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Case study

Unveiling the colour palette of Arraiolos carpets: Material study of carpets from the 17th to 19th century period by HPLC-DAD-MS and ICP-MS

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ABSTRACT

Wool samples collected from thirteen Arraiolos carpets from the 17th–19th century belonging to the National Museum of Ancient Art (NMAA, Lisboa, Portugal) collection were analysed to identify the natural dyes and mordants employed in the traditional dyeing process, in a way to complement and improve actual knowledge on this rugs. Natural dyes were extracted from Arraiolos historical wool fibres using a mild extraction method, followed by high-performance liquid chromatography with diode array and mass spectrometry detection (HPLC-DAD-MS) for compound identification. Colourimetry was used to measure colour parameters in all historical samples. Quantification of mordants in the historical fibres was carried out by inductively coupled plasma-mass spectrometry (ICP-MS). Weld, indigo, spurge flax, brazilwood, madder and cochineal were identified as dye sources in the fibres. Alum was the most commonly used mordant, but the presence of iron and zinc was also detected in some darker samples. The use of madder and cochineal is not referred in the available historical dyeing recipes. This study also proved that the actual visual perception of these carpets is strongly affected by the natural dyes photodegradation, which was mostly unaccounted for before.

1. Introduction and research aims

The origin of Arraiolos embroidered carpets is rather obscure but by the late 1600s they are mentioned in the inventories of Portuguese aristocratic households and churches [1,2]. Production of these carpets was more significant during the 17th and 18th centuries, ceasing almost completely by the second half of the 19th century [1,2].

Classification of historical carpets is nowadays done based solely on stylistic considerations. Earlier carpets present a strong influence of the oriental carpets, which were popular in Portugal and in Europe at the time [1,3]. Carpets attributed to the 17th century usually show a very rich colour palette and presence of oriental motifs. By the end of the 17th century, the industry is completely settled in Arraiolos, and 18th century carpets were usually embroidered with a large central medallion and a border. It is also in this period that the most characteristic Arraiolos pattern "animal pattern" shows up [1–3]. The original oriental influence and rich colour palette almost vanished by the end of the 18th century, and 19th century carpets usually present a duller colour palette and simpler patterns [1–3].

Some of the materials used on the manufacture of these carpets were locally provided, like sheep wool for the embroidery and linen or hemp for the canvas, while others, like some dyes used to colour the wool, were imported [1]. Historical literature concerning the Arraiolos carpets is very scarce and the only description concerning the colour palette used in their making is found in a document from the 19th century [4]. According to those recipes, blue colour hues were obtained with indigo blue dyes (*Isatis tinctoria* L. or *Indigofera tinctoria* L.); the reds with brazilwood (*Caesalpinia* spp.) or brazilwood and spurge flax (*Daphne gnidium* L.); yellows with weld (*Reseda luteola* L.); the greens were dyed with indigo and weld; the browns with brown natural wool dyed with spurge flax; and the black with logwood (*Haematoxylum campechianum* L.).

The majority of red and yellow dyes require the use of mordant for an effective dyeing process [5]. When the mordant used is an inorganic salt, the metal ion combines with the fibre and dye to form a coordination compound, influencing the fibre colour hue and

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ensuring that the colour stands fast against washing [5]. Alum and "*caparosa*" (iron, copper or zinc sulfate) are referred to as mordants in historical recipes [4].

Previous material analysis of three Arraiolos carpets identified weld, spurge flax, indigo and brazilwood in the colour wool yarns [6,7]. Alum was identified in most of the samples, but iron was also found in high amounts especially for the dark coloured hues [6,7].

The aim of this work was to perform a wider study on the materials used in the manufacture of historical Arraiolos carpets along the centuries. Thirteen carpets from the 17th–19th century period were studied in order to identify the natural dyes and mordants used for their making. The results obtained for the six most representative carpets are presented in this manuscript and data concerning the other seven is presented as Supplementary data, Fig. S1 and Table S1. Colour of the dyed wool fibres was measured by colourimetry, and dye chromophores were identified by liquid chromatography coupled with diode array detection and mass spectrometry (LC-DAD-MS). Mordant ions quantification was achieved by inductively coupled plasma-mass spectrometry (ICP-MS).

2. Experimental

2.1. Materials and reagents

The following reagents (analytical grade) were used: *N,N*-dimethylformamide and nitric acid (65%) from Panreac (Barcelona, Spain), EDTA dissodium salt from Sigma-Aldrich (Milwaukee, WI, USA). Methanol, acetonitrile and formic acid (HPLC gradient grade) from Merck (Darmstadt, Germany) were used in LC-DAD-MS sample preparation and analysis. For mordant quantification, 1 g dm^{-3} single element standard solutions of aluminium, iron, copper and zinc (Merck) were used. Water from a Millipore Simplicity UV system (Billerica, MA, USA) was used throughout this work.

