

Article

Dye Analysis of a 17th-Century Mattens Workshop Tapestry Based on Raphael's Drawing, *The Miraculous Draught of Fishes*

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Abstract: This paper describes the identification of dyes on fifty yarn samples from a tapestry created by the well-known 17th-century Flemish workshop of the Mattens family. The design of the tapestry is based on the first of ten drawings known as the *Acts of the Apostles* by the famed 16th-century Italian painter Raphael. The drawings were commissioned by Pope Leo X and translated into tapestries by Pieter van Aelst; these original tapestries are still in the collection of the Vatican Museums. The present work was reproduced over a century later from the original drawing and is one in a possible set of nearly fifty known copies of the original tapestry cycle. Most of the Mattens yarn samples were found to be dyed by weld, indigo, and madder, as well as a few using brazilwood and lichen, but no insect dyes were detected. A significant finding in the present study was the detection of the dye component pseudoindirubin 1, alongside indigotin and indirubin, as well as yarns that only yielded the latter two dyes. The implication of using this new marker as objective evidence of the use of both woad and most likely Asian indigo is explored. The historical and conservation significance of the dyestuffs identified is also discussed.

Keywords: dyestuff; LC-DAD-MS; *Acts of the Apostles*; tapestry; pseudoindirubin



Citation: Chen, V.J.; Smith, G.D.; Holden, A.; Arft, S. Dye Analysis of a 17th-Century Mattens Workshop Tapestry Based on Raphael's Drawing, *The Miraculous Draught of Fishes*. *Heritage* **2024**, *7*, 1221–1236. <https://doi.org/10.3390/heritage7030059>

Academic Editors: Georgios P. Mastrotheodoros, Anastasia Rousaki, Eleni Kouloumpi and Diego Tamburini

Received: 8 January 2024

Revised: 9 February 2024

Accepted: 22 February 2024

Published: 27 February 2024



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1. Introduction

Miraculous Draught of Fishes (Figure 1) in the collection of the Indianapolis Museum of Art at Newfields is a large decorative wool hanging tapestry that measures 13.5 ft × 16.3 ft and was manufactured in the 17th century by the Flemish workshop of the Mattens family [1]. Of note, it bears both the monograms of the workshop (intertwined HM) and the city of creation (BB for Brussels-Brabant). Its design consists of a wide ornate border surrounding a large central panel depicting the biblical story of Jesus performing the miracle of the catch of fishes by four of his future disciples Simon Peter, Andrew, James, and John, as well as the father of the latter two, Zebedee, with combined elements from the Gospels of Luke 5: 1–11, Matthew 4: 18–22, and Mark 1: 16–20. The design of the central panel is based on the first of the set of ten drawings, known as the *Acts of the Apostles*, created by the renowned Italian artist Raphael between 1515 and 1516 [2–5]. These drawings, also referred to as cartoons, were commissioned by Pope Leo X to be translated into tapestries intended for decoration of the lower walls of the Sistine Chapel. The wall hangings were eventually manufactured by the Flemish tapissier Pieter van Aelst between 1520 and 1523 [2–5]. Today, the complete set of ten original tapestries is still in the collection of the Vatican Museums.

Large tapestries such as the *Acts of the Apostles* were luxury items, affordable only by the wealthiest echelons of European society for adornment of their living and working spaces [6]. This, combined with the fame of their designer, Raphael, led to copies being desirable among the aristocracies in Europe. Since their conception in the 16th century, approximately fifty sets of the *Acts of the Apostles* tapestries of various completeness are known to have been made, and only the smallest of the originals depicting the release

of St. Paul was never duplicated [7,8]. Some of the rewoven sets were commissioned while others were made for commercialization in open markets. These tapestries, based on Raphael's 16th-century designs, form a group of historical artworks that has been the subject of special interest in European art history [7].



Figure 1. *Miraculous Draught of Fishes*, Indianapolis Museum of Art at Newfields, The Clowes Collection, 2016.372. (a) recto image; (b) verso image with locations and numbers of sampled yarns. (Courtesy of Newfields).

Although the Indianapolis copy of *Miraculous Draught of Fishes* was very likely part of a larger cycle of tapestries, it is unknown whether any of the others still survive or where they are located. Four other sets of *Acts of the Apostles* attributed to the Mattens workshop are, however, known to exist. These include a group of nine tapestries at the Apostolic Palace in Loreto, Italy [9], a set of eight tapestries currently in the Alma Mater Museum in Zaragoza, Spain [10], a collection of three tapestries at the Glencairn Museum in Pennsylvania [11], and a single tapestry depicting *The Sacrifice at Lystra* listed as part of a Christie's auction in 2003 [12]. How these tapestries and the one at Newfields are related, and the circumstances under which they were made and distributed, are interesting questions for future art historical investigation.

Provenance research [1] revealed the tapestry at Newfields was once in the possession of the German entrepreneur and art patron Baron Maximilian von Heyl (1844–1925) of Darmstadt, Germany. In 1958, the tapestry was acquired by the late Dr. George Henry Alexander Clowes (1877–1958), an Anglo-American physician scientist and art connoisseur who lived in Indianapolis and once led pharmaceutical research at Eli Lilly and Company. Although previously held on long term loan to the Indianapolis Museum of Art, The Clowes Fund eventually gifted the artwork to the museum in 2016.

Since arriving in Indianapolis, the tapestry had been exhibited for approximately fifty years both at Clowes Memorial Hall on the campus of Butler University and later at Newfields. Because of its age and extensive exhibition history, where it was continuously subjected to the effects of light and the weight of gravity, the tapestry suffered aesthetic and structural deterioration. Figure 1 shows the stark color differences between the front (recto) of the artwork and the back (verso); the latter has seen far less light and retains some of the vibrancy of its original appearance. In 2019, Newfields was awarded a Bank of America Art Conservation Project grant to conserve the tapestry and to conduct a technical study of the object [13]. As part of the conservation effort, dye analysis was performed to document the dyestuffs used on the tapestry, as well as to identify fibers possibly from 20th-century repairs. The results from the dye analysis of fifty yarn samples from the tapestry by liquid chromatography coupled to a diode-array detector and mass spectrometer (LC-DAD-MS) is reported along with the significance of the dye identifications, including relatively recently

discovered marker compounds to distinguish European and Asian indigo sources. These data from a tapestry recreated in the 17th century from Raphael's 16th-century cartoons complement what has already been published about the dyes used to create the first set of *Acts of the Apostles* tapestries held by the Vatican Museums [14].

