, madder, turmeric, and weld were readily identified based on the detection of laccaic acids, alizarin, curcuminoids, and flavones, respectively (Additional file 1: Figures S3, S4, S9–S12). Interestingly, luteolin was identified (based on retention time) in the mordanted weld-dyed sample but not in the un-mordanted sample. In the latter, weld identification was based on spectra corresponding to flavones found at retention times other than luteolin (Additional file 1: Figure S12). Only one signal confirming the presence of saffron was detected in both the un-mordanted and the mordanted saffron-dyed paper (Additional file 1: Figure S7). For henna and safflower, only very noisy spectra were found, often indistinguishable from similar spectra in un-dyed aged paper (Additional file 1: Figures S2, S5, and S6). Therefore, two adjustments were made in the protocol to improve the identification of the dyes: (i) the volume of the extraction solution used to treat the paper sample was reduced from 500 to 150 µL, increasing the concentration of analytes while the extraction was still effective; (ii) the injection volume into the HPLC–DAD was increased from 20 µL to 60 µL. After these adjustments, the identification of the dyes was possible in all the aged model samples (Additional file 1: Figures S2–S12).

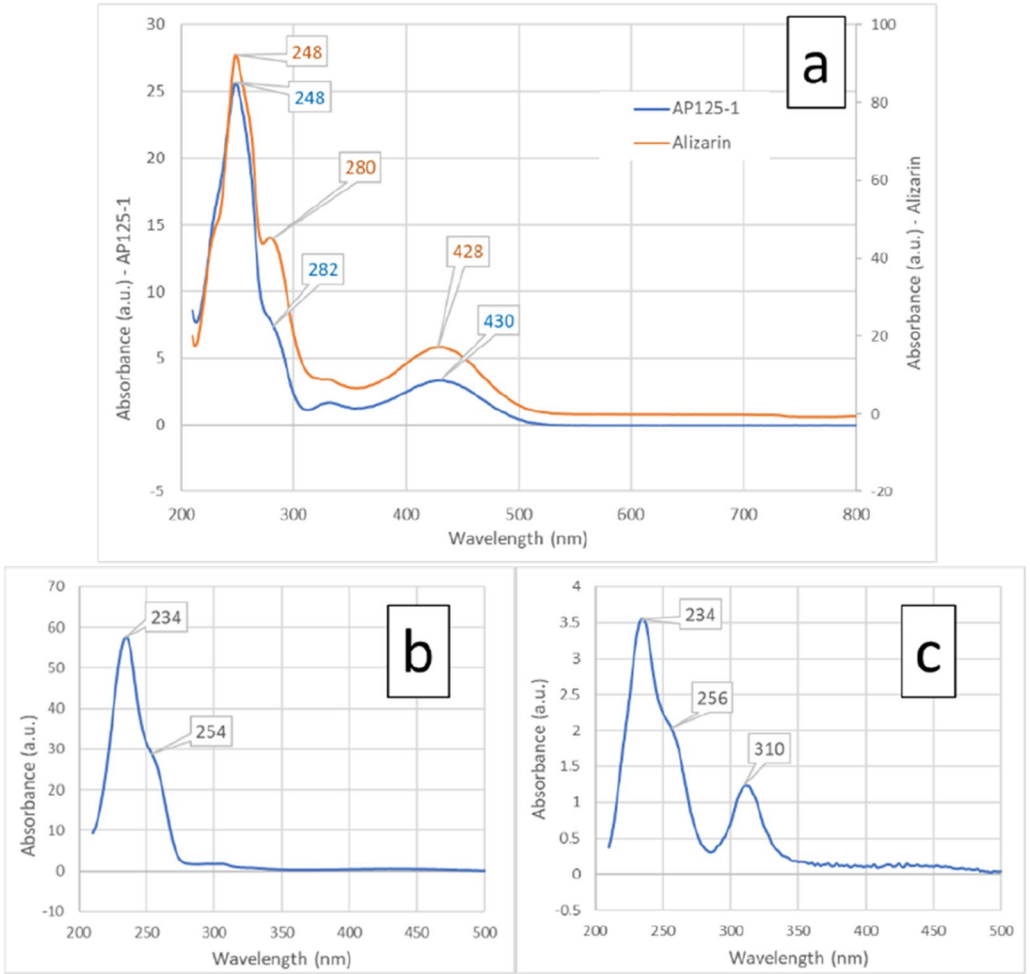

Fig. 4 UV–vis spectra associated with madder, recorded during HPLC–DAD analysis of **a** standard alizarin (orange line; retention time: 22.0 min) and sample AP125-1 (blue line; retention time: 21.8 min). Despite similarities with the spectrum of alizarin, the spectra from **b** sample AP125-1 (retention time: 21.9 min) and **c** sample AP125-1 (retention time: 22.0 min), the differences in wavelengths show that these spectra do not correspond to alizarin and thus are not indicative of the presence of madder

Historical samples

The results show that six dyes were used in the historical manuscripts studied, including henna, madder, lac, safflower, turmeric, and weld, while saffron was not detected in any of the samples. Although saffron is mentioned in historic sources as one of the yellow dyes used to colour paper, it is probably not found because it was an expensive dye in medieval times for many reasons, such as the high cost of labour, transportation, and demand, and remained a luxury item that only the wealthiest could afford [56, 57].