2.2. Arraiolos carpets sampling

Thirteen historical carpets from the 17th–19th century period (catalogue nrs. 19, 24, 25, 29, 30, 36, 38, 40, 55, 74, 88, 89 and 114) were selected from the National Museum of Ancient Art collection (NMAA, Lisboa, Portugal). Embroidery wool yarns with a length between 3 and 5 mm were sampled with fine point tweezers and spring bow scissors from thread ends in damaged areas or in the backside of the carpets. Each sample was individually stored in an *Eppendorf* tube protected from light.

2.3. Colourimetric studies

A portable spectrophotometer equipped with a Xenon lamp and a photo-diode sensitive to the 360–750 nm spectral range from Datacolor (Zurich, Switzerland) was used for colorimetric studies (L*, a* and b*- CIELab space defined by Commission Internationale de l'Eclairage in 1976). Black and white standards were used for calibration. Iluminant CIE D65; 10° of observation angle and specular component excluded. Analyses were performed at three different points of each wool sample, with the average value used for data interpretation.

2.4. Analysis of natural dyes

2.4.1. Natural dyes extraction procedure

Samples of approximately 2.0 mg of dyed wool were placed in vials and 1.0 mL of 0,1% EDTA in water/DMF (1:1, *v/v*) was added. The vials were capped and kept at 100 °C for 30 min. Vials were cooled to room temperature, and vacuum was used to evaporate the solvent. Dried samples were redissolved in 250 μL MeOH/H_2O (1:1, *v/v*) and filtered through a 0.45 μm filter [8]. Blue and green samples were redissolved in 250 μL MeOH/DMF (1:1, *v/v*) and filtered through a 0.45 μm filter [7].

2.4.2. LC-DAD-MS analysis [7]

An LCQ Fleet Thermo Finnigan mass spectrometer instrument equipped with an ESI source, an ion trap mass analyzer and a PDA detector was used (San Jose, CA, USA). The conditions of MS analysis were: capillary temperature of 300 °C; source voltage of 5.0 kV, source current of 100.0 μA, and capillary voltage of −20.0 V in negative ion mode and 22.0 V in positive ion mode. Analytes were detected in full MS mode: in negative ion mode two segments were used, 10% CID from 0–15 min and 30% CID from 15–30 min; in positive ion mode, 30% CID was used from 0–30 min. Column temperature was set at 30 °C and tray temperature was set at 24 °C. The DAD detector was set at 200–800 nm. The MS and DAD equipments were coupled to an LC system equipped with an autosampler (Surveyor Thermo Finnigan). The analytical column was a reversed phase Fortis-C18, (Fortis Technologies) (C18, particle size 3.0 μm, 150 × 2.1 mm). The mobile phase consisted of acetonitrile (A) and water acidified with 0.1% formic acid (B). The gradient used was 0–90% A from 0–20 min, then 90% A from 20–30 min. The injection volume was set to 10 μL.

2.5. Mordant quantification

2.5.1. Sample preparation

Historical fibres of 0.1–2.0 mg were placed in polypropylene tubes and digested with 0.5 mL of concentrated HNO_3 in an ultrasonic bath without temperature control. Acidic digestion proceeded until complete fibre dissolution (approximately 2 h). The solution was then diluted to 5 mL using ultrapure water.

2.5.2. ICP-MS analysis

Measurements were carried out using a ThermoScientific Element XR ICP-MS instrument, equipped with a sector field mass spectrometer of reverse Nier-Johnson geometry. Sample introduction was accomplished by means of a MicroMist nebulizer (sample uptake rate of 200 μL/min) (Glass Expansion), mounted onto a cyclonic spray chamber (Glass Expansion). Instrument settings and data acquisition parameters used were: Rf power 1250 W; auxiliary gas flow rate 0.800 L/min; cool gas flow rate 16.000 L/min; sample gas flow rate 0.993 L/min; mass resolution 4000 m/Δm; segment duration 200 ms; sample time 10 ms; E-scan type and 36 sweeps; total measurement time per sample 126 s.

Concentrations for all target elements (Al, Fe, Cu, Zn) were determined via external calibration versus a standard solution, containing 35 μg/L of the analyte elements. This standard solution was prepared by dilution of commercially available 1 g/L single element standard solutions (Merck) with 0.14 M HNO_3. High purity water–purified by means of a Milli-Q system (Millipore) – and HNO_3 – purified by sub-boiling distillation in PFA equipment – were used for dilution.

3. Results and discussion

Thirteen carpets from the 17th–19th century period were studied in order to identify the natural dyes and mordants used for their making. The results obtained for the six most representative carpets are presented in this manuscript (catalogue nrs. 24, 25, 40, 55, 74 and 88; Fig. 1) and data concerning the other seven carpets (catalogue nrs. 19, 29, 30, 36, 38, 89 and 114) is presented as Supplementary data, Fig. S1 and Table S1.

