

Article

A First Approach to the Study of Winsor & Newton's 19th-Century Manufacture of Madder Red Lake Pigments

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Abstract: This paper focuses on the first investigation of the 19th-century manufacture of red lake pigments obtained from madder by Winsor & Newton (W&N), prominent artists' colourman at that time. The first approach to their manufacture was carried out by studying the madder entries of the company's book P1, found in the W&N 19th Century Archive Database. Eleven production records were discovered under names such as Rose Madder, Madder Carmine, Madder Lake and Madder Rose. Three main methods of synthesis were identified and reproduced, revealing three main steps: washing of the madder roots (*Rubia tinctorum* L.); extraction in acid media and complexation with Al³⁺ using alum; and precipitation by the addition of salts such as ammonium carbonate and sodium borate. The syntheses were followed by UV-VIS spectroscopy, and the pigments were further characterised by colourimetry, Energy-Dispersive X-Ray Fluorescence Spectrometry (XRF), Fourier Transform Infrared Spectroscopy (FTIR) and High-Performance Liquid Chromatography-Diode Array Detector (HPLC-DAD). They all exhibited a rose hue in a highly insoluble aluminate matrix. Although the dye extraction was incomplete, alizarin, purpurin and pseudopurpurin were identified. An analytical comparison with a Rose Madder 19th-century oil paint tube was also performed by micro-FTIR and microspectrofluorimetry. This work intends to be foundational to a systematic study of the W&N's 19th-century madder colours aiming to contribute new knowledge towards their identification and preservation in heritage objects.

Keywords: madder; 19th-century manufacture; Winsor & Newton; multi-analytical characterisation; heritage preservation



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1. Introduction

Since antiquity, madder has been one of the most important sources of red colours. Used as dyes and pigments, these colours have been found in treasured artworks [1–4]. The first reference to its use as a dye dates back to the seventh century BC found in a neo-Babylonian tablet kept at the British Museum. The earliest it has been identified as a pigment was also in ancient objects such as Cypriot pottery of the 8th–7th century BC [1,3].

Madder colours are extracted from the roots of plants from the Rubiaceae family, but the most relevant species for dyeing are *Rubia peregrina* L. (wild plants) and *Rubia tinctorum* L. (cultivated plants), the latter being the most used for dyeing in western Europe from the Middle Ages to the 19th century [1–7]. Their composition differs quantitatively but qualitatively is based on anthraquinone compounds in the form of glycosides and respective aglycones (Figure 1). The main anthraquinones responsible for the colour are alizarin (1,2-dihydroxyanthraquinone), followed by purpurin (1,2,4-trihydroxyanthraquinone) and pseudopurpurin (1,3,4-trihydroxyanthraquinone-2-carboxylic acid) (Figure 1) [1–3].

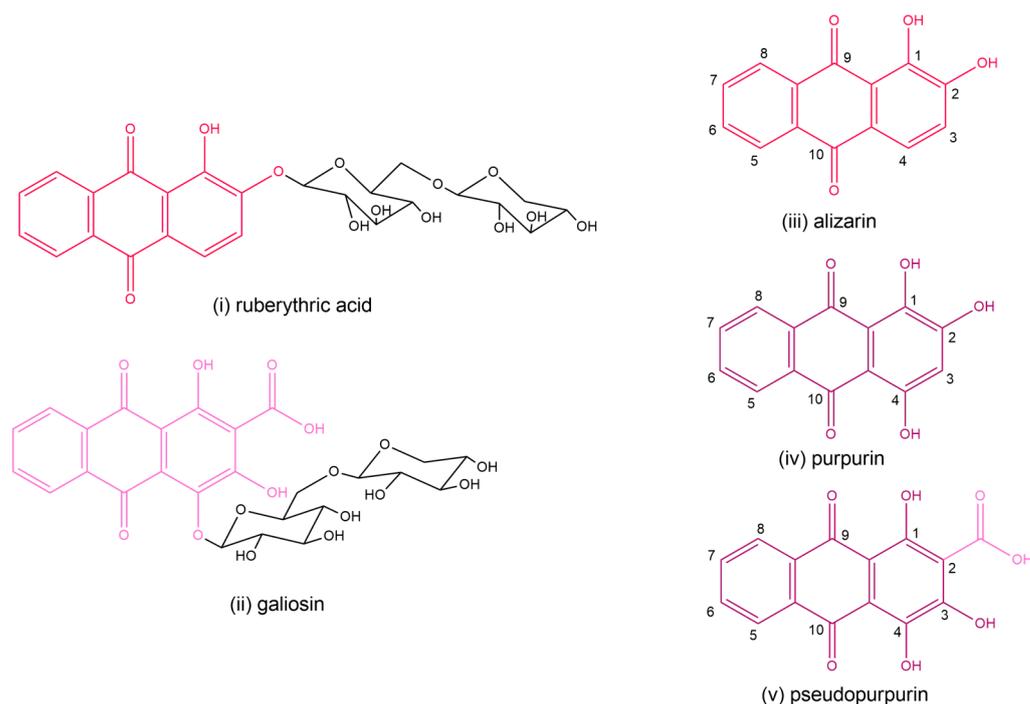


Figure 1. Molecular structures of the principal components found in madder roots.

Madder lake pigments are obtained by precipitation with salts such as alum ($\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$), forming aluminium (Al^{3+}) coordination complexes that are yet to be fully identified [8,9]. The proposals follow the model by Kiel and Heertjes, in which Al^{3+} coordinates to two alizarin ligands through the 9-C=O and the 1-OH, and the model by Wunderlich, in which Al^{3+} coordinates to two alizarin ligands through the catechol of hydroxyl groups at positions 1 and 2, and calcium ions (Ca^{2+}) close the structure by coordinating two alizarin ligands through the 9-C=O and the 1-OH [10–12]. Identification of madder lake pigments is a well-known challenge in the field of conservation, not only due to their complex composition but also because of the low dye concentrations in the pigment formulation as well as the degradation mechanisms that may occur. The latter can cause undesirable changes in the heritage objects' original visual appearance [8,13–15]. Nevertheless, great efforts have been made to improve their detection in heritage objects, including by in situ techniques such as Raman Microscopy, Fibre Optics Reflectance Spectroscopy (FORS) and Hyperspectral Imaging and Microspectrofluorimetry [16–21]; however, unequivocal identification is still only possible by fingerprinting techniques using micro-samples such as High-Performance Liquid Chromatography-Diode Array Detector (HPLC-DAD) and Surface-enhanced Raman spectroscopy (SERS) [22–24].

Madder colours can range from orange through different shades of red to purple and brown, depending on the manufacturing conditions, such as the pH of extraction, pH of precipitation and different complexing agents and additives [1,2,5,6,25]. Although much documentary evidence is found for their dyeing processes throughout history, there is a knowledge gap concerning pigment production. Furthermore, it was common to use madder lakes prepared with the dye extracted from shearings of textiles [1,2,5,7,25]. This paradigm changed in the 19th century when remarkable developments in the manufacture of madder lake pigments were accomplished and enabled their industrial production [6,7,26]. However, their production was considered very expensive, which unfortunately led to their adulteration by adding other colourants and/or cheaper materials [26,27]. Nonetheless, even after the discovery of synthetic substitutes, madder colours continued to be manufactured and sold by Winsor & Newton (W&N), a leading paint manufacturer of the 19th century [27]. Table 1 presents the colour names associated with madder red lake pigments, which appeared in W&N's catalogues throughout the 19th century [27].