2. Materials and Methods

2.1. Materials

The chemicals used, if not specified, were of the highest grade available: oxalic acid, dihydrate, 99+% extra pure (#129601000, Acros Organics, Morris Plains, NJ, USA); pyridine, anhydrous, 99.5+% (#43799, Alfa Aesar, Ward Hill, MA, USA); methanol, Optima LC/MS grade (#A456-4, Fisher Scientific, Fair Lawn, NJ, USA); acetonitrile, Optima LC/MS grade (#A944-1, Fisher Scientific, USA); formic acid, Optima LC/MS grade (#A117-50, Fisher Scientific, USA); sodium bicarbonate (#S8875-500G, Sigma-Aldrich, St. Louis, MI, USA). Deionized water was purified (18 M Ω) first through a Milli-Q[®] Direct 8 Water Purification System and then an LC-Pak cartridge.

2.2. Samples

The fifty wool yarns studied, shown in Table 1, were collected from the verso of the tapestry where the colors were less faded. Figure 1b denotes the sampling locations. They were selected at locations carefully determined to have no impact on the integrity of the textile and based on factors such as representation of color diversity and a sufficiently large amount of loose yarn available. Every effort was made to use a minimum amount of sample for each analysis to retain a portion of the available sample for future studies.

Table 1. Sample yarns, dyes identified, extraction solvent(s) used, and dye components detected. Extraction solution abbreviations are given in Section 2.3, and dye component codes are listed in Table 2. Some minor components present in low amounts were only observed by selected ion extraction of the full scan MS chromatogram.

Sample	Visual Color	Dyestuff	Ext. Solvent (2nd Solvent)	Dye Components
1	red	madder	OAPW	M1,M2,M3,M4,M5,M6
2	mustard	weld	OAPW	W1,W2,W3,W4,W5,W6,W7,W8
3	orange-brown	weld, madder	OAPW	W1,W2,W3,W4,W5,W6,W7,W8; M3,M4,M5,M6
4	dk blue	indigo	DMSO	I1,I2,I3,I4
5	dk pink	weld, brazilwood	OAPW	W1,W2,W4,W5,W6,W7; U
6	bright red	madder	OAPW	M1,M2,M3,M4,M5,M6
7	lt blue	indigo	DMSO	I1,I2,I3,I4
8	mustard	weld	OAPW	W1,W2,W3,W4,W5,W6,W7,W8
9	dk pink	weld, lichen	OADM	W1,W2,W3,W4,W5,W6,W7,W8; O2,O3,O4,O5,O6,O7
10	light brown	weld, indigo	OAPW	W1,W2,W3,W4,W5,W6,W7,W8; I2,I3
11	green	weld, indigo	OADM	W1,W2,W3,W4,W5,W6,W7,W8; I3
12	orange	unknown	OAMAW	unidentifiable dyes
13	brown	unknown	OAPW	unidentifiable dyes
14	black	unknown	DMSO	unidentifiable dyes
15	pink	weld, indigo	OADM	W1,W2,W3,W4,W5,W6,W7,W8; I1,I3
16	red	lichen, weld, indigo	OAPW (DMSO)	W1,W2,W3,W4,W5,W6,W7,W8; O1,O3,O4,O5,O6,O7; I3
17	mustard	weld	OAMAW	W1,W2,W3,W4,W5,W6,W7,W8
18	brown	weld, madder	OAMAW	W1,W2,W3,W4,W5,W6,W7,W8; M3,M4,M5,M6
19	brown	weld, madder	OAMAW	W1,W2,W3,W4,W5,W6,W7,W8; M1,M2,M3,M4,M5,M6
20	cream	weld, madder	OAPW	W1,W2,W3,W4,W5,W6,W7,W8; M4,M5,M6,I3
21	peach	madder	OAPW	M3,M4,M5,M6
22	green-blue	weld, indigo	OADM	W1,W2,W3,W4,W5,W6,W7,W8; I1,I2,I3,I4
23	blue	indigo	OADM	I3
24	brown	brazilwood	OAPW	U

Table 1. Cont.

Sample	Visual Color	Dyestuff	Ext. Solvent (2nd Solvent)	Dye Components
25	pink	lichen, some indigo	OAPW (DMSO)	O1,O2,O3,O4,O5,O6,O7; I3
26	green-blue	weld, indigo	OADM	W1,W2,W3,W4,W5,W6,W7,W8; I3,I4
27	purple	weld, indigo, madder	OADM	W1,W2,W3,W4,W5,W6,W7,W8; M5,M6; I1,I2,I3,I4
28	tan	brazilwood	OAPW	U
29	blue	indigo	DMSO	I1,I2,I3,I4
30	grey	weld, indigo	OADM	W1,W2,W3,W4,W5,W6,W7,W8; I3
31	blue	indigo	OADM	I1,I2,I3,I4
32	pink	weld, madder	OADM	W1,W2,W3,W4,W5,W6,W7,W8; M5,M6
33	yellow brown	weld	OAPW	W1,W2,W3,W4,W5,W6,W7,W8
34	rust red	weld, madder	OAPW	W1,W2,W3,W4,W5,W6,W7,W8; M3,M4,M5,M6
35	bright orange	weld, madder	OAPW	W1,W2,W3,W4,W5,W6,W7,W8; M3,M4,M5,M6
36	orange	weld, madder	OAPW	W1,W2,W3,W4,W5,W6,W7,W8; M4,M5,M6
37	red	madder	OAPW	M1,M2,M3,M4,M5,M6
38	yellow	weld	OAPW	W1,W2,W3,W4,W5,W6,W7,W8
39	tan	brazilwood	OAPW	U
40	light tan	unknown	OAPW	unidentifiable dyes
41	tan	tannin, unknown	OAPW	unidentifiable dyes
42	orange	weld, madder	OAPW	W1,W2,W3,W4,W5,W6,W7,W8; M3,M4,M5,M6
43	green	weld, indigo	OAPW	W1,W2,W3,W4,W5,W6,W7,W8; I3
44	yellow	weld	OAPW	W1,W2,W3,W4,W5,W6,W7,W8; I3
45	pink	weld	OAPW	W1,W2,W3,W4,W6,W7
46	purple	weld, lichen, indigo	OADM	W1,W2,W3,W4,W5,W6,W7,W8; O3,O4,O5,O7; I1,I2,I3,I4
47	blue-green	weld, indigo	OAPW	W1,W2,W3,W4,W5,W6,W7; I1,I2,I3,I4
48	yellow-green	weld, indigo	OAPW	W1,W2,W3,W4,W5,W6,W7,W8; I3
49	gray	weld	OADM	W1,W2,W3,W4,W5,W6,W7,W8
50	red	madder	OAPW	M1,M2,M3,M4,M5,M6