The colourimetric analysis of the different samples is presented in Table 1. For simplicity, samples of the different carpets studied were grouped according to the identified chromophores. The

Table 1
Colourimetric data and LC-DAD-MS identification of natural dyes in wool samples collected from Arraiolos tapestries with catalogue numbers 24, 25, 40, 55, 74 and 88 from NMAA collection.

ID	Colour	CIEL*a*b* coordinates			rt (min.)	LC-DAD data (nm)	LC-MS data (m/z)		Identification	Possible dye source
		L*	a*	b*			ESI⁻	ESI⁺		
88_01	Bl	22.33	−2.66	−8.73	16.49	245, 276, 313, 487	**491**, 447, 357, 327	–	Carminic acid	Cochineal + Indigo or Woad
					26.58	251, 286, 319, 607	–	**263**, 235, 219	Indigotin	
24_02	Gr	33.41	−8.88	−0.38	15.99	246, 267, 327	**609**, 447, 285	–	Luteolin di-O-glucoside	Weld + Indigo or Woad
24_04	Gr	37.19	−1.46	16.96	16.42	244, 268, 339	**609**, 447, 285	–	Luteolin	
24_07	Bl	18.23	−4.78	−2.45	17.33	248, 266, 348	**447**, 285	–	3′,7-di-O-glucoside	
25_08	Gr	28.20	−10.80	−1.13	18.09	245, 266, 331	**431**, 269	–	Luteolin 7-O-glucoside	
25_10	Gr	33.30	−7.11	16.04	18.22	247, 269, 341	**461**, 299	–	Apigenin 7-O-glucoside	
55_06	Gr	28.26	−7.57	−1.40	20.57	252, 265, 348	**285**, 241, 217, 199,	–	Chrysoeriol 7-O-glucoside	
74_02	Gr	41.39	−6.99	25.11	26.60	252, 285, 320, 605	175, 151, 133	**263**, 235, 219	Luteolin	
74_03	Gr	33.03	−8.27	12.15			–		Indigotin	
88_02	Gr	48.51	−1.27	24.18						
88_03	Gr	33.72	−6.95	10.72						
88_04	Rs	46.10	14.42	10.35	16.67	240, 276, 308, 493	**491**, 447, 357, 327, 299	–	Carminic acid	Cochineal + Madder
					18.02	245, 277, 315, 491	**491**, 447, 357	–	dcIV	
					18.42	245, 277, 315, 491	**491**, 447, 357	–	dcVII	
					24.74	252, 274, 423	–	**241**, 213, 185, 157	Alizarin	
					26.31	256, 288, 479	–	257, 229	Purpurin	
88_05	R	44.23	21.12	15.86	18.02	247, 266, 407	**269**, 254, 223	–	Morindone	Madder (*Morinda* spp.)
					18.21	259, 284, 415	**239**, 195	–	Xanthopurpurin	
					24.73	249, 278, 426	–	**241**, 213, 185, 157	Alizarin	
					26.30	256, 294, 479	–	**257**, 229	Purpurin	
25_01	Y	36.67	4.69	22.69	24.72	250, 278, 426	–	**241**, 213, 185, 157	Alizarin	Madder
74_08	O	52.41	15.04	24.40	26.29	256, 293, 479	–		Purpurin	
88_06	R	40.01	31.18	17.91						
25_02	Y	51.49	3.32	24.39	16.04	245, 267, 335	**609**, 447, 285	–	Luteolin di-O-glucoside	Weld
40_01	Y	65.04	1.39	49.66	16.43	245, 267, 335	**609**, 447, 285	–	Luteolin	
55_02	Y	56.08	4.28	33.18	17.33	254, 267, 348	**447**, 285	–	3,7′-di-O-glucoside	
74_04	Y	55.73	9.27	37.87	18.12	244, 265, 324	**431**, 269	–	Luteolin 7-O-glucoside	