Table 1. Availability of colours associated with madder red lake pigments in powder and oil paint tubes throughout the 19th century from W&N, adapted from L. Carlyle, 2001 [27].

W&N 19th-c. Madder Red Colours	Oil Paint Tube		Powder	
	First Appearance	Last Appearance	First Appearance	Last Appearance
Pink Madder	1835	-	1835 ¹	-
Rose Madder	1835	-	1835 ¹	-
Madder Carmine	c. 1840	-	c. 1840	-
Madder Lake	c. 1840 ²	-	not in powder	
Extra Madder Carmine Deep	c. 1861	c. 1861	not in powder	
Extra Madder Carmine Bright	c. 1861	-	1864	-
Extra Madder Carmine	1864	-	1864	-
Scarlet Madder	1886	-	1892	-
Crimson Madder	1886	-	not in powder	
Rose Madder (pink shade)	1900	-	not in powder	
Pink Madder Lake	not in oil		c. 1840	c. 1849
Rose Madder Lake	not in oil		c. 1840	c. 1849

¹ Not listed again until 1851. ² Not listed again until 1861.

This work resulted from the first investigation of the madder records found on the W&N 19th century Archive Database, enabling a unique insight into the company's workshop practices using madder. The W&N 19th century Archive Database is a fundamental primary source of information on the commercial availability and preparation of 19th-century artists' materials. Its study has demonstrated that W&N was committed to supplying the most durable products possible [28–32]. This investigation is being carried out in the framework of two funded projects, namely "REDiscovering madder colours: Science & Art for the preservation and creation of cultural heritage" (2022.02909.PTDC) and "Magic Lantern—Study, Safeguard, Uses and Reuses in 19th-Century Portugal" (PTDC/ART-PER/1702/2021). Their joint objective is to improve the identification of madder colours in complex matrices as those found in heritage objects such as historical hand-painted magic lantern glass slides. Another goal is to establish a correlation between the manufacturing conditions (e.g., pH of precipitation, different complexing agents and additives) and the stability of madder colours towards their preservation.

2. Materials and Methods

2.1. Materials

Madder roots and gum arabic were purchased from Kremer Pigmente[®]. Potassium aluminium sulfate ($\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) and sulfuric acid (H_2SO_4) were purchased from Fluka[®], ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) from Alfa Aesar[®] and sodium borate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) from Sigma-Aldrich[®]. Alizarin and purpurin analytical standards were purchased from Merck[®] and Aldrich[®], respectively. Pseudopurpurin was isolated following the protocol described by V. Daniels [33]; the analysed final product presented a purity of 80–87%, with purpurin also being detected. HPLC-DAD analyses of the latter compounds may be seen in Figure A1.

For the HPLC-DAD extractions and analyses, all solvents were HPLC grade. Millipore ultrapure water was used.

2.2. Synthesis Methods for Madder Lake Pigments

Investigation of the W&N 19th century Archive Database was focused on the sub-topic madder on the manuscript book P1 as further detailed below. Eleven production records pertaining to the manufacture of madder red lake pigments were discovered; see Table A1. It was possible to organise eight production records in three main representative formulations: Rose Madder, Madder Lake and Madder Rose, whose synthesis methods are described in Table 2.

Table 2. Formulation name and code of the synthesis methods of madder red lake pigments.

Formulation Name Code	Synthesis Methods
Madder Rose MR	<ol style="list-style-type: none"> 1. Wash 5 g of madder powder with 100 mL of water (repeat 5 times); 2. Dissolve 8.57 g of alum in 30 mL of hot water (near boiling); 3. Pour the above solution into the madder roots; 4. Decant the supernatant liquor into 88 mL of distilled water; 5. Slowly add an aqueous solution of carbonate of ammonia (1.2 M) and stir occasionally; 6. Filter the precipitate.
Madder Lake ML	<ol style="list-style-type: none"> 1. Let 5 g of madder powder rest in 100 mL of water for 1 h; 2. Decant the supernatant and let the madder rest in 100 mL of water for 30 min; 3. Decant the supernatant and wash the madder 3 times; 4. Dissolve 10.48 g of alum in 30 mL of hot water (80 °C); 5. Run through the above solution into the madder roots placed in a cotton filter bag and collect the red extract; 6. To the red extract, add immediately, one at a time, three solutions of sodium borate: 1.9 g in 10 mL, 0.24 g in 5 mL and 0.06 g in 2.5 mL; 7. Filter the precipitate.
Rose Madder RM	<ol style="list-style-type: none"> 1. Prepare a solution of 0.5 mL of sulfuric acid in 4 mL of water; 2. Pour the solution into the madder roots after step 5 of the Madder Lake recipe. 3. After 30 days, add 16 mL of boiling water; 4. Add immediately, one at a time, three solutions of sodium borate: 0.5 g in 2.5 mL, 0.06 g in 1.25 mL and 0.03 g in 1.25 mL; 5. Filter the precipitate.

The above materials were interpreted based on previous works [28–32]. As most production records call for 28 to 42 lbs (12.7 to 19 kg) of madder, all materials were scaled down from industrial to laboratory scale, and quantities in British measures were converted to SI units [27]. All madder red lake pigments produced were thoroughly washed with water, air-dried and then ground to a powder.

pH measurements throughout the syntheses were carried out with a Sartorius Docu-pH Meter. Calibration was performed with pH 4 and 7 buffer solutions from Panreac.

2.3. Analytical Equipment and Experimental Conditions

2.3.1. Colourimetry

For measuring colour, a handheld spectrophotometer Lovibond® TR 520 with a dif-fused illumination system, 8° viewing angle, and a 48 mm integrating sphere was used. The measuring aperture was 8 mm in diameter. Equipment calibration was performed with white and black references. Colour coordinates were calculated defining the D65 illuminant and the 10° observer. The colour data are presented in the CIE-Lab 1976 system. In the Lab cartesian system, L*, relative brightness, is represented by the z-axis. Variations in relative brightness range from white (L* = 100) to black (L* = 0). The (a*, b*) pair represents the hue of the object. The red/green y-axis plots a* ranging from negative values (green) to positive (red). The yellow/blue x-axis reports b* going from negative (blue) to positive numbers (yellow).

The colour was measured on paint references prepared with gum arabic (10% solution). The lake pigments were first ground with pure water and then ground with the gum arabic solution. The paints were applied on filter paper with a paintbrush and allowed to dry.