The degree of reliability of the identifications was not the same for all samples: for twelve samples, at least one dye used to stain the paper could be confidently identified, and the identification of the selected marker was consistent with the UV–vis spectrum and retention time. On the other hand, spectra suggesting the presence of a dye were identified for many samples, but the spectra and/or retention times only approximately matched the standards and references used for comparison. In many cases that we consider potential identifications, it is likely that the dyes have been degraded and the degradation products are multiple and not easily identified. The individual dyes and their relative confidence levels are discussed below.

Henna Identification of henna proved more difficult than for other dyes. Among the samples from historical manuscripts, the detection of lawsone can be considered reliable for four samples: AP5, AP73-3, AS3, and AS7. For these samples, spectra were found with the two most intense absorbance peaks at the same wavelengths as the standard lawsone spectrum (Fig. 3, Additional file 1: Figure S13) and with comparable retention times (about

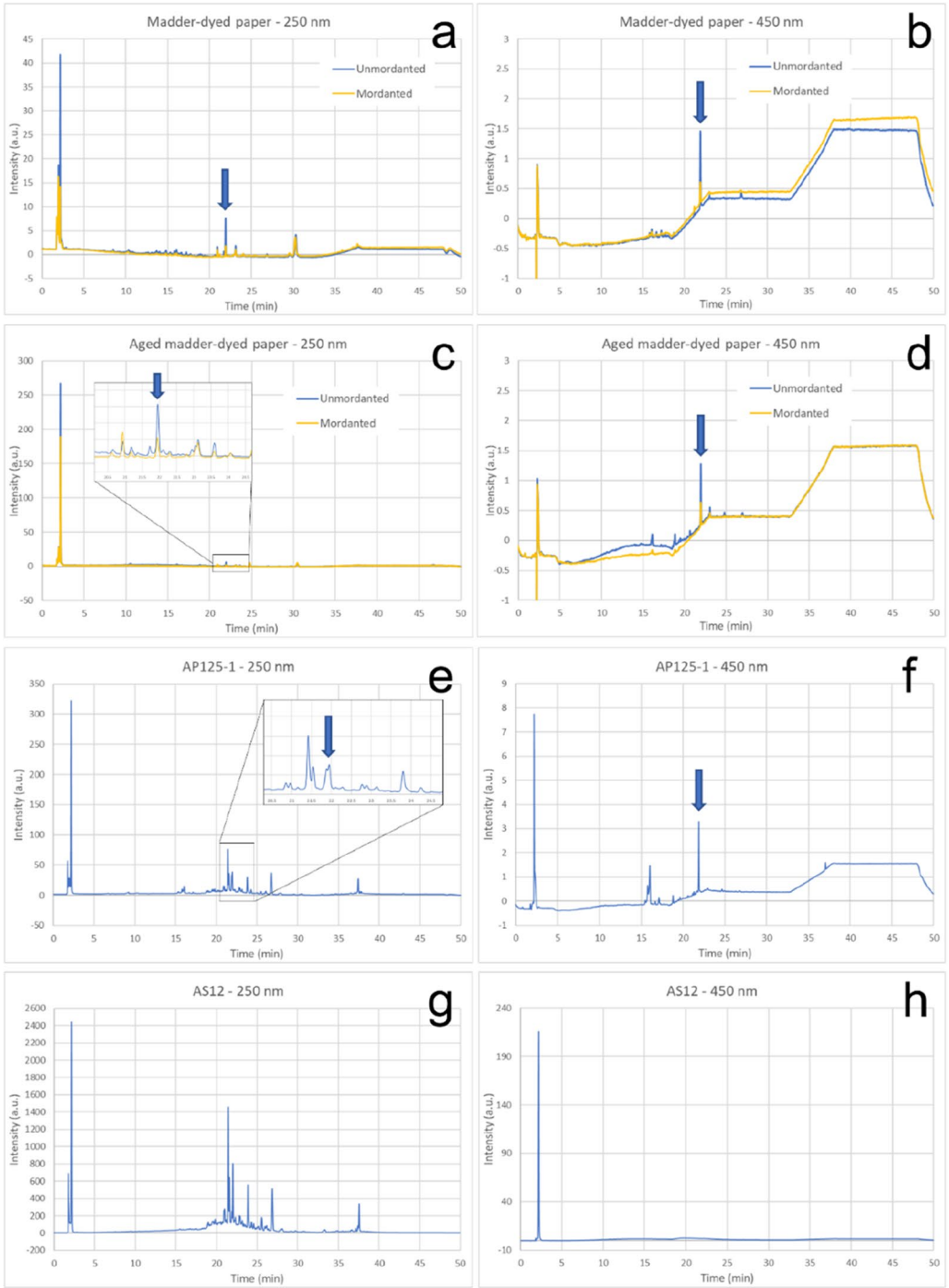

Fig. 5 Examples of chromatograms of the extracts of model papers and historical manuscripts. The arrow indicates the peak of alizarin. **a** and **b**: chromatograms recorded at 250 nm and 450 nm, respectively, of model paper dyed with madder without (blue) and with alum mordant (yellow); **c** and **d**: chromatograms recorded at 250 nm and 450 nm, respectively, of aged model paper dyed with madder without (blue) and with alum mordant (yellow); **e** and **f**: chromatograms recorded at 250 nm and 450 nm, respectively, of historical manuscript AP125-1; **g** and **h**: chromatograms recorded at 250 nm and 450 nm, respectively, of historical manuscript AS12