2.3. Dye Extraction

One or more of five different solvent systems were used for dye extraction from the sample yarns depending on the circumstances and the results of preliminary analysis. A 5 mM oxalic acid solution in pyridine/water 1:1 (OAPW) can extract most natural dyes well except indigotin, the principle blue compound in indigo [15], although the amount of the indigoid extracted with OAPW is still sufficient to determine if indigo is a major dyestuff present. A 4 mM oxalic acid solution in methanol/acetone/water 3:3:4 (OAMAW) is also well suited to the extraction of most natural dyes [16,17], and it has the advantage of a lower background signal at the expense of indigotin extraction efficiency. The presence of indigo can, however, be confirmed through a second extraction of the recovered fiber by neat DMSO [18]. Alternatively, a 5 mM oxalic acid solution in DMSO/water 199:1 (OADM) can obtain clear evidence for the mixture of flavonoid yellow dyes and indigo in one extraction, for instance in green colored yarns. Finally, a 5 mM oxalic acid solution in equal parts DMSO and water (OADM) provides much increased recovery of flavonoid components at the expense of about 50% decreased indigotin. Importantly, the use of these mild extraction procedures preserves biologically specific dye glycosides that can be useful in specifying plant and animal species used in dye production.

The extraction of the colorants involved heating a textile yarn segment (350 to 900 µg) at 80 °C for an hour in the desired extraction solvent. The specific extraction method used for each sample is listed in Table 1. Since residual OAMAW and OAPW extraction solvents can interfere with LC-DAD-MS analysis, they were removed after dye extraction by a gentle stream of nitrogen with slight warming of the sample. The dried residue was then redissolved in 1:1 methanol/water for instrumental analysis. Due to its high boiling point, extracts containing DMSO were directly used for analysis. Before analysis, samples were

clarified of solid materials by centrifugation in a Beckmann microfuge at 13,000 rpm for 5 min before the supernatant was removed by pipette and placed into an LC autosampler vial glass insert. A blank was run before each sample to verify the absence of carryover from the previous injection.

2.4. LC-DAD-MS

Dye separation was performed on a Thermo Accela LC system connected in sequence to a DAD and an LTQ electrospray ionization MS detector [17]. The entire system was controlled by Thermo Xcalibur 4.0 software. Dye separation was carried out using a Restek Ultra C18 reverse phase column (150 mm × 4.6 mm, 5 μm particles) eluted at 0.2 mL/min using a water–acetonitrile gradient system containing 0.1% formic acid. The column was equilibrated at 10% acetonitrile, and 6 min after sample injection, a linear gradient of acetonitrile was applied increasing from 10 to 90% in 70 min. This chromatographic method was intended to be generic, capable of identifying a wide array of natural and synthetic colorants, and it was chosen to afford sufficient resolution to identify the dye components. The DAD was set to record spectra in the range 200–800 nm at 20 Hz, 1 nm bandwidth, scan step 1 nm, and a rise (response) time 0.02 s. The MS collected a full-scan mass spectrum in the m/z range 50–1000, followed by two tandem mass scans of spectra for fragment ions resulting from helium collision-induced dissociation (CID) of the highest and second highest ion detected in the full-scan MS, respectively. The MS scan sequence alternated between positive and negative ionization modes [17].

2.5. Data Interpretation

Because the tapestry was woven in the 17th century well before the invention of synthetic dyes, the 50 wool yarns examined in this study were expected to be colored by natural dyestuffs derived from sources such as plants, insects, and microorganisms. Many of these dyestuffs have been well studied and are known to contain multiple color components, allowing their identification by detection of these key marker compounds. Whenever possible, dyestuff identification should be based on the identification of more than one of these known natural dye components since many dye compounds appear in multiple dyestuffs. The physiochemical data of the dye components used to guide identification of the dyestuffs from the tapestry are collected in Table 2. These data were culled from a combination of previous studies by this laboratory [17,19–21], as well as data published by others, as discussed in Section 3. Dye identification was based mainly on the mass of molecular ions of the analytes detected supported by their UV-vis spectra when they could be measured. The tandem mass spectral data were only used for confirmation and thus are not included in Table 2.

Table 2. Dye components, abbreviations, and the analytical data used to identify dyestuffs in sample yarns. ND = not detected, br = broad, sh = shoulder, w = weak.

Dyestuff	Dye Components	Code	Retention Time (min)	Negative Ion (m/z)	λ_{\max} (nm)
weld	luteolin-7,3'- <i>O</i> -di-glucoside	W1	28.5	609	340
	luteolin-7- <i>O</i> -glucoside	W2	31.8	447	348
	apigenin-7- <i>O</i> -glucoside	W3	34.7	431	333
	chryseriol-7- <i>O</i> -glucoside	W4	35.3	461	347
	luteolin-3'- <i>O</i> -glucoside	W5	35.9	447	332
	luteolin	W6	43.05	285	347
	apigenin	W7	47.7	269	334
	chryseriol	W8	48.6	299	346
indigo	isatin	I1	33.3	ND	294, ~400 (br)
	pseudoindirubin 1	I2	48	500	~440, ~560
	indigotin	I3	63.3	261 (w)	607
	indirubin	I4	66	261 (w)	540

Table 2. Cont.