2.3.2. Energy-Dispersive X-ray Fluorescence Spectrometry (XRF)

XRF analyses were performed on an ArtTAX spectrometer of Intax GmbH, equipped with a molybdenum (Mo) anode and an Xflash detector refrigerated by the Peltier effect (Sidrift). The primary X-ray beam is focused to a diameter of 70 µm using polycapillary X-ray mini lens. The characteristic X-rays emitted by the sample are detected by a silicon drift electro-thermally cooled detector with a resolution of 160 eV at Mn-Kα. The experimental parameters used were 40 kV of voltage, 300 µA of intensity and 300 s of acquisition

time. Measurements were carried out in a helium atmosphere to enable the detection of aluminium (Al).

2.3.3. UV-VIS Absorption Spectroscopy

The UV-VIS absorption spectra were recorded on a Cary 100 Bio UV-VIS Varian spectrophotometer, at room temperature. The spectra were acquired in the range 200–800 nm, with an average scan time of 0.1 s/nm and scan rate of 600 nm/min.

UV-VIS absorption spectra were acquired for the solutions obtained throughout the syntheses in poly(methyl methacrylate) cuvettes.

2.3.4. Fibre Optics Reflectance Spectroscopy (FORS)

Reflectance spectra were acquired with Ocean Optics equipment composed of a single-beam dispersive fibre optic spectrometer (model MAYA 2000 PRO) equipped with 2048 linear silicon CCD array detector (Hamamatsu). MAYA 2000 PRO has a spectral response from 200 nm to 1050 nm. The illumination is an Ocean Optics HL-2000-HP with 20 Watt halogen light source in a single optical path covering the 360–2400 nm range. Spectra were obtained with an integration time of 8 ms and 15 scans to average. The measuring head, in a 45°/45° (illumination/acquisition angles) configuration, gives a diameter of analysis of about 2 mm. As reference, a Spectralon[®] standard was used. FORS spectra were acquired in reflectance but are presented as apparent absorbance, $A' = \text{Log}10(1/R)$.

FORS analysis was performed on the paint references described above.

2.3.5. High-Performance Liquid Chromatography with a Diode Array Detector (HPLC-DAD)

HPLC-DAD analysis of the madder roots was carried out by placing 0.01 g of the ground material with 1 mL of 1:1 (*v/v*) solution of methanol:water and heating in a water bath at 80 °C for 30 min. Then the extract was centrifuged for 10 min, and the supernatant liquid was filtered through a 0.45 µm filter [3]. Its chromatographic profile may be seen in Figure A2.

The extraction of the dye molecules from the madder lake pigments was revealed to be very challenging as they are highly insoluble. Several extraction methods were tried. In all experiments, c. 2 mg of pigment powder was used. The one used in this work resulted from adding 300 µL of 1:1 (*v/v*) solution of methanol:HCl to the pigment sample and heated in an ultrasonic bath at 60 °C for 1 h. Then the extract was evaporated under nitrogen flow, and the residue was dissolved in 200 µL of methanol. Although this method showed better results until the present moment, the obtained results are far from the desired since the complete extraction of the free dye molecules was not possible, and further optimisation is needed. The other extraction methods experimented with, showing worst results, were (i) 1 mL of solution of oxalic acid (0.2 M):methanol:acetone:water (0.1:3:3:4, *v:v*) added to the pigment sample and heated in a water bath at 60 °C for 30 min [32]; (ii) two consecutive extractions of the pigment sample: a first one with 200 µL of dimethylformamide:methanol (2:1, *v/v*) heated in a water bath at 80 °C for 10 min, after which the extract is reserved, followed by a second one with 200 µL of solution of oxalic acid (0.5 M):methanol:acetone:water (0.1:3:3:4, *v:v*) heated in a water bath at 80 °C for 15 min, after which the residue is evaporated under nitrogen flow and dissolved in 200 µL of methanol:water (1:2, *v/v*) plus the extract from the prior DMF extraction [3]; and (iii) 300 µL of methanol:HCl (30/1, *v/v*) and (iv) 300 µL of methanol:HCl (70/30, *v/v*) added to the pigment sample and heated in an ultrasonic bath at 60 °C for 1 h [34].

The HPLC-DAD analysis data were obtained by the Analytical Laboratory LAQV/REQUIMTE—Chemistry Department, FCT|NOVA—Portugal. The analysis was carried out in a Dionex Summit (Sunnyvale, CA, USA) HPLC-DAD system with a DAD Dionex Ultimate 1000, an autosampler and a gradient pump. The sample separations were performed in a reversed-phase column, Phenomenex Luna C18, with a 5 µm particle size column (250 mm × 4.6 mm), with a 1 mL/min flow rate with the column at a constant temperature of 30 °C. The samples were injected with a 20 µL loop. The elution gradient consisted of two

solvents, A: 99.9% acetonitrile + 0.1% trifluoroacetic acid (*v/v*) and B: 99.9% water + 0.1% trifluoroacetic acid (*v/v*). An elution program was used with a linear increase in the ratio of A to B from 5:95 to 30:70 over 25 min, followed by a second linear gradient to 100:0 until 40 min of run and then 10 min of isocratic 100% A (re-equilibration time). The eluted peaks were monitored at 430 nm and 500 nm.

2.3.6. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared analyses were carried out with a Nicolet Nexus spectrophotometer coupled to a Continuum microscope (15x objective) with an MCT-A detector cooled by liquid nitrogen. The pigments were analysed in transmission mode between 4000 and 650 cm^{-1} , with a resolution of 8 cm^{-1} and 128 scans, using a Thermo diamond anvil compression cell. The spectra are shown here as acquired, without corrections or any further manipulations, except for the removal of the CO_2 absorption at ca. 2300–2400 cm^{-1} .

2.3.7. Microspectrofluorimetry

Fluorescence excitation and emission spectra were recorded on a Jobin-Yvon/Horiba SPEX Fluorog 3-2.2 spectrofluorimeter hyphenated to an Olympus BX51 M confocal microscope, with spatial resolution controlled with a multiple-pinhole turret, corresponding to a minimum 2 μm and maximum 60 μm spot, with 50 \times objective. Fluorescence spectra were corrected for the wavelength response of the system. Beam splitting is obtained with standard dichroic filters mounted at 45°; they are located in a two-place filter holder. Standard dichroic filters of 500 and 600 nm were used to collect the emission and excitation spectra, respectively. Emission spectra were acquired exciting at 490 nm, and excitation spectra were performed collecting the signal at 610 or 620 nm. Both were acquired in a 30 μm spot (pinhole 8) and the following slit set: emission slits = 3/3/3 mm, and excitation slits = 5/3/0.8 mm. The optimisation of the signal, through mirror alignment in the optic pathway of the microscope, was performed for all pinhole apertures following the manufacturer's instructions. Spectra were collected after focusing on the sample (eye view) followed by signal intensity optimisation (detector reading). Emission and excitation spectra were acquired in the same spot whenever possible.

Microspectrofluorimetry analysis was performed on the paint references described above.