16.7 min—only for AS3 was the retention time slightly higher at 17.7 min). In several other samples, we found signals potentially indicative of the presence of lawsone, and thus of henna, but with lower confidence. In four of the samples: AP56-4, AP87, AS1, and AS8, signals were found with spectra similar to those of lawsone around

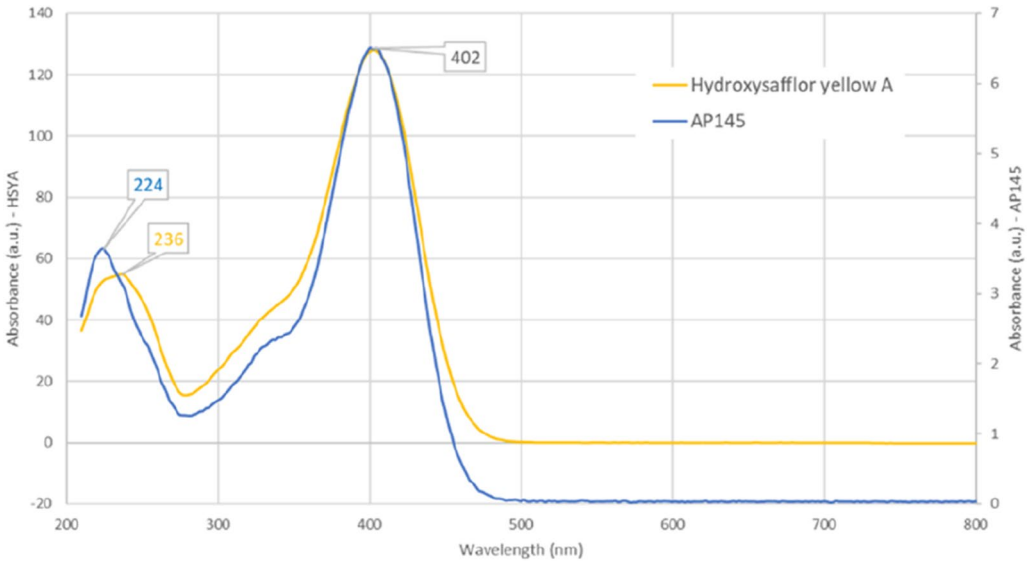

Fig. 6 UV–vis spectra recorded during the HPLC–DAD analysis of standard Hydroxysafflor yellow A (yellow line; retention time: 10.0 min) and sample AP145 (blue line; retention time: 10.1 min)

16.7 min, but with higher noise, likely suggesting very low concentrations of the compound (Fig. 3, Additional file 1: Figure S14). In two other samples: AP45-1–2 and AP129-2, signals with very comparable spectra to lawsone were found, but at slightly shorter retention times (about 14.5 min—Additional file 1: Figure S15). These signals could correspond to degradation products of lawsone, although the collected data (UV–vis spectra) are not sufficient to confirm the identity of these compounds.

Madder The identification of madder in the historical manuscripts was based on the detection of alizarin eluting around 22 min. This marker was confidently identified in three samples: AP45-1–2, AP125-1, and AS4 (Figs. 4, 5 and Additional file 1: Figure S16).

In many other samples, spectra similar to that of alizarin were identified around 22.0—22.8 min. An example is shown in Fig. 4: the spectra show a very intense peak with the same shape as the most intense peak in the spectrum of alizarin around 230–250 nm with a shoulder around 255–285 nm. However, the other main peak of the alizarin spectrum, a broader peak at 430 nm, is not present in these spectra. In some cases, a broad peak with low intensity at 300–315 nm is seen instead.