Dyestuff	Dye Components	Code	Retention Time (min)	Negative Ion (<i>m/z</i>)	λ_{\max} (nm)
madder	lucidin primeveroside	M1	35.1	563	405
	ruberythric acid	M2	35.9	533	416
	pseudopurpurin	M3	50.4	299	493
	munjistin	M4	51.2	283	419
	alizarin	M5	57.6	239	429
	purpurin	M6	63.2	255	480
brazilwood	uroolithin C		36.4	243	307, 345
lichen	unknown orcein	O1	36.3	374	475 (br)
	β/γ -aminoorcein isomer 1	O2	37.01	483	517, ~544 (sh)
	α -aminoorcein	O3	40.7	361	515, ~544 (sh)
	β/γ -aminoorcein isomer 2	O4	41.6	483	526, 552
	β/γ -hydroxyorcein	O5	42.5	484	~480 (br)
	β/γ -hydroxyorcein	O6	48.1	484	~482 (br)
	α -hydroxyorcein	O7	49.4	362	471 (br)
tannin	ellagic acid	E1	31.5	301	366

3. Results

The results of the 50 samples from the tapestry are summarized in Table 1. Forty-five yielded data for colorants that are assignable with confidence to the dyestuffs weld, indigo, madder, brazilwood, and lichen based on the characteristic data shown in Table 2.

3.1. Weld

The dyestuff weld (*Reseda luteola*) was detected in 31 samples, making it the most prevalent dyestuff identified in the sample yarns from the tapestry. Twelve marker compounds from weld have recently been isolated in sufficiently pure form to allow structural characterization by high-resolution mass spectrometry and two-dimensional proton NMR spectroscopy [22]. Additionally, several publications on the characterization of weld dyestuff on textiles have included chromatograms from reverse phase columns similar to the present study showing consistent relative order of elution and relative peak height of the marker compounds [22–27]. By comparison to these data, the corresponding dye markers in the present analyses could be assigned. When sufficient material was present, eight of the twelve marker compounds could be confirmed, as shown in Table 2. Unfortunately, the remaining four were obscured by high sample background, presumably due to the age and condition of the historical textile. Therefore, the two small peaks for apigenin-6,8-di-*C*-glucoside and luteolin-7,4'-di-*O*-glucoside, that are reported to elute before luteolin-7,3'-di-*O*-glucoside (W1) [22,27], are not included in the present marker panel shown in Table 2; the same is true for apigenin-4'-*O*-glucoside and luteolin-4'-*O*-glucoside, which have only been described by van der Klift et al. and in trace amounts [22].

Consistent with published data [22–27], luteolin-7,3'-di-*O*-glucoside (W1), luteolin-7-*O*-glucoside (W2), and luteolin (W6) were the three predominating peaks in our data, although their relative ratios were variable between samples, with W1 usually being the smallest of the three. The remaining peaks, including those for apigenin-7-*O*-glucoside (W3), chrysoeriol-7-*O*-glucoside (W4), luteolin-3'-*O*-glucoside (W5), luteolin (W6), apigenin (W7), and chrysoeriol (W8), were smaller and variable in height, to the extent that in some instances W5 and W8 were not observed even by ion-extraction. Furthermore, the sum of peak height for the respective glycosides and aglycons maintained the expected ratio luteolin > apigenin >> chrysoeriol [28].

Figure 2 shows two characteristic chromatograms of extracts of weld: (a) the yellow yarn sample 2, which contains strong signals of weld, and (b) the cream-colored sample 20, which, based on peak size, contains a mixture of low amounts of weld together with the

red dyestuff madder, as evident by comparison with (c) the chromatogram from red yarn sample 1 that contains strong peaks of madder (vide infra). Sawwort (*Serratula tinctoria*), which contains similar flavonoid components to weld, is another possible yellow dyestuff that could have been used. However, previous studies have shown that chrysoeriol is only found in weld [28–30], and apigenin is either very low or undetectable in sawwort [28,29]. Another possible flavonoid-containing yellow dyestuff, dyer’s broom (*Genista tinctoria*), can be ruled out by the absence of the marker compound genistein [30,31], that under the chromatography conditions used would elute just ahead of apigenin.

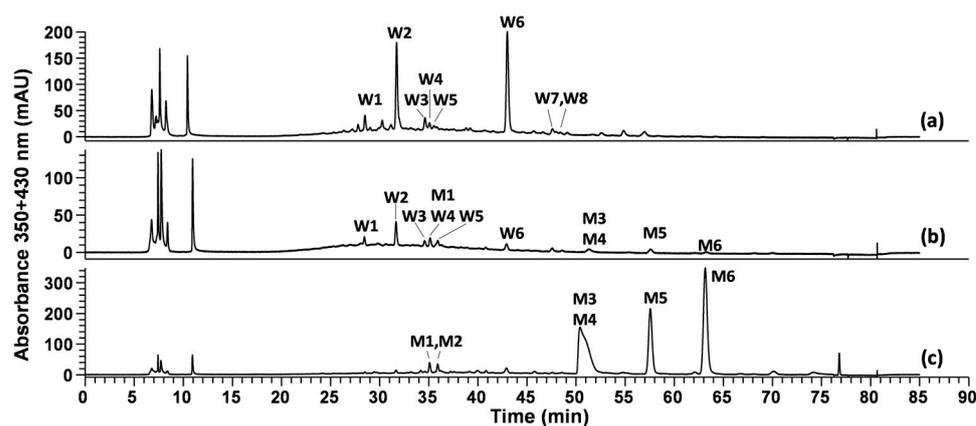


Figure 2. Chromatograms of extracts from (a) yellow yarn sample 2, (b) cream yarn sample 20, and (c) red yarn sample 1. The peaks are labeled with the codes as given in Table 2 for the dye components identified.

Since all the flavonoid-containing samples in this study contained significant peaks for apigenin and its glycoside, but no trace of genistein, it is most likely that they were dyed with weld instead of sawwort or dyer’s broom. As summarized in Table 1, out of a total of thirty-one weld-containing samples, eight were found to be only weld, and almost all of those had a noticeable yellowish color. Some, like the pink yarn 45 and the gray yarn 49, revealed only weld components. The rest were mostly in binary combination with another dyestuff to create non-primary colors, including nine samples with madder, nine samples with indigo, one with lichen, and another with brazilwood. Additionally, three were detected as a mixture of three dyestuffs: two with lichen and indigo and one with indigo and madder.