74_05	Y	56.43	9.43	47.62	20.58	253, 266, 348	**285**, 243, 241, 217,	–	Apigenin 7-O-glucoside	
88_07	Y	51.42	3.78	30.08			199, 175, 151, 133		Luteolin	
88_08	Bl	45.98	−5.66	−0.38	17.34	243, 269, 348	**447**, 285	–	Luteolin 7-O-glucoside	Weld? + Indigo or Woad
					26.61	253, 285, 319, 607	–	**263**, 235, 219	Indigotin	
24_06	W	51.14	2.72	16.13	–	–	–	–	–	No dye source identified
25_05	Br	19.90	3.87	5.00						
25_06	Bg	50.70	4.62	24.38						
25_07	Bg	53.29	4.15	16.44						
55_03	Bg	60.54	3.02	17.00						
74_14	Bg	56.56	9.41	26.91						
88_09	W	60.27	2.78	16.57						
24_03	Bl	38.54	−4.56	2.05	26.55	245, 286, 331, 606	–	**263**, 235, 219	Indigotin	Indigo or Woad
24_08	Bl	23.97	−3.29	−8.92						
25_03	Bl	24.02	−4.25	−11.77						
25_09	Bl	42.78	−6.33	−2.94						
40_08	Bl	36.67	−6.44	−10.28						
55_05	Bl	39.38	−7.47	−5.12						
55_08	Bl	18.17	0.60	−10.48						
74_01	Bl	25.93	−4.40	−7.04						
74_07	Bl	49.27	−5.77	7.09						
74_10	Bk	18.11	−0.75	−0.33						
55_04	O	44.51	14.30	26.32	15.99	243, 277, 323	**609**, 447, 285	–	Luteolin di-O-glucoside	Weld + Madder
74_06	R	35.11	32.91	21.91	16.45	243, 277, 323	**609**, 447, 285	–	Luteolin	
74_13	O	42.31	25.56	26.74	17.37	250, 267, 346	**447**, 285	–	3,7′-di-O-glucoside	
					20.62	250, 267, 347	**285**, 217, 199, 175	–	Luteolin 7-O-glucoside	
					24.74	252, 274, 423	–	**241**, 213, 185, 157	Luteolin	
					26.31	256, 288, 479	–	**257**, 229	Alizarin	
									Purpurin	
74_09	Rs	45.02	20.72	15.65	16.47	240, 276, 308, 493	**491**, 447, 357, 327, 299	–	Carminic acid	Cochineal
74_11	Gy	32.58	2.37	4.85	24.74	252, 274, 423	–	**241**, 213, 185, 157	Alizarin	Madder + Indigo or Woad
74_12	Gy	42.89	2.41	12.71	26.31	256, 288, 479	–	**257**, 229	Purpurin	
					26.55	245, 286, 331, 606	–	**263**, 235, 219	Indigotin	
25_04	Rs	36.81	31.41	13.25	16.47	240, 276, 308, 493	**491**, 447, 357, 327, 299	–	Carminic acid	Cochineal + Madder + Weld
					17.37	250, 267, 346	**447**, 285	–	Luteolin 7-O-glucoside	
					24.74	252, 274, 423	–	**241**, 213, 185, 157	Alizarin	
					26.31	256, 288, 479	–	257, 229	Purpurin	
55_01	OBr	29.24	22.90	18.94	15.99	243, 277, 323	**609**, 447, 285	–	Luteolin di-O-glucoside	Weld + Brazilwood + Madder
					16.45	243, 277, 323	**609**, 447, 285	–	Luteolin 3,7′-di-O-glucoside	
					17.37	250, 267, 346	**447**, 285	–	Luteolin 7-O-glucoside	
					18.80	259, 307, 333	**243**	**245**	Type C compound	
					20.62	250, 267, 347	**285**, 241, 217, 199, 175, 133	–	Luteolin	
					24.74	249, 278, 429	**239**, 211	–	Alizarin	
					26.31	256, 290, 479	**255**, 227	–	Purpurin	