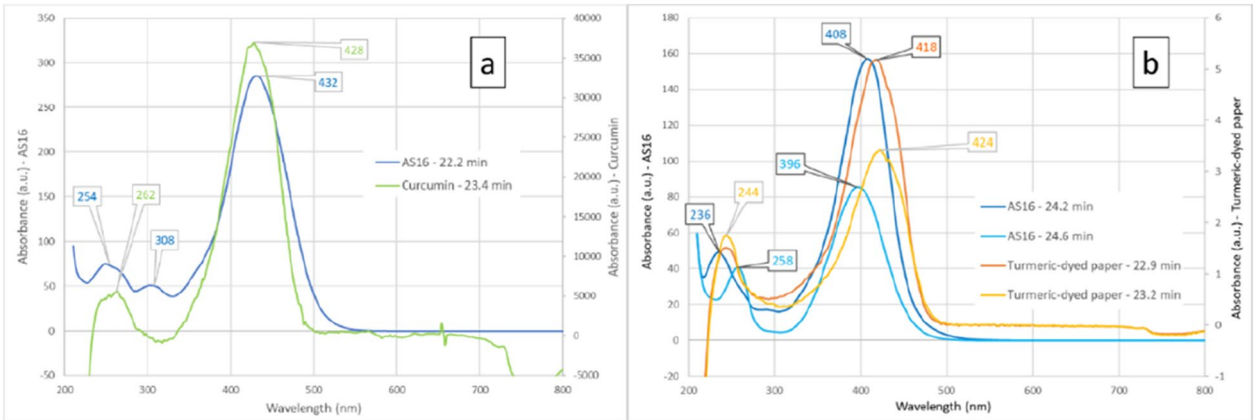

Fig. 7 UV–vis spectra associated with turmeric, recorded during the HPLC–DAD analysis of: **a** standard curcumin (green line; retention time: 23.4 min) and sample AS16 (blue line; retention time: 22.2 min); **b** Bisdimethoxy- (orange line; retention time: 22.9 min) and demethoxycurcumin (yellow line; retention time: 23.2 min) in turmeric-dyed model paper, and two spectra from AS16 (Dark blue and light blue lines; respective retention times: 24.2 and 24.6 min)

Comparison with the UV–vis spectrum of purpurin, another main compound of madder, from the literature [58] confirmed that this is also not the compound detected. Although these spectra were also identified in sample AP125-1, which was shown to contain madder, we do not consider them to indicate the presence of madder. We consider both the most intense absorbance peak in the spectrum (248 nm) and the peak around 430 nm to be fundamental for the identification of alizarin, while the peak in the 230–280 nm range cannot be considered specific, since many organic compounds absorb radiation in this range. Therefore, the absence of the broader absorbance peak at 430 nm suggests that the unknown spectra are not consistent with alizarin. If the product is derived from alizarin, the absence of the peak at 430 nm would indicate a significant change in the structure of the compound; however, the retention time in all cases is very similar to that of alizarin, which would be unlikely in the case of such a structural change.

Lac Lac dye was confidently identified in three samples: AS2-2, AS2-3, and AS4. In each of these samples, we found at least three signals with spectra very similar to those of standard laccaic acid and lac-dyed model samples (Additional file 1: Figures S17–S19), although some discrepancies in wavelength and the presence or absence of some absorbance peaks suggest differences in molecular structures. This is also reflected in the variation of retention times between samples. However, the UV–vis spectra are not sufficient to speculate on the structure of the detected compounds.

Interestingly, we found a signal in many samples suggesting the use of lac. This peak at about 23.2 min was found in a total of 21 samples, including the three samples where lac identification was confident: AP2, AP6, AP22-1, AP25, AP45-1–1, AP45-1–2, AP87, AP131, AP145, AP146, AP151, AS1, AS2-1, AS2-2, AS2-3, AS4, AS5, AS7, AS9, AS11, and AS13. The spectrum corresponding to this signal (Additional file 1: Figures S18, S19) is similar to laccaic acid "1" in Fig. 2: the shapes of the two spectra are comparable, but the wavelengths of the absorbance peaks are different, except for the most intense absorbance at 286 nm. However, it should also be noted that the wavelengths of absorption in the spectra of the model samples dyed with lac can vary considerably