3. Results and Discussion

3.1. Research in the W&N 19th Century Archive Database

An initial assessment of the significance given to madder red/purple lakes by W&N in the 19th century can be made by analysing all sub-topics under those terms (Figure 2). As previously reported by Vitorino et al., there are more than eight thousand database records on red/purple lake pigments [29]. From these, 35% pertain to madder. However, it is relevant to note that W&N also had access to the manuscript books by George Field (1777–1854), one of the most important colour chemists in the 19th century, who greatly influenced W&N pigment manufacture, especially of madder red lake pigments [26,27]. Field's books are not included in the W&N archive database.

Its relevance is also evident if we consider that, at the time the W&N Archive Database was created in 2006 [35], the majority of the madder records were restricted due to their commercial sensitivity. Recently, this restriction has been removed, prompting the beginning of this research.

Due to the high number of database records, this first approach to studying W&N's 19th-century manufacture of madder red lake pigments was carried out by analysing the madder entries of the manuscript book P1. This book belonged to Arthur Henry Newton, son of W&N's founder Henry Charles Newton, and it is primarily dedicated to pigment manufacture between 1846 and 1858. It includes several comments on the production records, significantly assisting with their laboratory reproduction, as will be shown below. Furthermore, he was well aware of the potential of madder as he wrote: "*The root of the Rubia Tinctoria or madder plant, so valuable for the solidity of its colours in dyeing, is invested*

naturally with tingent matter in a series of states, and of colours from the lightest yellow, on the one extreme to the deepest purple (. . .)." (URC P1P022AL01).

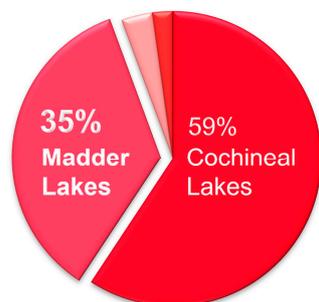


Figure 2. Distribution of the red/pink lakes in the pigment sub-topics from W&N's database; 59% of cochineal lakes [29], 35% of madder lakes, 2% of lac lakes and 4% of other lake pigments, mostly of unidentified dye sources.

In book P1, there are 35 database entries under the sub-topic madder, of which 29 correspond to the pigment manufacture of madder reds (11), browns (10), purples (5) and yellows (3). The 11 database records on the manufacture of madder red lake pigments appear under several names, such as Madder Rose, Madder Lake, Rose Madder and Madder Carmine (Table A1). These can be related to W&N's 19th-century trade names (Table 1).

Eight production records fall into three main representative formulations, hereafter referred to as Rose Madder, Madder Lake and Madder Rose, as shown in Table 2. The other three production records correspond to different synthesis methods and were left out, namely, a recipe for Liquid Madder Lake (P1P030AL03), and the other two are experiments for a Crimson Madder (P1P205AL12) and a Madder with lime water (P1P299AL01).

It is important to emphasise that in this preliminary work, with a limited number of records, it is not possible to establish a correlation between the identified formulations and W&N's 19th-century products. This can only be achieved by a systematic study of all W&N's records on the manufacture of madder colours and an analytical comparison with W&N's historical materials.

3.2. Main Steps for the W&N's 19th-Century Manufacture of Madder Red Lake Pigments

In Figure 3, we present the three essential steps of the three main methods of synthesis identified: (i) washing of the ground madder roots (*Rubia tinctorum* L.); (ii) extraction in acid media and complexation with Al^{3+} using alum ($AlK(SO_4)_2 \cdot 12H_2O$); and (iii) precipitation by the addition of salts such as ammonium carbonate ($(NH_4)_2CO_3$) and sodium borate ($Na_2B_4O_7 \cdot 10H_2O$).

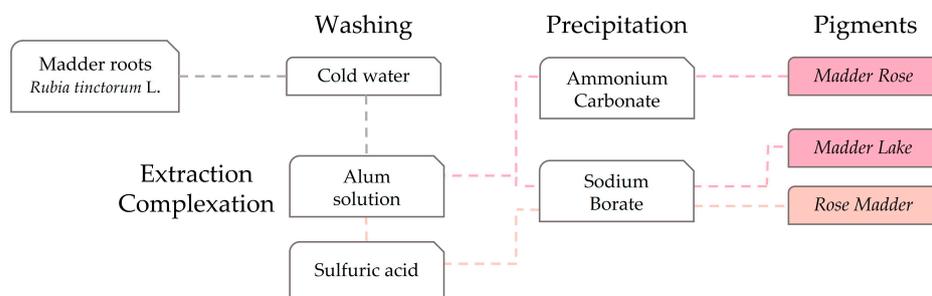


Figure 3. Scheme of the main steps of W&N's 19th-century manufacture of madder red lake pigments.

The importance of washing the madder roots is clear throughout the records, as it is stated: "Take 7lbs [or any quantity] of the finest Crop Madder powder, infuse and perfectly diffuse it in any quantity of pure, cold water, which decant;—repeat the same with a fresh quantity of water—again and again,—there being no danger of repeating such lavations too often; the first condition

toward a perfect Rose—color being the entirely removing all the dark brown and yellow-colors soluble in cold water from the root” (URC P1P025AL01), and “In fact the washing of the Madder Root with repeated water is simply getting rid of the fine fecula & dirty matter that would otherwise spoil the brilliance of the madder red extract” (URC P1P114AL13). Two washing methods were found, one for Madder Rose, in which we washed the ground madder roots five times, and another one for Madder Lake and Rose Madder, in which the water is left with the madder for longer periods of time. HPLC-DAD analyses reveal that this process reduces the alizarin content (Figure 4a), and XRF results show that the presence of elements calcium (Ca) and iron (Fe) is also significantly reduced when compared with the final product (Figure 4b). The pH values of the water washings were always between 6 and 7.