Table 1 (*Continued*)

ID	Colour	CIEL*a*b* coordinates			rt (min.)	LC-DAD data (nm)	LC-MS data (m/z)		Identification	Possible dye source
		L*	a*	b*			ESI⁻	ESI⁺		
24_05	Y	50.73	3.60	21.16	18.80	259, 307, 333	**243**	**245**	Type C compound	Brazilwood
40_12	Bg	53.68	9.23	30.79						
55_07	Y	53.19	6.46	22.19						
55_09	Bg	63.34	8.79	25.22						
40_02	Br	23.41	6.67	10.07	16.01	223, 253, 320	**609**, 447, 285	–	Luteolin di-O-glucoside	Weld + Brazilwood
					16.42	244, 265, 332	**609**, 447, 285	–	Luteolin 3,7′-di-O-glucoside	
					17.39	243, 266, 348	**447**, 285	–	Luteolin 7-O-glucoside	
					18.04	243, 268, 332	**431**, 269	–	Apigenin 7-O-glucoside	
					18.82	246, 267, 331	**243**	**245**	Type C compound	
40_03	Bl	48.34	−7.51	−6.55	18.80	246, 267, 331	**243**	**245**	Type C compound	Brazilwood + Indigo or Woad
40_07	Bl	28.45	−3.53	−15.22	26.58	253, 282, 606	–	**263**, 235, 219	Indigotin	
40_04	Gr	33.89	−9.38	11.97	15.03	224, 256, 309	**339**, 177	–	Daphnin	Spurge flax + Indigo or Woad
40_05	Gr	39.82	−7.27	23.37	15.70	223, 244, 322	**339**, 177	–	Daphnetin 8-O-glucoside	
40_06	Gr	24.06	−9.12	4.49	16.01	224, 255, 323	**609**, 447, 285	–	Luteolin di-O-glucoside	
					16.42	243, 268, 329	**609**, 447, 285	–	Luteolin	
					16.84	225, 261, 324	**515**, 339, 177	–	3,7′-di-O-glucoside	
					17.42	243, 266, 348	**447**, 285	–	Daphnetin derivative	
					18.08	243, 268, 332	**431**, 269	–	Luteolin 7-O-glucoside	
					20.57	250, 267, 347	**285**, 243, 175, 151, 133	–	Apigenin 7-O-glucoside	
					26.51	245, 286, 607	–	**263**, 235, 219	Luteolin Indigotin	
40_09	Rs	56.52	11.65	25.84	17.41	243, 266, 348	**447**, 285	–	Luteolin 7-O-glucoside	Weld + Brazilwood
40_10	Br	38.53	8.06	17.40	18.12	224, 243, 445	**283**, 265, 173	–	Brazilein	
					18.80	246, 267, 331	**243**	**245**	Type C compound	
40_11	Rs	44.67	18.52	27.20	18.14	224, 243, 445	**283**, 265, 173	–	Brazilein	Brazilwood
					18.80	246, 267, 331	**243**	**245**	Type C compound	
24_01	Y	49.40	4.30	25.70	16.01	224, 253, 319	–	**611**, 449, 287	Luteolin di-O-glucoside	Spurge flax + Brazilwood
					16.44	243, 267, 334	–	**611**, 449, 287	Luteolin 3,7′-di-O-glucoside	
					16.89	260, 323	**177**, 149	–	Daphnetin derivative	
					17.37	244, 269, 337	**447**, 285	–	Luteolin 7-O-glucoside	
					18.02	244, 267, 324	**431**, 269	–	Apigenin 7-O-glucoside	
					18.80	259, 307, 333	**243**	**245**	Type C compound	
					20.57	250, 267, 347	**285**, 243, 175, 151, 133	–	Luteolin	
					22.21	255, 317	**351**, 307	–	Daphnoretin	

Bg: beige; Bk: black; Bl: blue; Br: brown; Gr: green; Gy: grey; O: orange; OBr: Orange-Brown; R: red; Rs: rose; W: white; Y: yellow.
In bold: major ions.

identification of the natural dyes used was carried out by LC-DAD-MS analysis of dyed wool extracts obtained using an EDTA/DMF extraction procedure [7,8] (Table 1).

Weld was reportedly used in Arraiolos carpets to obtain yellow hues [4] and, in fact, it has already been detected in previously analysed carpets [6,7].

Analysis of the samples collected in the NMAA carpets enabled the identification of weld in several yellow, green, brown, blue and reddish samples. Phenolic compounds extracted from these samples absorb in the spectral region below 350 nm, confirming their flavone structure, and their elution pattern and mass spectra correspond to the luteolin, apigenin and chrysoeriol derivatives reported in weld extracts [6,9,10]. A detailed analysis of the chromatographic profile of a weld dyed Arraiolos historical sample containing nine flavone derivatives has already been published [7].

Indigo was identified in several green and blue samples. It was also identified in black sample 74_10 (Table 1), probably resulting from a very concentrated dyeing bath. Green dyes are rare [5] and green hues were usually obtained by sequentially dyeing the fibre with blue and yellow dyes. Arraiolos recipes refer the use of weld and indigo to dye wool fibres in green hues [4] and that combination has already been detected previously in Arraiolos carpets [6,7]. The identification of indigotin as the chromatographic peak eluting at approximately 26.50 min was done based on its characteristic UV-Vis and mass spectra [11,12] (Table 1). As reported in the literature [11,12], indigoids are generally detected in the ESI positive mode, presenting low intensity signals. The samples yielded the expected ionization pattern (Table 1), but no identification of the dye source was made, as it is not possible to distinguish between the two main sources of indigotin, indigo and woad, in historical samples using HPLC.

Despite spurge flax being mentioned in the traditional Arraiolos recipes, the combination with indigo to dye in green hues is not described in the historical recipes. Spurge flax and indigo were found together in green samples 40_04, 40_05 and 40_06 (Table 1). Spurge flax chemical composition is very similar to weld, the major difference between these two dyes are the coumarins daphnetin, daphnin and daphnoretin, that are found in spurge flax (Fig. 2) [6,13]. Daphnetin 7-*O*-glucoside (daphnin) was detected at 15.03 min and daphnetin 8-*O*-glucoside was detected at 15.70 min based on the UV-vis data and mass fragmentation pattern obtained (Table 1). Di-coumarin daphnoretin was identified at 22.21 min, in yellow sample 24_01.