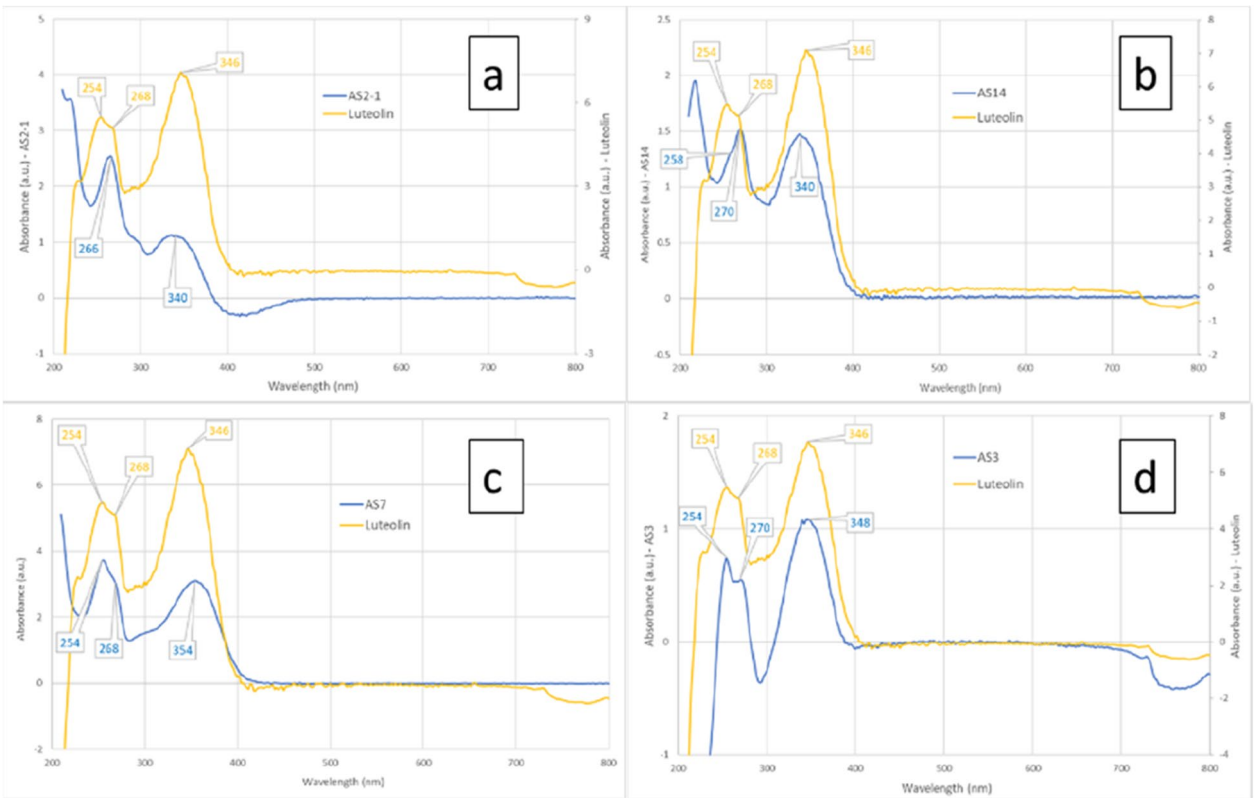

Fig. 8 UV–vis spectra associated with flavonoids, possibly due to dyeing with weld, recorded during the HPLC–DAD analysis of: **a** sample AS2-1 (retention time: 8.9 min); **b** sample AS14 (retention time: 11.9 min); **c** sample AS7 (retention time: 17.8 min); **d** sample AS3 (retention time: 23.1 min). In all panels, the yellow spectrum corresponds to the HPLC–DAD analysis of standard luteolin (retention time: 19.3 min)

Table 1 Summary of dyes identified in the historical samples from the two collections examined

Sample	Dyes						
	Henna	Lac	Madder	Safflower	Saffron	Turmeric	Weld
AP 2	–	o	–	–	–	–	–
AP 5	+	–	–	–	–	–	–
AP 6	–	o	–	–	–	–	–
AP 16–2	–	o	–	–	–	–	–
AP 18	–	o	–	–	–	–	–
AP 22–1	–	o	–	–	–	–	–
AP 25	–	o	–	–	–	–	–
AP 45–1-1	–	o	–	–	–	–	–
AP 45–1-2	o	o	+	–	–	–	–
AP 56–4	o	–	–	–	–	–	–
AP 73–3	+	o	–	–	–	–	–
AP 87	o	o	–	–	–	–	–
AP 89	–	–	–	–	–	–	–
AP 111	–	–	–	–	–	–	–
AP 125–1	–	–	+	–	–	–	–
AP 129–2	o	–	–	–	–	–	–
AP 130	–	o	–	–	–	–	o
AP 131	–	o	–	–	–	–	o
AP 145	–	o	–	+	–	–	–
AP 146	–	o	–	–	–	–	–
AP 151	–	o	–	–	–	–	–
AS 1	o	o	–	–	–	–	–
AS 2–1	–	o	–	+	–	–	o
AS 2–2	–	+	–	–	–	–	–
AS 2–3	–	+	–	–	–	–	–
AS 3	+	–	–	–	–	–	o
AS 4	–	+	+	+	–	–	–
AS 5	–	o	–	–	–	–	–
AS 6	–	–	–	–	–	–	–
AS 7	+	o	–	–	–	–	o
AS 8	o	–	–	–	–	–	–
AS 9	–	o	–	–	–	–	o
AS 10	–	–	–	–	–	–	–
AS 11	–	o	–	–	–	–	–
AS 12	–	–	–	–	–	–	–
AS 13	–	o	–	–	–	–	o
AS 14	–	–	–	–	–	–	o
AS 15	–	–	–	–	–	–	–
AS16	–	–	–	–	–	+	–
AS17	–	–	–	–	–	–	–

"+" indicates confident identification of the dye

"o" indicates potential identification

from compound to compound, although the shape of the spectrum remains very similar (Additional file 1: Figure S4).