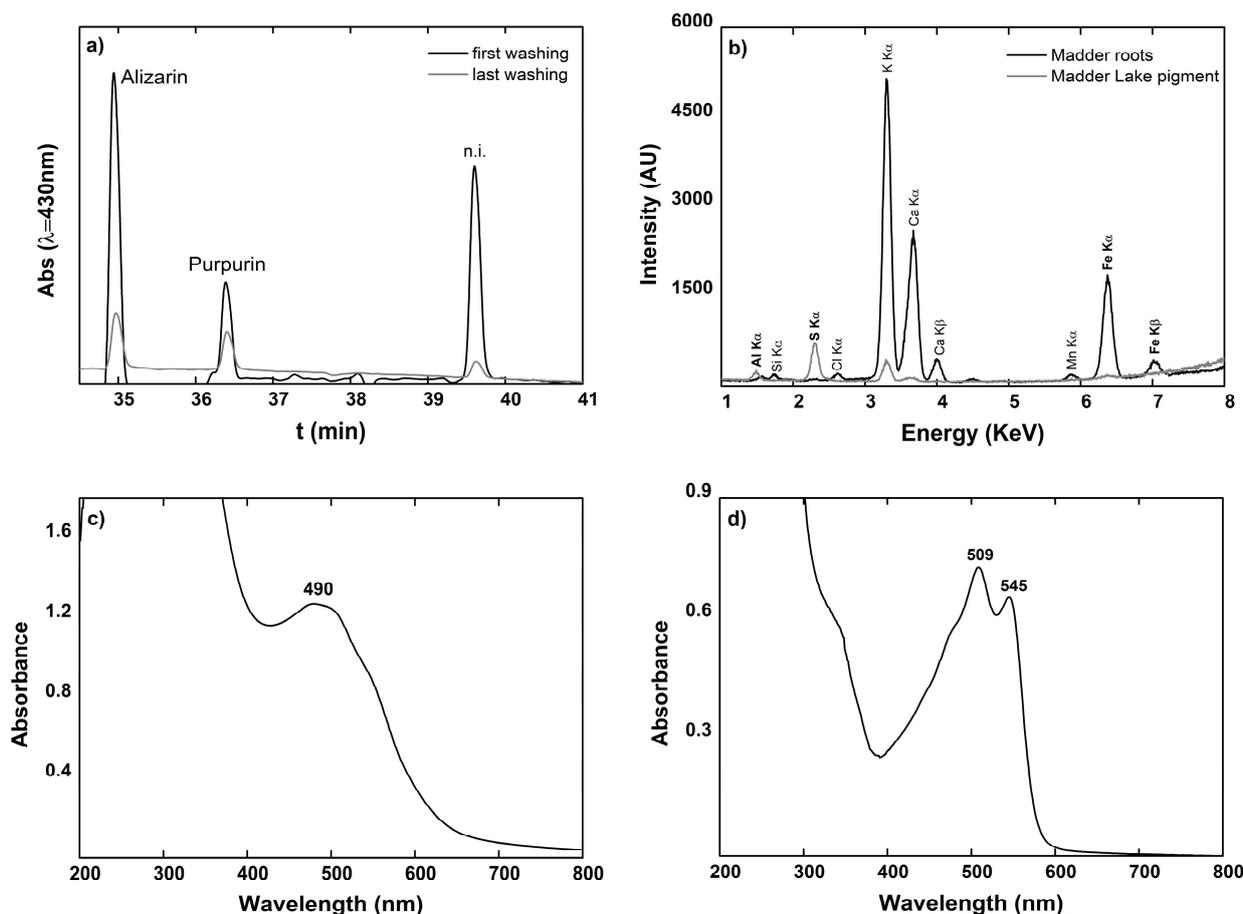


Figure 4. (a) Chromatograms at 430 nm of solutions of the first and last washing of the production of Madder Lake pigment (n.i.—non-identified); (b) XRF spectra of the madder roots and a Madder Lake pigment (ML3); (c) UV-VIS spectrum of the solution of the madder roots washing; and (d) UV-VIS spectrum of the madder solution after the addition of alum (madder red extract).

After washing, colour extraction is performed in acid media by adding a concentrated hot solution of alum ($\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$), which decreases the pH to 2–3. This favours the extraction of pseudopurpurin [33]. Regarding this step, there is also reference that “Attention to this is expedient to success, the aluminous salt taking up spontaneously a moderate proportion of color only;—precipitated in which state it affords but a comparatively weak pigment—but as the alum crystallises without color, the color it thus gives up is retained in chemical combination in the tincture affording all the richness of color required, at the same time that the beauty and transparency of the pigment is improved by the spontaneous precipitation of terrene impurities” (URC P1P025AL01). In Madder Rose, alum is added directly to the madder roots, and the madder red extract is afterwards decanted. In Madder Lake and Rose Madder, the alum solution is poured through a cotton filter bag where the madder roots are, and the

red extract is collected in a recipient below the filter. However, for the Rose Madder, this step is still to be better understood as there is the extra addition of sulfuric acid (H_2SO_4), further lowering the pH. In this work, this was done to the madder roots after the alum was run through, but as will be shown below, the resulting pigments do not correspond to what was expected: “a bright scarlet tinted & transp’ madder rose of excellent strenght in oil” (URC P1P114AL13). Furthermore, precipitation did not always occur, probably due to the low pH. Ingredients such as sulfuric acid are always more challenging to work with when reproducing historical recipes, as their purity and quantity conversion can significantly influence the processes and final products [28,29]. Further experiments must be conducted to determine the role of sulfuric acid in producing W&N’s madder reds.

Figure 4c,d show the UV-VIS spectra of the madder roots in water before and after alum extraction, respectively, demonstrating that extraction and complexation with aluminium (Al^{3+}) occur in one single step. The UV-VIS spectrum of the madder red extract is very similar to that of purpurin and/or pseudopurpurin complexes with Al^{3+} presenting maxima at 509 nm and 545 nm [9,36].

The final step is the precipitation of the madder lake pigments by adding salts such as ammonium carbonate ($(NH_4)_2CO_3$) and sodium borate ($Na_2B_4O_7 \cdot 10H_2O$) to the madder red extracts. The first is only used for Madder Rose, and sodium borate is used for Madder Lake and Rose Madder. The final pH, obtained after precipitation, was always around 4, except for one replication of Rose Madder, where a higher quantity of sodium borate had to be used for precipitation to occur, resulting in a final pH of 6.

The records show that the Madder Rose lake pigments were “of a colour literally as beautiful as the rose, and surpassing in truth and purity of hue all other red pigments” (URC P1P025AL01). On the other hand, Madder Lake formulations may be revealed to be “not so strong as might have been expected, but was very bright having a scarlety pink colour” (URC P1P127AL05).

Interestingly, contrary to what was found for W&N’s cochineal formulations, no reference to the use of extenders such as calcium carbonate ($CaCO_3$) or calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) was found [29]. The complete study of all production records in the future will allow us to infer whether this is a characteristic of W&N’s 19th-century madder colours.

3.3. Characterisation of the Madder Red Lake Pigments

All formulations were repeated three times to assess reproducibility. Each madder lake pigment produced was analysed by colourimetry, UV-VIS Fibre Optic Reflectance Spectroscopy (FORS), Energy Dispersive X-Ray Fluorescence Spectrometry (XRF), Fourier Transform Infrared Spectroscopy (FTIR) and High-Performance Liquid Chromatography-Diode Array Detector (HPLC-DAD). A summary of the results is presented in Table 3.

Table 3. Summary of the analytical results obtained by colourimetry, FORS, XRF, FTIR and HPLC-DAD for all madder lake pigments produced following the protocols described in Table 2.

