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Yellow Lake Pigments from Weld in Art: Investigating the Winsor & Newton 19th Century Archive

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Abstract: Weld (*Reseda luteola*) was one of the main sources of yellow dyes used for dyeing textiles and to prepare artists' pigments in Europe until the 19th century. For the first time, this work explores the technology of preparing weld lake pigments in the 19th century by Winsor & Newton (W&N), a renowned supplier of artists' materials. Five recipes were discovered in the W&N 19th century Archive Database and reconstructed in the laboratory. W&N was extracting weld in neutral and basic media, and preparing the insoluble lake by complexation with Al^{3+} in the form of alum ($KAl(SO_4)_2 \bullet 12H_2O$) or hydrated alumina ($Al(OH)_3$). Five yellow lake pigments were successfully obtained and characterized by High-Performance Liquid Chromatography-Diode Array Detector (HPLC-DAD) and Fourier Transform Infrared Spectroscopy (FTIR). Their chromatographic profiles display as main yellows, luteolin 7-*O*-glucoside (Lut-7-*O*-glu) or both Lut-7-*O*-glu plus luteolin 3′,7-*O*-glucoside (Lut-3′,7-*O*-glu). In two of the processes, the presence of gypsum ($CaSO_4 \bullet 2H_2O$) was unequivocally detected by FTIR, being formed as a by-product. This work offers the first identification of weld lake pigments' characteristic infrared bands. The W&N Database proved again to be a unique source of information on 19th-century artists' materials and their commercial preparation. The knowledge gain is essential to ensure effective conservation and authentication procedures.

Keywords: weld lake pigments; yellow lakes; luteolin; 19th century; Winsor & Newton; conservation

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1. Introduction

Yellow dyes were used in artworks for millennia up until the advances in modern chemistry. *Reseda luteola* L., or weld, was one of the most important dyes in Europe up until the 19th century, and the primary source for organic yellows [1]. These were used in the textile industry as a source of yellow and green colors and prepared as artists' pigments to create precious masterpieces [1–3].

Although weld was possibly identified in textiles from Xinjiang [4,5], in 17th-century Arraiolos carpets, Portugal [6] and in Southern Swedish painted wall hangings from the 18th–19th centuries [7], assessing its conservation condition and the causes of degradation in artworks is still in its early stages. To understand the degradation mechanisms that are in play in such complex matrices as found in our cultural heritage, it is necessary to have reference materials prepared with as much historical accuracy as possible. These are used to assess the natural evolution of these colors and simulate by accelerated ageing experiments with a limited number of variables the aging of these systems.

Methanol:water extracts of *Reseda luteola*, which gave the highest flavonoid yield, have shown that the main chromophore is luteolin 7-*O*-glucoside (Lut-7-*O*-glu), followed by luteolin 3′,7-*O*-glucoside (Lut-3′,7-*O*-glu). Luteolin (Lut), apigenin 7-*O*-glucoside (Api-7-*O*-glu), chrysoeriol glycoside (Chry-gly), luteolin 4′-*O*-glucoside (Lut-4′-*O*-glu), are also found, with apigenin (Api), apigenin-6,8-di-*C*-glucoside (Api-6,8-*C*-glu), and a luteolin di-*O*-glucoside (Lut-di-*O*-glu) found in lower amounts [6,8–10]. When analyzing dyed textiles, weld is identified as the yellow used by the presence of "luteolin-type" flavonoids. In 17th-century Arraiolos carpets, the yellow historical samples analyzed with LC–MS contained primarily Lut-7-*O*-glu, small amounts of apigenin-6,8-di-*C*-glucoside, Lut-3,7-*O*-glu and its isomer, as well as Api-7-*O*-glu and Lut, see Figure 1 [6]. Moreover, for the dyed textiles from Xinjiang, the identification of Lut-7-*O*-glu, along with other "luteolin-type" and "apigenin-type" flavonoids, led to the proposal of the use of weld in the samples analyzed [4,5].