In 4 of the remaining historical samples: AP16-2, AP18, AP73-3, and AP130, a signal suggestive of lac use was found at 23.2 min, but with slightly different spectra than the one just discussed (Additional file 1: Figure S18). Notably, the four spectra also have absorbances around 246, 286, and 610 nm, but the relative intensities and shape of the most intense absorbance peaks (< 400 nm)

vary from sample to sample. In addition, sample AP130 shows another signal with spectra similar to that of laccaic acid "3" (Additional file 1: Figure S19). The presence of more than one signal with spectra comparable to laccaic acids makes the identification of lac in this sample more confident. Finally, in AP5 and AP6, we found a signal at 28.7 min (Additional file 1: Figure S20) with a spectrum similar to laccaic acids "1" and "4". Although in AP6 we also found the signal at 23.2 min discussed above, sample AP5 had no other signals with comparable spectra to the laccaic acids. Since the signal at 28.7 min was not found in any other sample at the same retention time, this signal cannot be associated confidently to the presence of lac.

Safflower Three samples from historical manuscripts were determined with confidence to have been dyed with safflower: AP145, AS2-1, and AS4 (Additional file 1: Figure S21). In all cases, identification was based on the signal corresponding to hydroxysafflor yellow A (HSY-A), the major dye of safflower when used as a yellow rather than a red dye [16, 59]. The peak of HSY-A was found in all samples at 10.1 min, with spectra exactly matching those of the standard (Fig. 6). Several other signals (up to 23 in AP145) with very similar spectra eluting between 12 and 21 min were found in all three samples. These signals could correspond either to the other yellow chromophore compounds naturally occurring in safflower [59] or to their degradation products (Additional file 1: Figure S22).

Turmeric Only one sample, AS16, was found to be dyed with turmeric. The major marker of turmeric, curcumin, was identified with good correspondence of the spectrum, although the retention time differed by about 1 min from the expected retention time of the standard (22.2 min compared with 23.5 min of the standard). It was also considered whether this signal might correspond to one of the demethoxy forms of curcumin that occur naturally in turmeric [51] and were detected in the turmeric-dyed models at slightly shorter retention times than curcumin. However, the spectrum shows closer correspondence to that of curcumin (Fig. 7). Two other signals were found at higher retention times with spectra similar to those of the two curcuminoids, but differences in the absorption wavelengths as well as in the retention times and elution order may suggest that these peaks correspond to curcuminoid-derived compounds (Additional file 1: Figure S23).

Weld Based on the retention time of the standard (19.3 min), luteolin was not identified in any of the historical samples examined; however, signals with very similar spectra, albeit at different retention times, were found in 8 of the historical manuscripts. These signals suggest that these samples: AP130, AP131, AS2-1, AS3, AS7, AS9, AS13, and AS14, were dyed with a flavonoid dye, probably weld (Fig. 8).

The retention times and spectral characteristics of the signals suggesting the use of weld can be divided into four categories: (A) eluted at 8.9 min, observed in AS2-1; (B) eluted at 11.6—11.9 min, observed in AS13 and AS14; (C) eluted at 16–5—17.8 min, observed in AP130 and AS7 (and AS13, although the spectrum is very noisy and not very clear due to low intensity); (D) eluted at 22.4—23.5 min, observed in AP131, AS3 and AS9 (Additional file 1: Figures S24–S27).

The presence of several signals potentially associated with weld, with spectra comparable to those of standard luteolin but with different retention times, could be explained in several ways. First, weld is known to contain several flavonoids such as luteolin, apigenin, and chrysoeriol [52]. These compounds may also be present as glycosides in which multiple sugar moieties are bound to the hydroxy groups [60]. The extraction method used here is unlikely to break the glycoside bond [48], so multiple forms of each flavonoid could be present in the same sample. The spectra of both the flavonoids mentioned above [61] and their glycosidic forms are similar to that of luteolin, with the glycosides having only one additional absorbance around 210 nm [60, 62]. This absorbance is present in some of the recorded spectra but is not consistent with retention times. The glycosides would be expected to elute earlier than the corresponding aglycosides because of their higher polarity, so they might correspond to peaks eluting before luteolin (groups A and B). These signals might also correspond to degradation products of the flavonoids as some of them are known to have spectra similar to luteolin [63, 64]. The flavonoids would probably elute at about the same time as luteolin and could therefore correspond to the signals in groups C and D.