Red anthraquinone dyes were, for the first time, detected in Arraiolos carpets in this work, and these dye sources are not described in the historical Arraiolos literature [4]. The main colouring component for cochineal, carminic acid, was identified alone in sample 74_09, and together with other chromophores in samples 88_01, 88_04 and 25_04, as the chromatographic peak eluting at approximately 16.50 min; observed fragmentation (Table 1) was characteristic of the anthraquinones' fragmentation pattern and of a C-glycoside molecule [12]. Two minor compounds, dcIV and dcVII, were found in cochineal dyed sample 88_04 (Table 1). Both UV-Vis and mass spectra are very similar to those of carminic acid. These two compounds have already been described by other authors [14,15], being likely isomers from the carminic acid, but no chemical structure has been proposed so far. The identification of these two additional peaks in the samples does not allow

Fig. 1. Fibre sampling location of the six studied carpets from NMAA collection: nr. 24 (18th century, eight samples), nr. 25 (17th–18th century, 10 samples), nr. 40 (19th century, 12 samples), nr. 55 (17th century, nine samples), nr. 74 (17th century, 14 samples) and nr. 88 (17th century, nine samples).

the determination of the scale insect species used in the dyeing process.

Madder is a scarlet dye extracted from perennial herbaceous plants of the *Rubiacea* family, of which there are about 35 species [16]. The composition of the extracted anthraquinones differs between the varieties of *Rubiaceae*, but in general, it is very difficult to determine which madder source was used in the dyeing process. Alizarin and purpurin are found in most of madder species, and have been identified in the present work as the chromatographic peaks eluting at approximately 24.70 and 26.30 min, respectively (88_04, 88_05, 88_06, 74_06, 74_08, 74_11, 74_12, 74_13, 25_01, 25_04, 55_01 and 55_04; Table 1) based on their UV-Vis and mass fragmentation pattern [12]. Besides alizarin and purpurin, red sample 88_05 presented two other chromatographic peaks (Table 1). At r_t = 18.02 min, a molecular deprotonated ion at *m/z* 269, yielding two fragments at *m/z* 254 ([M-H-CH_3]$^-$) and *m/z* 223 ([M-H-CO-H_2O]$^-$) was assigned as morindone, an anthraquinone colouring matter that is only found in *Morinda* spp. [17]. Xanthopurpurin,

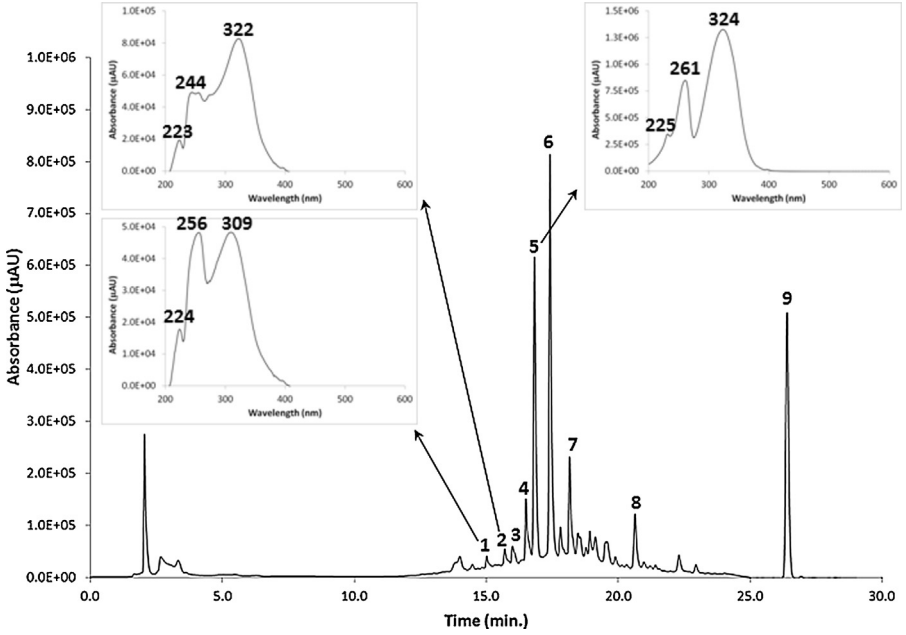

Fig. 2. Chromatographic profile (DAD detection at 290 nm) of sample 40_06, showing DAD spectra of the identified coumarins. Peak identification as follows: (1) Daphnin, (2) Daphnetin 8-*O*-glucoside, (3) Luteolin di-*O*-glucoside, (4) Luteolin 3,7′-di-*O*-glucoside, (5) Daphnetin derivative, (6) Luteolin 7-O-glucoside, (7) Apigenin 7-O-glucoside, (8) Luteolin and (9) Indigotin.