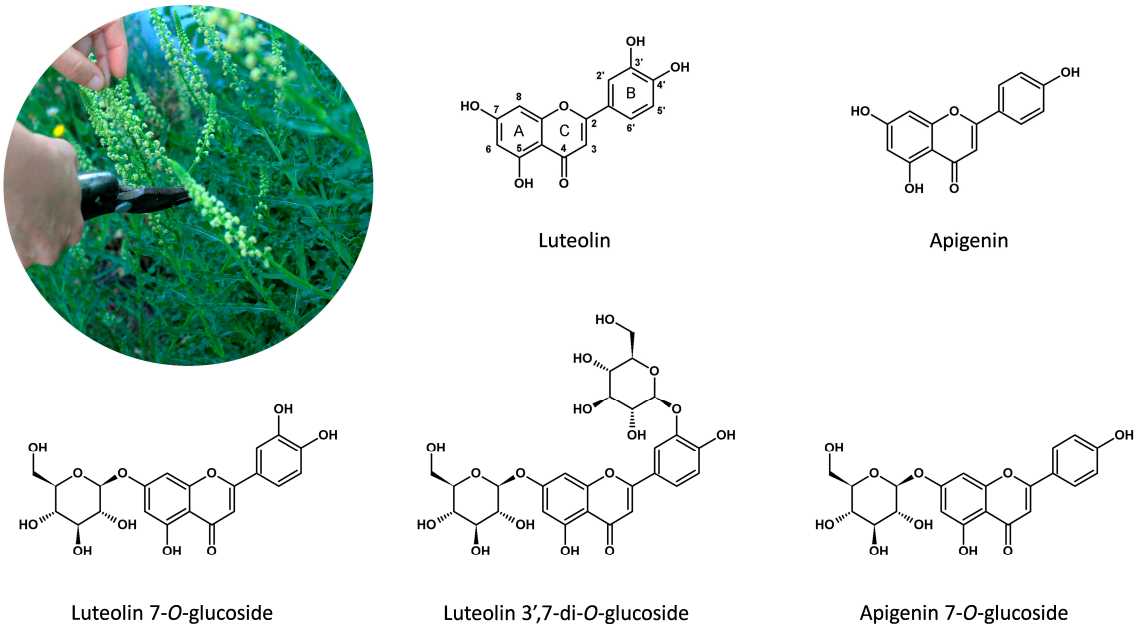


Figure 1. Collection of *Reseda luteola* in its native environment; structures for the main chromophores found in *Reseda luteola* yellows: luteolin, apigenin, luteolin 7-*O*-glucoside, luteolin 3′,7-di-*O*-glucoside, and apigenin 7-*O*-glucoside.

Generally, most dyes were applied as lake pigments, formed by the colorant's precipitation with a complexing agent, such as alum, hence becoming a non-soluble pigment, in a process analogous to the mordanting of textiles [2]. Although these dye-metal complexes' exact structure is still unknown for most lake pigments, there are some proposals for luteolin-metal complexes [11–13]. Following a DFT/TDDFT study of the complexation sites of luteolin and apigenin, Amat et al. proposed that luteolin is preferentially co-precipitated or absorbed with Al^{3+}, or other metals in a bi-dentate mode involving the 4-keto-5-hydroxy site and with a Al:Luteolin 1:1 stoichiometry [11]. The same structure was proposed by Gao et al. for luteolin-Cr(III) complexes, while Dong et al. proposed the same coordination sites for complexation with manganese (II), although with an Mg:Luteolin 1:2 stoichiometry, which means the existence of a complexation network is expected involving the hydroxyl groups [12,13]. On the other hand, Smith et al. found that the aluminium ion-flavonoids complexes (present in dyed textiles and lake pigments) prevent the natural efficient and non-degradative dissipation of excitation energy by an intermolecular proton transfer involving the 5-OH and the 4=O groups, hence are more susceptible to degradation [14].