3.2. Indigo

Historically, the primary blue textile dyestuff was indigo [32], and it was detected in eighteen of the samples from the Indianapolis *Miraculous Draught of Fishes*. It is the second most common dyestuff found in this work. Indigo dyestuffs from several plants are known to contain the blue colorant indigotin (I3) as the major dye along with a small peak of its red isomer indirubin (I4) and a trace amount of their oxidation product isatin (I1) [18,21,33]. Additionally, of the eighteen samples found to contain indigotin in the samples studied here, the dye pseudoindirubin 1 could also be detected in nine [33]. Of these nine, four showed an additional smaller intensity ion at m/z 500 eluting ~1.5 min after pseudoindirubin 1 that could be attributed to the putative pseudoindirubin 2 isomer [33]. The significance of the presence of pseudoindirubin will be discussed in Section 4.

The data for the indigo dyed sample 46 contain all the aforementioned indigo-related dye compounds, as shown in Figure 3. Among the yarns examined from the tapestry, indigo was used singly in five samples, in binary mixtures with lichen in one, with weld in nine, and in triple admixture with weld and madder in one and with weld and lichen in two samples.

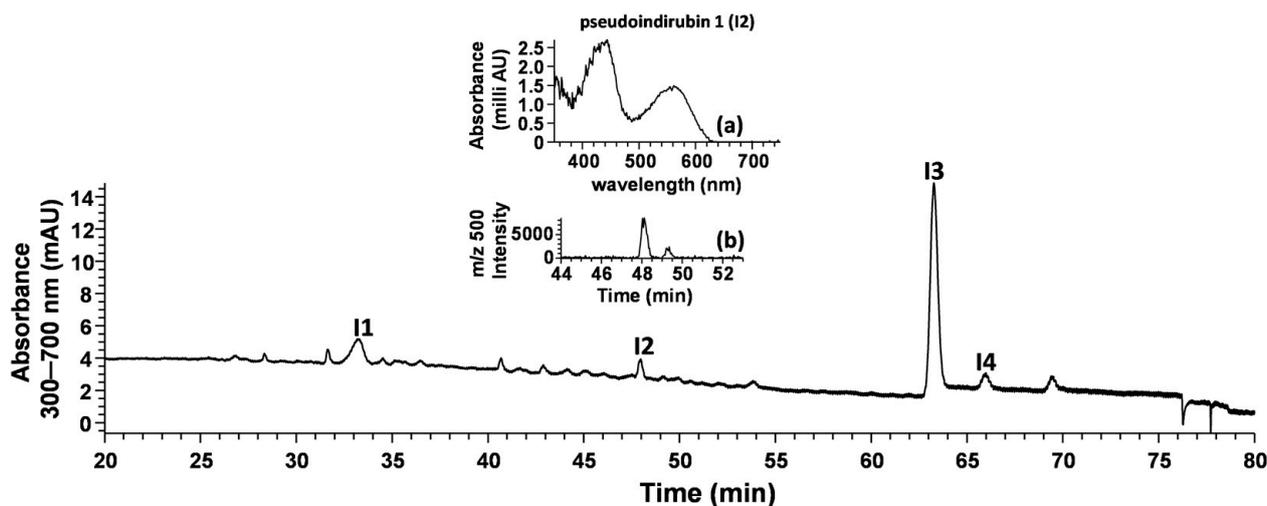


Figure 3. Chromatogram of the extract from blue yarn sample 46, likely dyed by woad, with characteristic dye components marked as in Table 2. Inset (a) shows the UV-vis spectrum of pseudoindirubin 1 (I2), while inset (b) shows a chromatogram for the extracted ion m/z 500 indicative of pseudoindirubin 1 (I2) and its putative isomer pseudoindirubin 2.

3.3. Madder

The dyestuff madder was found to be the main red colorant used in the tapestry, appearing in fifteen of the fifty samples, as shown in Table 1. Among the several madder species possible, all are known to contain anthraquinone-based colorants. However, common madder (*Rubia tinctorum*) can be distinguished by the presence of both alizarin (M5) and purpurin (M6) [34,35]. In addition, common madder also contains significant peaks for pseudopurpurin (M3) and munjistin (M4), which are the carboxylated forms of purpurin and xanthopurpurin (1,3-dihydroxy-anthraquinone), respectively [34,35]. These acidic compounds coelute under the chromatographic conditions used here, but they are easily identifiable by their mass differences [17,19]. The glycosides lucidin primeveroside (M1) and alizarin primeveroside, also known as ruberythric acid (M2), usually occur in low amounts due to endogenous enzymatic breakdown of the glycosides following harvest of the dye plant [35], but they were also detected. The identification of these colorants is exemplified by sample 1, as shown in Figure 2c. Based on these identifications, fifteen tapestry samples can be shown to contain common madder. The madder dyed samples are distributed such that five contain madder alone, nine have madder in binary combination with weld, and one has a triple dye combination of indigo, weld, and a trace amount of madder that might have originated from adventitious transfer due to physical contact with a strongly madder dyed area when the tapestry was rolled up, as seen before [17,19].

3.4. Brazilwood

The principal coloring materials in brazilwood (*Caesalpinia* spp.) are brazilin and brazilein [36]. These two dyes are known to be fugitive and not easily observed in historic textiles, but their degradation product urolithin C (U) can be readily detected due to its good chromatographic behavior coupled with characteristic UV-vis and mass spectra [37]. Urolithin C was identified as a single dye with strong signals in samples 5, 24, and 28, but only weakly in 39. The data for a tan yarn sample 39 are shown in Figure 4.