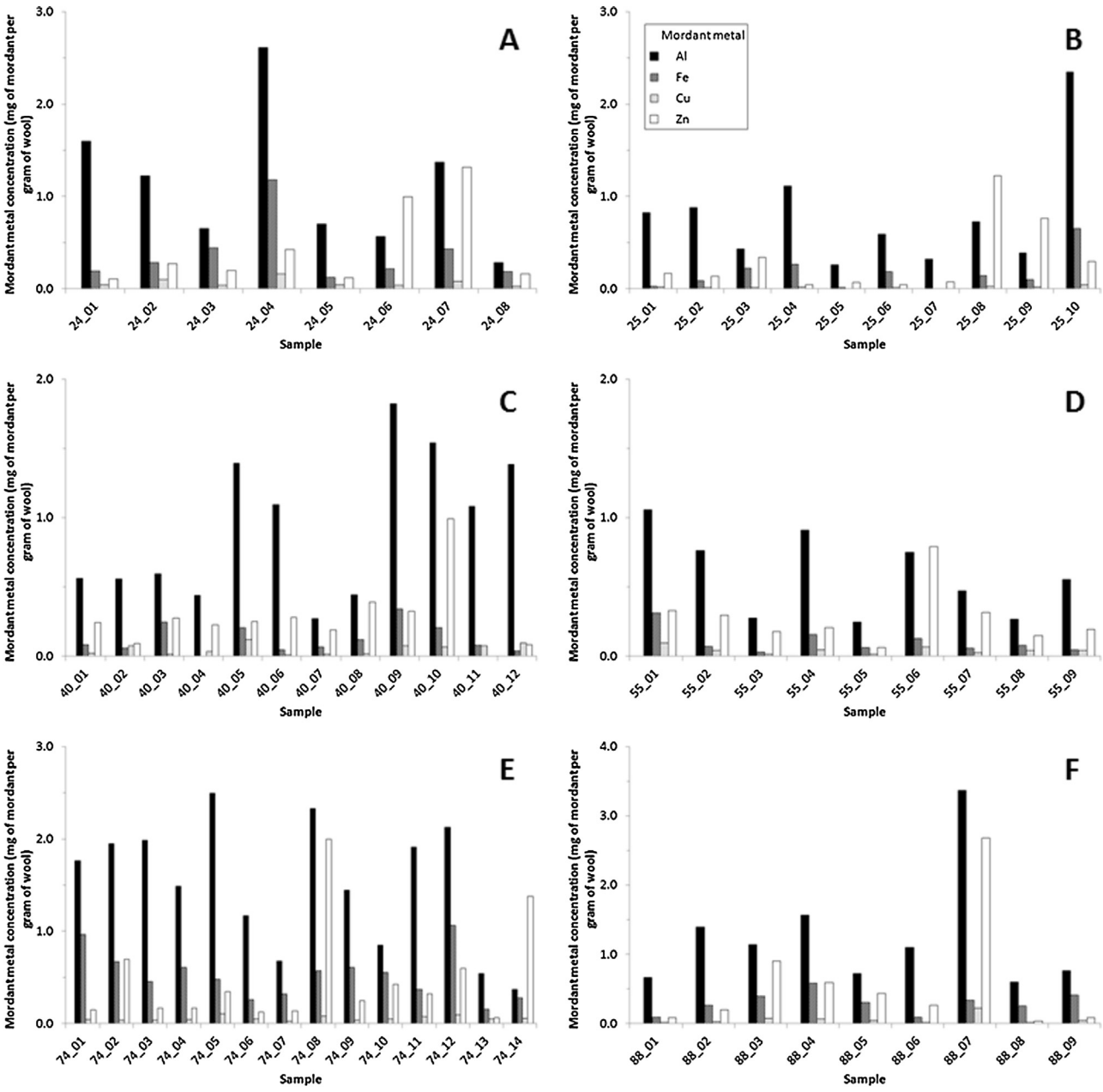

Fig. 3. ICP-MS mordant metal ion quantification in the Arraiolos rugs historical samples. NMAA carpet identification: A–nr. 24, B–nr. 25, C–nr. 40, D–nr. 55, E–nr.74 and F–nr. 88.

also found in *Morinda* spp., was identified at r_t = 18.21 min, with a molecular deprotonated ion of *m/z* 239 that yielded the fragment $[M\text{-}H\text{-}CO_2]^-$ = 195 amu.

Despite the fact that sample 24_01 nowadays presents a yellowish hue, it is thought to have been originally dyed in an orange/reddish hue. This conclusion is supported by the fact that the base of the embroidery stitches, which is less exposed to the effects of light, still presents a faded orange/reddish hue. No red chromophore, anthraquinone or homoisoflavonoid, were detected in these samples. Nevertheless, a compound with r_t = 18.80 min in the chromatographic profile of this sample extract was tentatively identified as Type C compound. Karapanagiotis et al. [18,19] describe the presence of two compounds in photodegraded samples of brazilwood, namely, Type B and Type C compounds. The two compounds have totally different UV and mass spectra [19], with Type B compound, tentatively identified as dehydro-brazilein, being associated with harsh extraction conditions (for example, HCl), while for Type C compound, with an UV and mass spectra similar to that obtained here, no indication on its possible chemical structure was given by the authors [18,19].