Within an interdisciplinary team of chemists, botanists, and heritage scientists, with 20 years of experience in studying and retrieving the "lost knowledge" on natural dyes found in historical documents and artworks [15–19], this work will be the first step of a

systematic study on the technology used in the past to produce weld lake pigments. For this first approach, we investigated recipes found in the Winsor & Newton (W&N) 19th century Archive Database, a unique primary documentary source covering handwritten formulation instructions and workshop notes of a leading artists' colormen that supplied prominent painters. The W&N Archive Database comprises a summary index-linked to digitalized page-images of 85 manuscript books (corresponding to 15.003 database records) and a digital collection of 47 W&N 19th-century trade and retail catalogues [20–22].

In a time of chemical development, especially of artificial dyestuffs, it is very interesting to note that W&N was producing at an industrial scale and selling natural yellow lake pigments during the 19th century [23]. In previous studies, we have proven that W&N was committed to primarily selling the most high-quality and durable products [18,24,25]. More importantly, we have demonstrated that research on the W&N Database enables pigment reconstructions with as much historical accuracy as possible. These references will be fundamental to advance analytical methodologies on the identification of weld lake pigments in artworks. In this work, for the first time, we disclose the infrared bands of weld lake pigments, complemented by their chromatographic profiles.

2. Materials and Methods

2.1. Materials

All solvents used were HPLC grade. For all chromatographic studies as well as dye extraction, Millipore ultrapure water was used. Luteolin ($C_{15}H_{10}O_6$), luteolin-7-O-glucoside ($C_{21}H_{20}O_{11}$) and luteolin-3′,7-di-Oglucoside ($C_{27}H_{30}O_{16}$) analytical standards were purchased from Extrasynthese®. Potassium aluminium sulfate ($AlK(SO_4)_2{\cdot}12H_2O$), potassium bicarbonate ($KHCO_3$), sodium borate ($Na_2B_4O_7{\cdot}10H_2O$), calcium carbonate ($CaCO_3$), and hydrated alumina ($Al(OH)_3$), were purchased from Sigma-Aldrich®, while potassium carbonate (K_2CO_3) was purchased from Merck®. Gum arabic to prepare paint references was purchased in pieces from Kremer Pigmente®.

Flowering branches of *Reseda luteola* were collected in June 2020 by A. Clemente, from wild populations near Bucelas, north of Lisbon, Portugal (38°54′21″ N–9°6′30″ W). The plant material was spread in a tray and air-dried in the dark, in a ventilated area at 20 °C.

2.2. Synthesis Methods for Weld Lake Pigments

Research on the W&N 19th century Archive Database was carried out under the sub-topic weld, which resulted in 12 database records. Among these, it was possible to identify seven records for the production of weld lake pigments, however, there are only five recipes as 3 of the records are copies, see Table 1. The remaining five database records include two notes on weld, two experiments to extract weld, and one recipe to prepare Yellow Carmine from weld, Persian berries and quercitron bark. The transcription of the production records used in this work may be consulted in Table S1, and the synthesis methods reproduced are described in Table 1. Interpretation of the materials used was based on our previous works [18,24,25], which allowed us to infer that the term 'whiting' used in the recipe *Yellow from Weld* corresponds to calcium carbonate ($CaCO_3$), 'Sub. Carb. Pot', used in the same recipe, is potassium bicarbonate ($KHCO_3$) and 'Pearlash', used in the other recipes, is potassium carbonate (K_2CO_3). It is important to note that the recipe *Yellow Lake. Cool tint.* refers to the use of alum (ammonia sort), however, it was chosen to use common alum ($KAl(SO_4)_2{\cdot}12H_2O$) in all recipes to facilitate a first comparison between them. For this reason, we also decided always to use weld flowers. The introduction of experimental variants such as using ammonium alum ($NH_4Al(SO_4)_2{\cdot}12H_2O$) will be investigated in the future. All materials were scaled-down from industrial to laboratory scale, and quantities in British measures were converted to SI units [22,23].

pH measurements were acquired throughout the syntheses. After 1 day left to precipitate, the lakes were centrifuged for 10 min at 2400 rpm, washed with distilled water, and centrifuged again for 5 min at 3000 rpm. The lakes were air-dried and ground in an agate mortar for 15 min each.