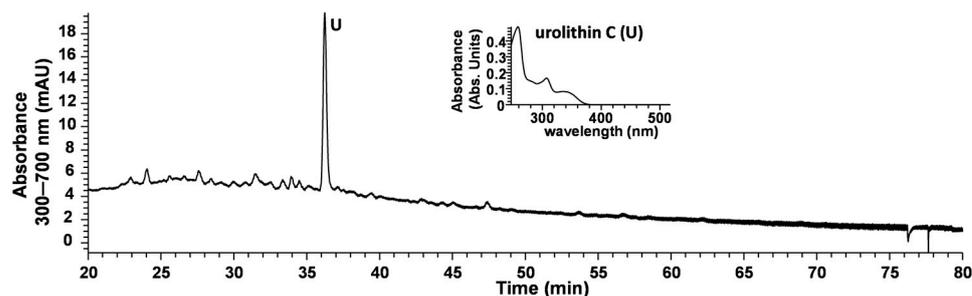


Figure 4. Chromatogram of the extract of tan yarn sample 39 showing the presence of urolithin C (U). Inset reveals UV-vis spectrum of urolithin C.

3.5. Lichen

Extracts from samples 9, 16, 25, and 46 were found to contain colorants exhibiting physiochemical properties indicative of orcein (orchil) dyes derived from precursors found in lichens [38–41]. Their chromatographic and spectral data are shown in Figures 5 and 6, respectively. These compounds are phenoxazone derivatives known to be the pink components obtained when certain species of lichen are extracted into dilute aqueous ammonia followed by prolonged incubation under aerated conditions [38,42]. Several lichen species have been used since antiquity in Europe as sources of orcein dyes for textiles [42,43], with those of *Rocella* spp. (*Lecanore* spp.) and *Ochrolechia* spp. being frequently mentioned in connection with European art [31,39,44,45]. The structures of orcein dyes have been described in the literature [38], and they fall into three primary color groups: hydroxy-orceins, amino-orceins, and amino-orceinimines, all of which are distinguishable by their UV-vis spectra.

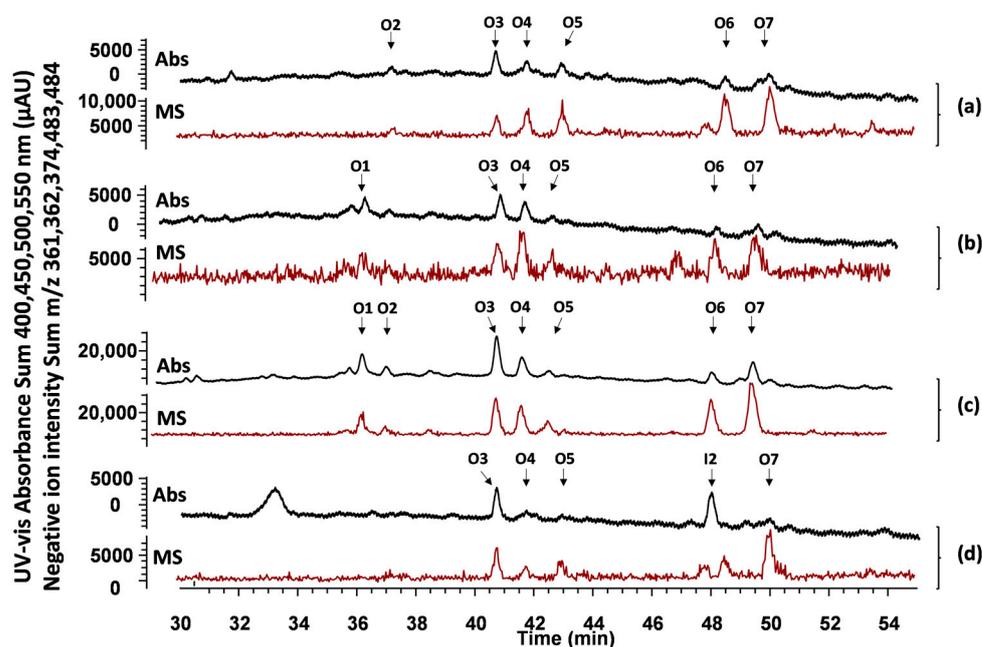


Figure 5. Data for the lichen dyed samples: (a) dark pink sample 9, (b) red sample 16, (c) pink sample 25, and (d) purple sample 46. The traces are based on absorption and corresponding ion extracted MS chromatograms as indicated.

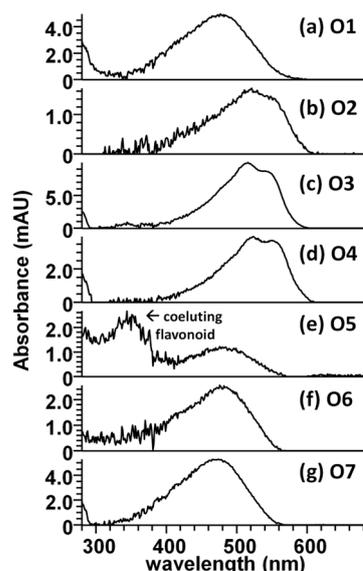
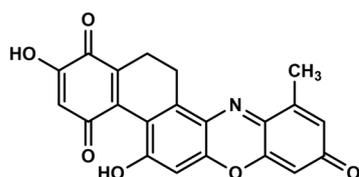


Figure 6. UV-vis spectra of the orceins O1–O7 detected in sample 25: (a) R.T. = 36.3 min, MW 375, an unknown hydroxyorcein; (b) R.T. = 37.0 min, MW 484, a β - or γ -aminoorcein; (c) R.T. = 40.7 min, MW 362, an α -aminoorcein; (d) R.T. = 41.6 min, MW 484, a β - or γ -aminoorcein; (e) R.T. = 42.5 min, MW 485, a β - or γ -hydroxyorcein; (f) R.T. = 48.1 min, MW 485, a β - or γ -hydroxyorcein; (g) R.T. = 49.4 min, MW 363, an α -hydroxyorcein.