Azo dyes Although no marker for the seven selected dyes could be identified in several samples, signals indicating the extraction of organic compounds were always detected throughout the chromatogram. In particular, in sample AS6, where visual assessment of the colour of the paper indicated the presence of synthetic dyes, we observed the presence of several signals with spectra similar to the literature spectra of azo dyes [65, 66] eluting between 17 and 20 min (Additional file 1: Figure S28). Although these spectra cannot be compared to standards, the combination of the visual assessment and the presence of these spectra suggests that the paper was dyed with azo dyes. Interestingly, the presence of these dyes could narrow the eighteenth/nineteenth century dating of the manuscript, as suggested by the visual assessment, to

the second half of the nineteenth century, when azo dyes were first produced [67].

After analysing a total of forty samples, the conclusive findings reveal that dyes were detected in thirty-four of them. The complete list of these dyes identified in the historical samples from the two collections studied is shown in Table 1.

Colorimetry

Except for AS6, all historical samples have similar a* values, ranging from −8 to 11.05. The a* value scales from red to green (positive to negative)—so one would have expected the red dyed samples to have higher a* values than the yellow ones. However, this does not appear to be the case. Instead, the lower end of the a* value mainly contains samples with mixed dyes. Since b* ranges from yellow (+) to blue (−), yellow samples should have the highest b* values. This is not the case, as the samples with only yellow dyes are in the middle of the overall range, below many samples with only red dyes (including AS6), some mixed samples, and some samples with no dye.

AS6 is the sample most different from all the others. The difference is mainly due to the a* value, which tends more towards red than all the others (51.38). For the b* value, the sample is in the middle of all the others (16.81). For the L* value, it is at the lower end (50.33). This difference can be attributed to the fact that this sample contains one of the azo dyes, but not a natural dye, as shown by the results from HPLC–DAD.

Conclusion

In summary, our developed method using HPLC–DAD was successfully applied to identify six of the seven dyes suggested in primary sources for dyeing Islamic and quasi-Islamic paper red and yellow: henna, madder, lac, safflower, turmeric, and weld. The absence of saffron is probably due to its scarcity in the mediaeval time and its exclusive use in luxurious manuscripts. The method can serve as a reference for the identification of natural dyes in additional paper manuscript collections from the mediaeval Islamic world, considering the potential influence of diverse aging and degradation processes on historical samples, leading to significant differences in the obtained analytical results. Our work also examined a variety of original historical sources in which dye recipes are cited providing a more comprehensive understanding of the subject in an analytical context. Finally, future research using liquid chromatography-mass spectrometry (LC–MS) could provide valuable supplementary information on the composition of the natural dyes and their potential degradation products detected in the current study.

Abbreviations

HPLC–DAD	High performance liquid chromatography with diode array detection
UV–VIS	Ultraviolet–visible spectroscopy
LC–MS	Liquid chromatography-mass spectrometry
AP	The manuscripts from the Ljubljana collection
AS	The manuscripts from the Ain Shams collection
TFA	Trifluoracetic acid
EDTA	Ethylenediaminetetraacetate
Na2EDTA	Disodium ethylenediaminetetraacetate

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40494-023-01117-w.