Formulation Name	Code	L*	a*	b*	FORS	XRF	FTIR	HPLC-DAD
Madder Rose	MR1	78.80 ± 0.35	32.87 ± 0.25	2.81 ± 0.08	511, 549 (sh)	S, K, Al	Aluminate	1. Pseudopurpurin 2. Alizarin 3. Purpurin
	MR2	78.82 ± 0.61	31.59 ± 0.58	3.00 ± 0.21	512, 546 (sh)			
	MR3	82.81 ± 0.46	24.79 ± 0.28	2.45 ± 0.24	513, 549 (sh)			
Madder Lake	ML1	85.61 ± 0.75	23.38 ± 1.37	5.37 ± 0.24	511, 547 (sh)	S, K, Al	Aluminate	1. Pseudopurpurin 2. Alizarin 3. Purpurin
	ML2	83.48 ± 0.53	23.21 ± 1.31	4.19 ± 0.21	512, 547 (sh)			
	ML3	85.12 ± 1.04	20.60 ± 1.75	3.69 ± 0.06	510, 547 (sh)			
Rose Madder	RM1	92.24 ± 0.07	5.98 ± 0.12	6.86 ± 0.06	508	S, K, Al, Fe		
	RM2	86.96 ± 1.03	16.18 ± 1.38	4.95 ± 0.1	504, 538 (sh)			
	RM3	89.67 ± 0.32	8.97 ± 0.4	7.61 ± 0.1	505, 538 (sh)			

As seen in Table 3 and Figure 5a, all madder lake pigments display a pink hue. Madder Rose and Madder Lake formulations were reproducible as their colour coordinates (a^* and b^*) tend to cluster (Figure 5a). It is also perceptible that Madder Rose lake pigments are

redder, with the highest a^* values. On the other hand, as noted before, reproducibility was not verified for the Rose Madder formulations, which are found to be less red (lower a^* value) and more yellow (higher b^* value), still exhibiting signs of the presence of iron (Fe) from the madder roots.

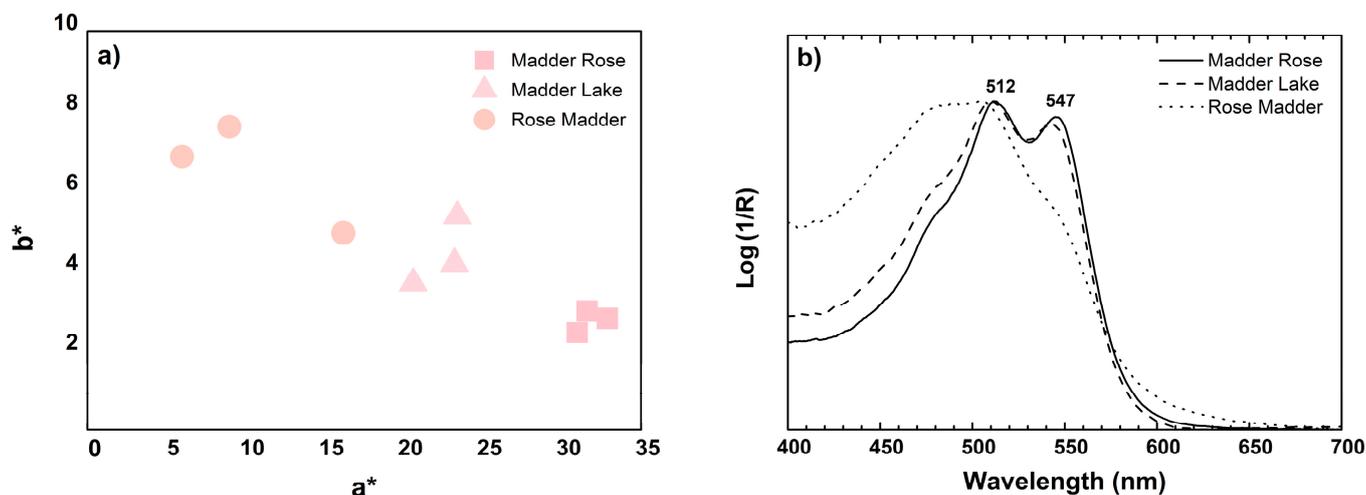


Figure 5. (a) Colour coordinates (a^* and b^*) for the madder lake pigments detailed in Table 3 and (b) representative absorbance spectra of the madder lake pigments. These analyses were carried out in samples painted with gum arabic on filter paper.

Figure 5b shows representative FORS spectra of all three formulations. Those of Madder Rose and Madder Lake are similar in shape and maxima around 512 nm and 547 nm, also observed in Al^{3+} -purpurin and pseudopurpurin complexes [9,36]. The FORS spectrum of Rose Madder is shifted to lower wavelengths, with the shape and maxima at 508 nm, similar to that of Al^{3+} -alizarin complexes [9,36].

Infrared analyses of most madder lake pigments (except for the RM2 lake pigment, whose infrared spectrum may be consulted in Figure A3) reveal the presence of an amorphous aluminate polymeric matrix with characteristic bands at 3343 cm^{-1} attributed to the stretching vibration of $-\text{OH}$ (broad band), at 1114 cm^{-1} assigned to the bending vibration of $\text{Al}-\text{OH}$, at 1644 cm^{-1} corresponding to the bending vibration of coordinated water and at 983 cm^{-1} assigned to the stretching vibration of $\text{Al}-\text{O}-\text{Al}$. There is also the overlap of the stretching vibration of SO_4^{2-} at 1114 cm^{-1} (Figure 6a) [37]. Additional bands of weak to medium intensities in the region of the asymmetric stretching vibration of CO_3^{2-} between 1500 and 1400 cm^{-1} and of the asymmetric stretching vibration of $\text{B}-\text{O}$ between 1400 and 1300 cm^{-1} are also observed. These are related to the use of the ingredients ammonium carbonate for the Madder Rose formulations and sodium borate for the Madder Lake and Rose Madder lake pigments. No infrared bands of the Al^{3+} -anthraquinone complexes were detected.

As mentioned above, the madder lake pigments were highly insoluble, making the dye extraction for HPLC-DAD analyses complicated; details can be found in the experimental part. Although it was possible to detect pseudopurpurin, alizarin and purpurin (HPLC-DAD data of the dye molecules in Figure A1), as shown in Figure 6b, a signal at the beginning of the run was observed corresponding to Al^{3+} -anthraquinone complexes exiting the column, indicating that the dye extraction was incomplete. This interferes with any quantitative analysis that could be carried out in this work. Optimisation of the dye extraction method of these madder lake pigments will be pursued in the future.

3.4. Comparison with a W&N 19th-Century Oil Paint Tube

An analytical comparison was made with a late 19th-century W&N oil paint tube labelled “Rose Madder” (dated according to the appearance and data on the label). As shown in Figure 7a, its infrared spectrum presents a direct match with a Madder Rose lake pigment

reconstruction, exhibiting the infrared fingerprint of an aluminate polymeric compound, as described above, in an oil binder, identified by its characteristic bands at 2928 cm^{-1} and 2856 cm^{-1} assigned to the stretching vibrations of $-\text{CH}$, at 1740 cm^{-1} attributed to the stretching vibrations of $-\text{C}=\text{O}$ and at 1464 cm^{-1} corresponding to the bending vibrations of $-\text{CH}$ [38]. The presence of an oxalate compound may also be suggested due to the bands at 1608 cm^{-1} and 1377 cm^{-1} assigned to the asymmetric and symmetric stretching vibrations of COO^- [39].