Each color group consists of the three members that are designated by prefixes α , β , and γ . The α -orceins have one orcinol substituent bonded to C-6 of the phenoxazine nucleus. β and γ have an additional one attached to C-3, such that the two orcinols are oriented with respect to each other either as *trans* in β - or *cis* in γ -orceins. Mass spectrometry can confirm the color grouping assignment as well as determine whether it is an α -, β -, or γ -orcein. However, being isobaric, the chromatographically distinct peaks for β - and γ -orceins cannot be assigned to their specific isomer without appropriate reference materials. Presumably due to their manner of preparation, the orceins formed are not present at the same concentrations as reflected by relative chromatographic peak heights. Additionally, given their light sensitivity, not all nine possible derivatives are expected on historic textiles [31,43–45]. Therefore, it is not surprising that the orcein signals are weak in the four tapestry samples analyzed here, and only in sample 25 are six orceins present in sufficient quantity such that good quality UV-vis and mass spectral data, as shown in Figure 5, were obtained to allow matching with published data [40,41]. Nonetheless, the ions for the same five or six orceins were detected in the other three samples within the expected retention times even though not all gave correspondingly good quality UV-vis spectra compared to those shown in Figure 6. An unknown analyte O1 eluting at 36 min in samples 16 and 25 gave spectra similar to those of the hydroxyorceins. Based on its UV-vis and mass spectral data, O1 is proposed here to be the structure shown in Scheme 1, which, if proven, could be an oxidative degradation product of α -hydroxyorcein.



Scheme 1. Proposed structure for the unknown orcein (O1).

Among the four samples, lichen dyes in binary combination were found for sample 9 with weld and in triple combination with weld and indigo for 16, 25, and 46. It is noteworthy

that the dye was not found by itself in any of the fifty samples. However, based on the known light sensitivity, it is possible that preferential sampling of brightly colored threads may have avoided instances where faded lichen alone was present.

3.6. Unidentified Dyestuffs

Five of the fifty samples studied contain multiple dyes that cannot currently be identified. Based on the absorption spectra of the colorants detected -which are not discussed here, we surmise that these five could be black synthetic dyes arising from modern repairs.

4. Discussion

Of the fifty samples from the tapestry studied in this work, forty-five yielded data of colorants that allow confident assignment to the dyestuffs, including weld, indigo, madder, brazilwood, and lichen. These are all dyestuffs known to have been used in European textiles including tapestries in the 17th century [31,43,46]. Weld, indigo, and madder, which are historically the most prevalent natural dyestuffs used in Europe, accounted for 89% of the identifications in the samples analyzed.

From the literature on dye history, woad was the blue dyestuff mostly used initially in Europe, and it, along with weld and madder, has been cultivated on the continent since medieval times [31,32,43,47–49]. However, Asian indigo was also known in Europe before the 16th century, but it was uncommon at this early date probably due to the commercial and diplomatic challenges in importing the dyestuff via land routes from Central Asia [32,43,47–49]. This situation started to change in the late 15th century when sea routes to the Far East were established, leading to an influx of Asian indigo into European markets [32,49]. Estimation of the relative usage of woad versus other sources of indigo dyestuffs by 17th-century European weavers could be challenging as the relevant historical archives are sparse and the availability of dyestuffs might be sporadic and dependent on personal contact.

A search for specific marker compounds useful for ascertaining the indigo plant source recently led Laursen and Mouri [33] to the discovery of the minor components pseudoindirubin 1 (I2), which is characterized by the molecular ion m/z 500 in negative ionization and exhibits a distinct UV-vis spectrum, and a likely isomer pseudoindirubin 2 of the same mass. The minor presence or total absence of these minor components was shown to correlate to certain geographic origins of indigo-producing plants [33]. Among the indigo-producing plants and dyed fibers examined by Laursen and Mouri [33], those that contain pseudoindirubin include woad (*Isatin tinctoria*), which is commonly found and historically widely used in Europe, rattlebox (*Crotalaria incana*) from the West Indies, and *yangua* (*Cybistax antisiphylitica*) from South America. Indeed, the present authors confirmed the presence of pseudoindirubin 1 and 2 along with indigotin and an unusually large chromatographic peak for indirubin in black and brown yarns from a late Nazca period woolen tunic that was radiocarbon dated to between 595 and 665 CE [21], consistent with the use of indigo from *yangua* in Pre-Columbian textiles [50]. Moreover, Laursen and Mouri found that pseudoindirubin 1 and 2 were absent in extracts of fiber dyed by Asian indigo dye plants such as Indian indigo (*Indigofera tinctoria*) and the Japanese *ryukyu-ai* (*Strobilanthes cusia*) and *sukuno-ai* (*Polygonum tinctorium*). Considering the exotic nature of *yangua* and rattlebox, these two dye plants were unlikely to be widely available in Europe in the 17th century. The detection of pseudoindirubins in approximately half of the blue samples from the tapestry studied here may indicate that indigo from different plant sources, probably both European woad together with Indian indigo, were used on the tapestry by the Mattens workshop. This discovery adds to the relatively sparse literature on this recently discovered, but potentially important, marker dye compound [21,33].

In addition to the primary colorants yellow weld, blue indigo, and red madder, their mixtures were used to create a wide range of hues in the 17th-century Mattens tapestry workshop, revealing an economical palette. The corpus of samples studied here are sufficiently large to show some interesting statistics of palette composition. Of the

50 colored yarns studied, the presence of weld dominates (43%) since yellow is mixed with blue to make green and with red to make orange. Concomitantly, indigo (25%) and madder (21%) are well represented, but at lower frequencies. As shown by the intensity of the chromatographic signals, weld used heavily alone confers a yellow or mustard color. In binary combination with madder, it produces colors ranging from orange to light brown. On the other hand, brown and orange can also be obtained by heavy dyeing with madder alone. In contrast, based on relative chromatographic peak heights, light application of madder and weld afford subtle hues such as pink, cream, and peach. Based on peak height, different proportions of weld and indigo make various shades of green, and by adjusting the amount of indigo used on the yarns, the intensity of blue is varied.

Dye degradation leads to aesthetic changes in tapestries; however, dye analysis can help indicate the original color, especially if the verso, which is usually less impacted by light exposure, is not visible. The resulting aesthetic condition issues in the tapestry being studied are illuminated by the chromatographic analysis. Weld is known to be more fugitive than indigo and madder [51]. As observed with other historical tapestries [51], areas of vegetation in many areas of the *Miraculous Draught of Fishes* tapestry appear blueish rather than the anticipated green. However, dye analysis of yarns from the corresponding areas in colorants from the object's verso showed the presence of the flavonoid components expected in weld, thus confirming the likely deep green original color of the recto. On the other hand, an accurate appreciation of how the extent of degradation correlates with color appearance would likely involve extensive and detailed study using reference material as well as model dye swatches (mock-ups) being exposed to light and oxygen under controlled conditions, followed by color measurements and careful quantitation of the changes of flavonoid components, as shown in two recent studies [52,53]. Furthermore, aside from light-induced degradation, physical erosion of the fiber might possibly be another factor of color change. For example, yarn samples 49 and 30 appear to be grey, which is not readily explained by the respective presence of components of weld alone (yellow?) or weld in combination with indigo (green?). We surmise that this may be due to degradation or physical erosion occurring on the surface layer of the thread, leaving only intact dyes within the textile fiber bundle to be detected.