The presence of both spurge flax and brazilwood in sample 24_01 could explain the orange/reddish colour observed in the base of the embroidery stitches. Brazilwood is known for its fast light degradation [20] and the colour fading in Arraiolos carpets has already been described by Pessanha [2], who stated that some areas originally dyed in red hues became brownish with time. Sample 24_01 was taken from the filling colour of the carpets studied (Fig. 1). Brazilwood dye photodegradation has a tremendous impact on the actual perception of these carpets when compared to what might have originally been intended by its makers. Despite the referred use of brazilwood in the Arraiolos historical dyeing recipes [4], it is now for the first time tentatively identified in these carpets. In the rose and brown samples 40_09, 40_10 and 40_11, the chromophore molecule of brazilwood, brazilein, was effectively

detected at r_t = 18.12 min (Table 1) based on their UV-Vis data and fragmentation pattern [12].

Although fibres 88_01, 74_11, 74_12, 40_03 and 40_07 nowadays present a blue/grey hue, they were probably originally dyed in purple, since red chromophores were detected along with indigotin in these samples. Red dyes most likely underwent light degradation and only the more stable blue dye remained visible. A similar situation probably occurred in the case of blue samples 24_07 and 88_08 (most likely originally dyed in green): yellow chromophores suffered degradation, thus resulting in a visible blue hue. As stated before, brazilwood reds are extremely light-fugitive, and that can be observed in wool samples 55_07, 55_09, 40_12 and 24_05. Instead of presenting the red hues characteristic of brazilwood dyeings, samples present nowadays beige and yellow hues. The chromophores in sample 25_01, taken from the background of the carpet, also suffered severe photodegradation, presenting nowadays a yellow hue, instead of the expected orange/red hues, characteristic of madder dyeings.

Extraction of white and beige samples (88_09, 74_14, 25_05, 25_06, 25_07, 55_03 and 24_06) didn't yield any recognizable dye on the chromatogram (Table 1).

Despite the reported use of other metal salts, alum has always been the most frequently used mordant for the red and yellow dyes [21], and appears in the Arraiolos historical dyeing recipes along with "*caparosa*" for darker hues [4].

Fig. 3 presents the ICP-MS mordant metal ion quantification in wool samples collected from the studied Arraiolos carpets. Al, Fe, Cu and Zn contents in blank solutions were below the limit of detection (LOD) of the analytical method (1 μg/L). Metal ion quantification was performed on several samples of actual untreated sheep wool and the amounts detected were much lower than those detected in the samples of the historical carpets (data not shown).

Overall, the results showed that concentrations of Al and Fe are much higher than those of Cu, which is only detected in residual amounts. Whenever copper salts were used nowadays as mordants to dye wool samples, the concentrations detected in the wool are normally much higher than those of Al and Fe [22,23] and, therefore, it can be assumed that copper salts have not been used as mordants in the carpets studied.

ICP-MS data show high amounts of Al, and sometimes Fe and Zn, in samples where only indigotin had been detected (samples 74_01, 74_07, 74_10, 25_03, 25_09, 55_05, 55_08, 40_08, 24_03 and 24_08; Table 1 and Fig. 3). Due to red and yellow dyes light fastness it is possible that some of these samples were also dyed with a currently undetectable mordant dye. However, this is unlikely to have occurred for all the samples, because originally blue wool was certainly used in the embroidery work.

Detectable amounts of Al, Fe and Zn were found in wool samples without extractable chromophores (88_09, 74_14, 25_05, 25_06, 25_07, 55_03 and 24_06; Table 1 and Fig. 3), with most of these samples having white, beige and brown hues. The white/brown colours could be attributed to the use of virgin wool, but the high contents of metals in some of these samples (samples 24_06 and 74_14; Fig. 3) suggest that these were likely originally dyed samples, where chromophore photodegradation prevents the identification of the dye source.

Some samples present high amounts of zinc (Fig. 3), but this could not be associated with a certain dye or hue. Zn salts have been seldom referred as mordants, with exception of some reports on their use together with weld to obtain yellow hues in Coptic textiles [24,25].

4. Conclusions

Weld, indigo, spurge flax and brazilwood were identified as natural dye sources, as already described in the Arraiolos historical dyeing recipes [4]. The anthraquinone-based natural dye sources madder and cochineal were described for the first time in historical Arraiolos. Unlike the dyeing recipes indicate, green hues were obtained not only by dyeing with weld and indigo, but also with spurge flax and indigo.

Chromophore photodegradation has a tremendous impact in the actual perception of these carpets when compared to what it might have originally been intended. This is particularly significant for the brazilwood degradation on the background field of several carpets.

Less important in terms of embroidery area but no less important in terms of visual perception is the effect of the photodegradation of the yellow flavonoid dyes has on some originally green hues which today appear as blue coloured areas.

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Appendix A. Supplementary data

Supplementary data (Fig. S1 and Table S1) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.culher.2013.04.005.

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