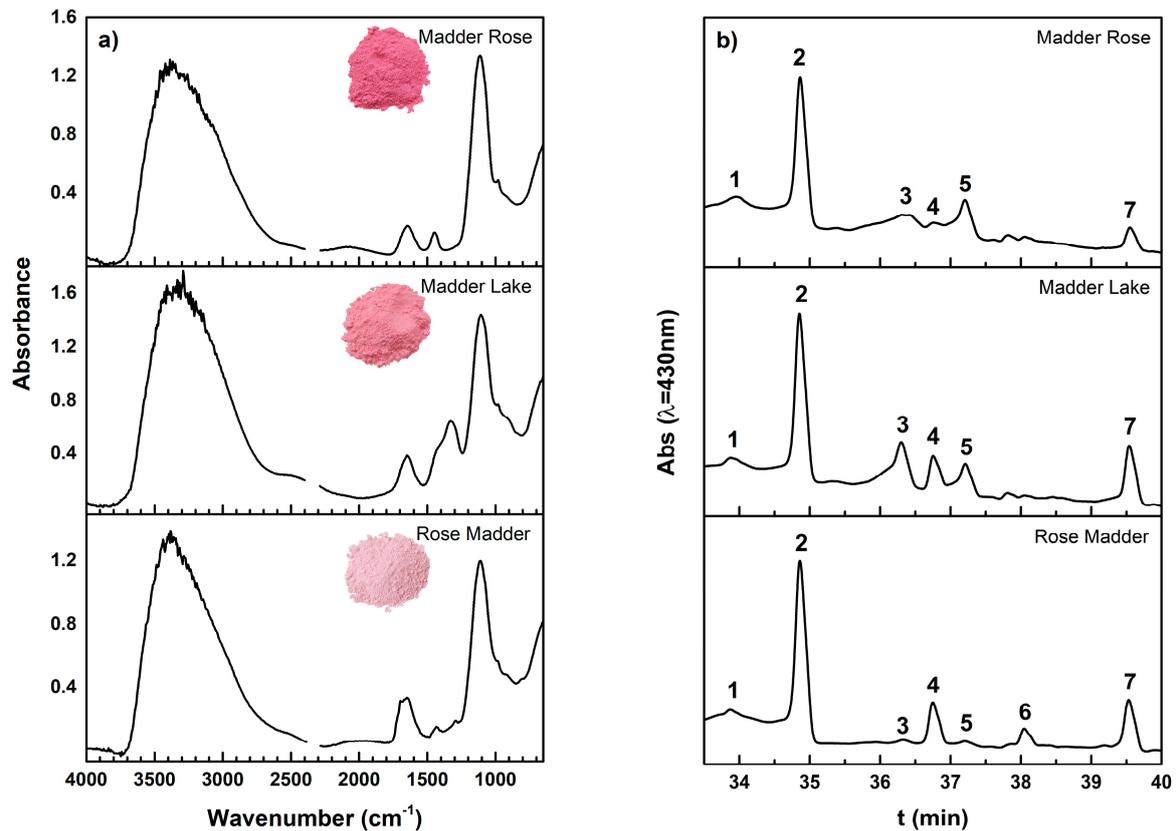


Figure 6. (a) Representative infrared spectra of the madder lake pigments produced and (b) chromatograms at 430 nm of MR1, ML1 and RM1 lake pigments; 1—pseudopurpurin, 2—alizarin, 3—purpurin; compounds 4–7 were not identified.

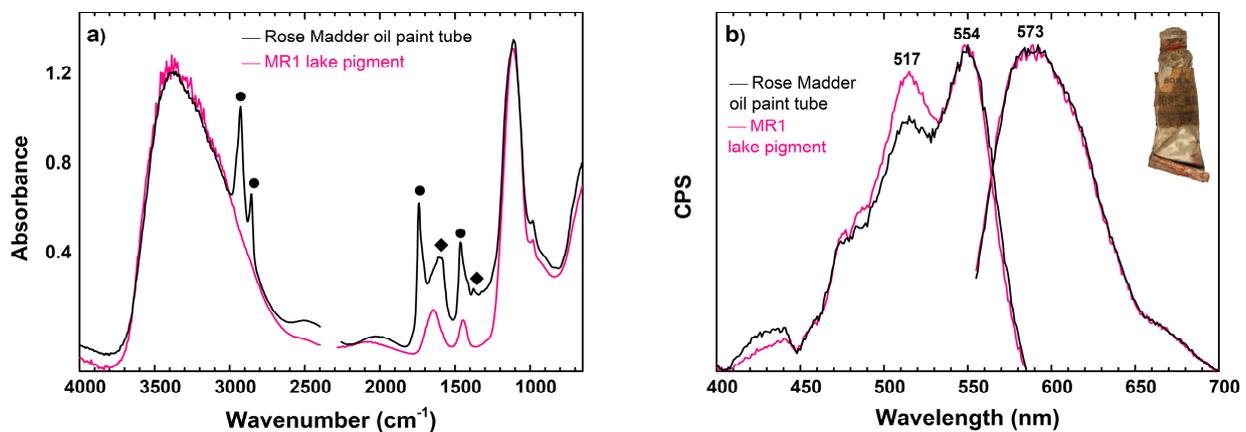


Figure 7. (a) Infrared spectra of a micro-sample from a Rose Madder W&N 19th-century oil paint tube and MR1 lake pigment; (●) bands assigned to the oil matrix and (◆) to an oxalate compound; (b) excitation and emission spectra acquired in painted samples of the Rose Madder 19th-century oil paint tube and MR1 lake pigment.

More importantly, by microspectrofluorimetry, a highly selective and sensitive in situ technique [15,19,36], it was also possible to find a very good match between the excitation and emission spectra of the historical W&N “Rose Madder” oil paint tube and MR1 lake pigment. As shown in Figure 7b, their spectra overlap very well, presenting excitation maxima at 517 nm and 554 nm and an emission maximum at 573 nm.

The powerful combination of these molecular techniques validates the Madder Rose lake pigment reconstruction as a historically accurate reference.

4. Conclusions

This work investigated the W&N 19th-century manufacture of madder red lake pigments for the first time. From 11 production records under the names Madder Rose, Madder Lake, Madder Carmine and Rose Madder, three main synthesis methods were found with three common steps: (i) washing of the madder roots from *Rubia tinctorum* L. with cold water, (ii) extraction in acid media and complexation with Al^{3+} using a solution of alum and (iii) precipitation using either ammonium carbonate or borate of sodium. All pigment reconstructions resulted in madder lake pigments with a rose hue, except for the Rose Madder formulation, which includes adding sulfuric acid. This strong acid significantly affects the process and the final product, and understanding its role in producing W&N’s madder reds is crucial and will be assessed in the future.

The presence of Al^{3+} -purpurin and/or pseudopurpurin complexes was observed in the solution before precipitation, which resulted in the formation of an amorphous aluminate polymeric matrix identified by FTIR. Dye extraction of the madder lake pigments was revealed to be more complex than expected; however, pseudopurpurin, alizarin and purpurin were detected by HPLC-DAD.

Although preliminary, this work enabled the successful preparation of a historically accurate madder lake pigment that was analytically validated by the infrared and microspectrofluorimetry analyses of a Rose Madder W&N 19th-century oil paint tube.