The dyestuffs brazilwood and lichen are observed infrequently in the analyses reported here, with each being detected at about 5–6% (4/72) occurrence. Their more limited availability combined with the low fastness of the dye components themselves may be the reason for their sparse usage by the Mattens workshop. Brazilwood gives a vibrant shade of red, while lichen dyes can produce a delicate pink, with both colors very much desired throughout history. While lichen prepared in boiling water gives an orange dye [42], it is not frequently reported, and the coloring principles appear not to have been fully characterized, although they are different from the phenoxazones just described [V. J. Chen, unpublished observation]. Identification of the phenoxazone compounds indicates that the pink dyes from lichen were used on the tapestry. Though known in northern Europe since before medieval times, in the 17th century the materials for both dyestuffs were most likely imported to Flanders, with brazilwood coming from South America [36,48] and lichen from the Canary Islands or southern European coastal areas around the Mediterranean Sea [42,43,54]. The detection of analyte O1, a probable oxidized product of α -hydroxyorcein with hypothetical structure shown in Scheme 1, and the specific identification of urolithin C instead of brazilein or brazilin, are consistent with the known instability of lichen and brazilwood, respectively. The high level of urolithin C detected in three of the four brazilwood dye samples (24, 28, and 39) suggests that they could at one time have been intensely scarlet, but now they appear only tan in color. Interestingly, sample 5, which, based on peak height, contained a low amount of urolithin C as well as several weld components, is still faintly pink in color. On the other hand, despite low amounts of colorant detected, the lichen dyed threads in samples 9, 16, 25, and 46 all still appear pink.

One notable observation in this study is the absence of the carminic acid-containing crimson red dyes from such scale insects as kermes or any of the cochineal varieties.

Though not as prevalent as weld, indigo, and madder, insect dyes are known to have been used in European tapestries in the 16th and 17th centuries [46,51,55–58]. If present even in low amounts, the major colorant carminic acid is readily detectable by LC-DAD-MS, and therefore, it is unlikely to have been missed here. Sampling omission could explain its absence, for instance if these precious insect dyes were only used on yarns used for special iconographic features such as Jesus's red garment, which provided no safe sampling locations for this study and therefore was not included in the corpus of yarns taken. It is entirely possible, though, that with madder, brazilwood, and lichen, the dyers felt the full range of maroon to pink hues could be met without the added expense of including insect red dyes.

There may be other geographic or regional reasons for the lack of insect dyes being used in the Mattens workshop. Studies using LC-DAD-MS have been reported on the dyes used on the original *Acts of the Apostles* tapestries made first from the Rapheal cartoons [14]. These works, still in the collection of the Vatican Museums, were made by another Flemish weaver Pieter Van Aelst some 150 years before the Newfields version of *Miraculous Draught of Fishes* [14]. As in the present study, no carminic acid was detected in more than one hundred and seventy-two samples from the original weaving analyzed from eight of the ten tapestries, except on a thread that was determined to be from a later restoration. The dyestuffs occurrence reported for the Vatican cohort is seventy-six identifications of indigo for blue (37%), fifty contained weld along with fourteen dyer's broom and 3 Scotch broom (combination of three 32%) for yellow, fifty-four had madder for red (26%), and eight were colored with tannin (4%). Interestingly, indigo appears as the most common colorant in the original set of tapestries.

5. Conclusions

Of the several sets of *Acts of the Apostles* attributed to the Mattens workshop, no dye analysis has been reported to the knowledge of the authors, except the present study on *Miraculous Draught of Fishes* at Newfields. This study yielded results from LC-DAD-MS showing that the dyes identified are consistent with known dyestuffs usage in European textiles of the period [32,46,47,51,55–58]. Additionally, the newly discovered dye marker pseudoindirubin 1 in a portion of the blue dyed yarns is adduced as a possible objective indication of the simultaneous use of both woad and most likely Asian indigo from India. On the other hand, cochineal, which is often detected in 16th- and 17th-century contexts, was not found on either the tapestry from the Mattens workshop at Newfields or the earlier original set produced by Peter van Aelst. Unfortunately, in practice, it may not be feasible to collect additional samples from these historical textiles for further dye analysis for confirmation of these unusual findings. Historic texts and archives may provide additional evidence to understand the period practices in sourcing dyestuffs, or through analysis of other similar tapestries from European workshops, which might focus on what factors influence dyers and weavers to choose those dyestuffs that appear less frequently in tapestries.

Author Contributions: Conceptualization, G.D.S. and A.H.; methodology, V.J.C.; investigation, V.J.C. and S.A.; writing—original draft preparation, V.J.C.; writing—review and editing, G.D.S., A.H. and S.A.; supervision, G.D.S.; project administration, G.D.S. and A.H.; funding acquisition, A.H. and G.D.S. All authors have read and agreed to the published version of the manuscript.

Funding: The *Miraculous Draught of Fishes* (2016.372) and accompanying conservation and reinstallation funding was generously provided by The Clowes Fund in honor of the director emeritus and longtime president of the Allen Whitehill Clowes Charitable Foundation, William Marshall. Additional conservation analysis support was provided by Bank of America through their Art Conservation Project grant program. Funding for lab operations was provided by Sarah and John Lechleiter, Kay Koch, The Carter Family Fund, The Frenzel Family Charitable Lead Trust, the R.B. Annis Educational Foundation, and Lilly Endowment, Inc.

Data Availability Statement: All reasonable requests for data will be considered.

Acknowledgments: The authors acknowledge the contributions of their Newfields colleagues in assisting with photography, sample collection, note keeping, art historical background, grant management, and artwork relocations. In particular, Erinn Bessler assisted in yarn sample collection and documentation, and Eric Lubrick captured the images shown in Figure 1.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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