Additional file 1: Table S1. Recipes from the original Arabic texts used for the study from the 10th to seventeenth centuries AD. **Table S2.**. Materials specified in the historical recipes, additives used, extraction method, colour obtained, time and place of use. **Table S3.** Botanical and binomial names, major constituents of the dye, molecular formula and chemical structure of the dyes used for the study. **Table S4.** Weight of the historical samples used for the HPLC–DAD analysis. **Table S5.** Elution gradients of the methods tested during optimisation of the HPLC–DAD method. Eluent A is acetonitrile, whereas eluent B is 0.1% w/w TFA in water. **Figure S1.** Chromatograms (recorded at 250 nm) of the mixture of standard marker compounds for different dyes, analysed with the methods listed in Table 5 in SF: a) Method 1, b) Method 2, c) Method 3. The identified peaks are indicated in the chromatograms. **Figure S2.** UV–vis spectra associated with henna, recorded during HPLC–DAD analysis of lawsone standard, dyed paper, and aged dyed paper (retention time: 16.3 – 16.7 min). **Figure S3.** UV–vis spectra associated with madder, recorded during HPLC–DAD analysis of alizarin standard, dyed paper, and aged dyed paper (retention time: 21.9 – 22.0 min). **Figure S4.** UV–vis spectra associated with lac, recorded during HPLC–DAD analysis of laccaic acid standard, dyed paper, and aged dyed paper. **Figure S5.** UV–vis spectra associated with safflower, recorded during HPLC–DAD analysis of hydroxysafflor yellow A standard, dyed paper, and aged dyed paper (retention time: 10.0 – 10.1 min). **Figure S6.** UV–vis spectra associated with safflower, recorded during HPLC–DAD analysis of dyed paper and aged dyed paper (retention time: 12 – 17 min). **Figure S7.** UV–vis spectra associated with saffron, recorded during HPLC–DAD analysis of unaged and aged model samples. **Figure S8.** Chromatograms (recorded at 250 nm) of reference dyed paper extracted with the MeOH/HCl method and the ACN/EDTA method. The arrows indicate the peaks corresponding to the characteristic compounds of the dye. a) Saffron-dyed paper, with and without mordant. b) Lac-dyed paper, with and without mordant. **Figure S9.** UV–vis spectra associated with turmeric, recorded during HPLC–DAD analysis of curcumin standard, dyed paper, and aged dyed paper (retention time: 23.4 min). **Figure S10.** UV–vis spectra associated with turmeric, recorded during HPLC–DAD analysis of curcuminoids in dyed paper and aged dyed paper (retention time: 23.0 – 23.2 min). **Figure S11.** UV–vis spectra associated with weld, recorded during HPLC–DAD analysis of luteolin standard, dyed paper, and aged dyed paper (retention time: 19.2 – 19.3 min). **Figure S12.** UV–vis spectra associated with weld, recorded during HPLC–DAD analysis of luteolin in dyed paper and aged dyed paper (retention time: 10—14 min). **Figure S13.** UV–vis spectra associated with henna (lawsone), recorded during HPLC–DAD analysis of samples AS7, AP5, AP73-3, and AS3 (retention time: 16.6 – 17.7 min). **Figure S14.** UV–vis spectra associated with henna, recorded during HPLC–DAD analysis of samples AS8, AP56-4, AP87, and AS1 (retention time: 16.6 – 16.7 min). **Figure S15.** UV–vis spectra associated with henna, recorded during HPLC–DAD analysis of samples AP45-1–2 and AP129-2 (retention time: 14.5 – 14.6 min). **Figure S16.** UV–vis spectra associated with madder (alizarin), recorded during HPLC–DAD analysis of samples AP45-2, AP125-1, and AS4 (retention time: 22.0 min). **Figure S17.** UV–vis spectra associated with lac (laccaic acid), recorded during HPLC–DAD analysis of samples AS4, AS2-2, and AS2-3 (retention time: 12 – 14 min). **Figure S18.** UV–vis spectra associated with lac (laccaic acid), recorded during HPLC–DAD analysis of samples AP2,

AP6, AP16-2,AP22-1, AP25, AP45-1, AP45-1–2, AP73-3, AP87, AP130, AP131, AP145, AP146, AP151, AS1, AS2-1, AS2-2, AS2-3, AS4, AS5, AS7, AS9, AS11, and AS13 (retention time: 23.2 – 23.3 min). **Figure S19.** UV–vis spectra associated with lac (laccaic acid), recorded during HPLC–DAD analysis of samples AP130, AS2-3 and AS2-2 (retention time: 22.0 – 23.8 min). **Figure S20.** UV–vis spectra associated with lac (laccaic acid), recorded during HPLC–DAD analysis of samples AP5 and AP6 (retention time: 28.7 min). **Figure S21.** UV–vis spectra associated with safflower (hydroxysafflor yellow A), recorded during HPLC–DAD analysis of samples AP145, AS2-1, and AS4 (retention time: 10.1 min). **Figure S22.** UV–vis spectra associated with safflower, recorded during HPLC–DAD analysis of samples AP145, AS2-1, and AS4 (retention time: 12.2 – 19.4 min). **Figure S23.** UV–vis spectra associated with turmeric (curcuminoids), recorded during HPLC–DAD analysis of sample AS16 (retention time: 22.2 – 24.6 min). **Figure S24.** UV–vis spectra associated with weld, recorded during HPLC–DAD analysis of samples AS2-1 (retention time: 8.9 min). **Figure S25.** UV–vis spectra associated with weld, recorded during HPLC–DAD analysis of samples AS13 and AS14 (retention time: 11.6 – 12.0 min). **Figure S26.** UV–vis spectra associated with weld, recorded during HPLC–DAD analysis of samples AP130, AS7, and AS13 (retention time: 16.6 – 17.8 min). **Figure S27.** UV–vis spectra associated with weld, recorded during HPLC–DAD analysis of samples AP131, AS3, and AS9 (retention time: 22.4 – 23.5 min). **Figure S28.** UV–vis spectra probably associated with azo dyes, recorded during HPLC–DAD analysis of sample AS6 (retention time: 17.6 – 20.5 min).

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Author contributions
HE conceptualization, methodology, investigation, writing—original draft preparation FDG methodology, investigation, writing IKC methodology, investigation, supervision MS conceptualization, methodology, supervision, reviewing and editing. All authors read and approved the final manuscript.

Availability of data and materials
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Declarations

Competing interests
The authors declare no competing interests.

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