This investigation intends to be the groundwork for comprehensively studying the W&N’s 19th-century madder colours. A complete evaluation of W&N’s 19th-century production records for madder colours will identify their primary manufacturing processes and pinpoint possible markers for W&N’s 19th-century madder products. It will enable the creation of a robust analytical database made with historically accurate references that will be used to improve our analytical methodology to identify madder reds in heritage objects.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A. Additional HPLC-DAD Analyses

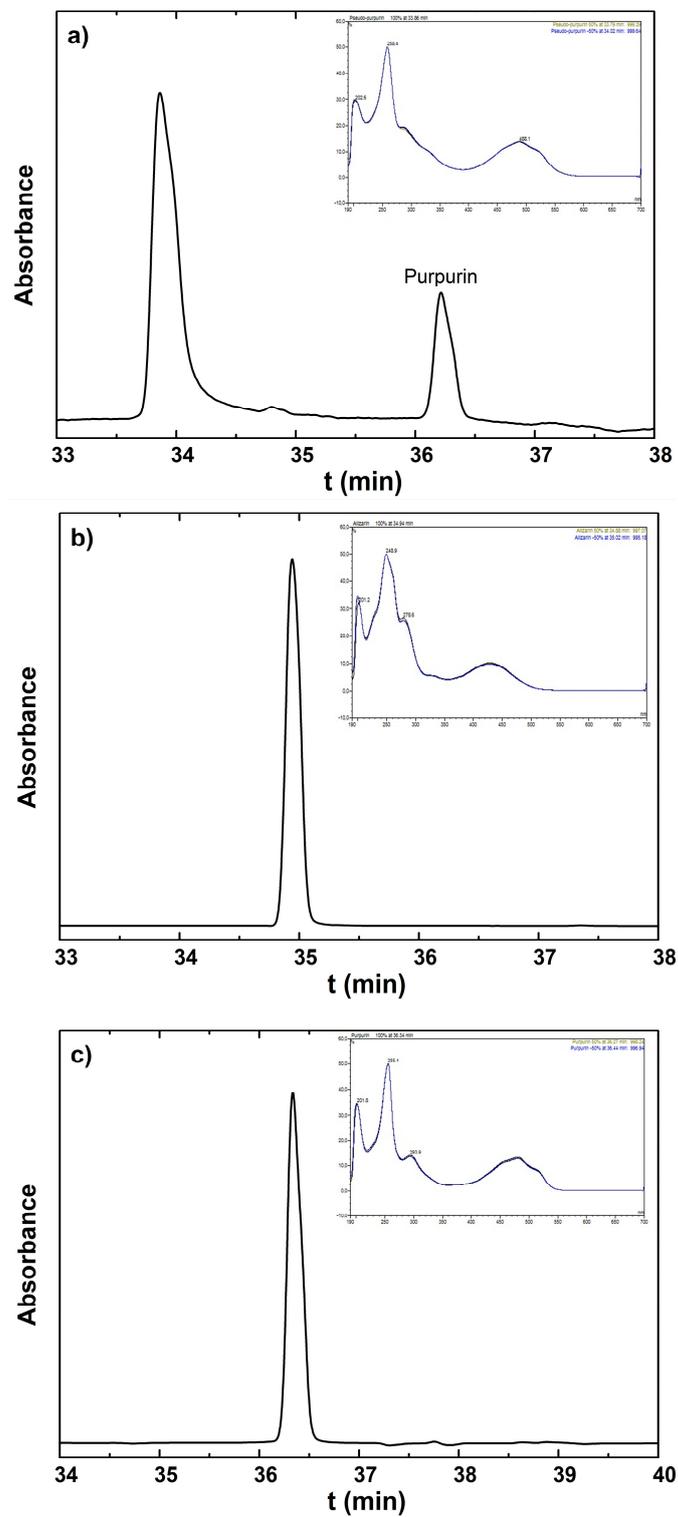


Figure A1. Chromatograms of (a) pseudopurpurin at $t = 33.9$ min with purpurin at $t = 36.3$ min ($\lambda = 500$ nm); (b) alizarin at $t = 35$ min ($\lambda = 430$ nm); and (c) purpurin at $t = 36.3$ min ($\lambda = 500$ nm). Insets of the corresponding UV-VIS spectra.

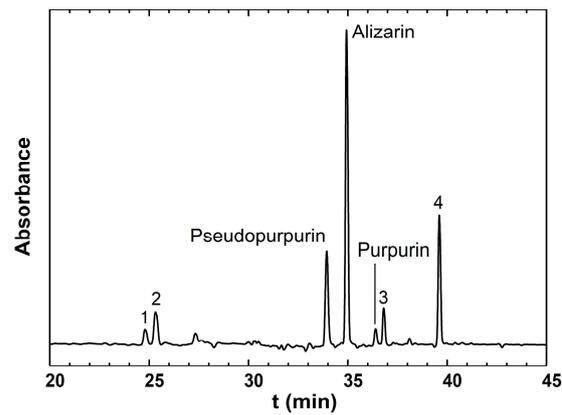


Figure A2. Chromatogram at 430 nm of water/methanol extract of the *R. tinctorum* roots used in this work; compounds 1–4 were not identified.

Appendix B. Additional Data on the W&N Production Records

Table A1. Formulation name, original production name and their unique recipe code (URC) for the eleven production records pertaining to the manufacture of madder red lake pigments in book P1.

Formulation Name Code	Original Production Name	URC *
Madder Rose MR	Madder Rose-colours	P1P025AL01 [¥]
	Madder Carmine for Water	P1P257AL01
Madder Lake ML	Madder Lake	P1P127AL05
	§	
Rose Madder RM	Rose Madder	P1P114AL13
	Madder Carmine	P1P120AL11
	Another formula [RM extra quality]	P1P320BL01
	Madder Carmine	P1P322AL01
-	Liquid Madder Lake	P1P030AL03
	Crimson Madder	P1P205AL12
	Madder with lime water	P1P299AL01

* The unique recipe code (URC) identifies the database record on the W&N Database. [¥] The URC P1P025AL10 also falls under the Madder Rose-colours production record. [§] This production record appears on the Rose Madder database record (URC P1P114AL13). In a database record (data from the RE database), the corresponding archive page can contain more than one production record (manufacturing data from the actual W&N archive).

Appendix C. Additional FTIR Analysis

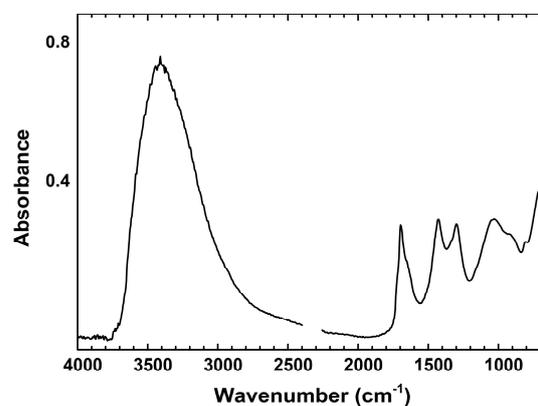


Figure A3. Infrared spectrum of RM2 pigment.

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