Table 1. Production name, recipe and pigment code of the synthesis methods for weld lake pigments, adapted from the original text transcribed in Table S1.

Production Name	Unique Recipe Code [§]	Pigment Code	Synthesis Methods
Yellow from Weld	4PP148AL01 (copy in P4P088L01)	WL1	A. To 10 mL of boiling water add 0.2 g of $CaCO_3$ and then slowly add 0.86 g of $KAl(SO_4)_2{\cdot}12H_2O$, always stirring. Leave it to rest and decant the solution; keep the precipitate. B. To 50 mL of boiling water add 2 g of weld flowers. Then add 0.014 g of $KHCO_3$ and leave it to boil during 20 min. Filter it and keep the solution. Put the solution B to boil. When boiling, add the precipitate A and leave it boiling for 1 h, always stirring. Leave it to rest for 1 day and filter the yellow lake pigment.
	4PP148AL14 (copy in P4P089L14)	WL2	A. To 10 mL of boiling water add 0.86 g of $KAl(SO_4)_2{\cdot}12H_2O$ and then slowly add 0.2 g of $CaCO_3$, always stirring. Leave it to rest and decant the solution; keep the precipitate. B. To 50 mL of boiling water add 2 g of weld flowers. Then add 0.014 g of $KHCO_3$ and leave it to boil during 20 min. Filter it and keep the solution. Put the solution B to boil. When boiling, add the precipitate A and leave it boiling for 1 h, always stirring. Leave it to rest for 1 day and filter the yellow lake pigment.
Yellow Lake. Cool tint.	P1P348AL01 (copy in X6P228L01 [¥])	WL3	To 50 mL of boiling water add 0.43 g of K_2CO_3. When dissolved add 2 g of weld flowers and leave it to boil during 20 min. Filter it and keep the solution. To the yellow solution add 0.86 g of $KAl(SO_4)_2{\cdot}12H_2O$, always stirring. Leave it to rest and filter the yellow lake pigment.
Weld Yellow	P4P100L10	WL4	To 50 mL of boiling water add 0.018 g of K_2CO_3 and then 4 g of weld flowers. Boil 10 min. Filter it and keep the solution. To the yellow solution add 0.107 g of $KAl(SO_4)_2{\cdot}12H_2O$ and then 0.07 g of $Na_2B_4O_7.10H_2O$, always stirring. Leave it to rest and filter the yellow lake pigment.
		WL5	To 50 mL of boiling water add 0.018 g of K_2CO_3 and then 2 g of weld flowers. Boil 10 min. Filter it and keep the solution. To the yellow solution, add 0.177 g of $Al(OH)_3$, always stirring. Leave it to rest and filter the yellow lake pigment.

[§] The unique recipe code is the code from the W&N Database that identifies a database record. [¥] Although this record is a copy, its title is "Experiment with Weld for Yellow Lake for Water Colours" and is dated 6 October 1854.

2.3. Paint References

Paint references were prepared using gum arabic as a 20% solution; the pieces were ground and then added to pure water. The lake pigments were first ground in a glass mortar with pure water and then ground with the binder. The paints were applied on filter paper with a paintbrush and allowed to dry. Filter paper was selected because no additives are present such as brighteners; this was confirmed by checking the filter paper under an UV-lamp (280 nm). The paint references were analyzed by colorimetry.

2.4. Equipment and Characterization Methods

2.4.1. Colorimetry

For measuring color, a portable spectrophotometer colorimetry Data Color International was used. Its measuring head's optical system uses diffuse illumination from a pulsed Xenon arc lamp over the 8mm-diameter measuring area, with 0° viewing angle geometry. Color coordinates were calculated defining the D65 illuminant and the 10° observer. The calibration was performed with a white bright standard plate and a total black standard. Color, as perceived by the human eye, may be represented in a three-dimensional system. The color data are presented in the CIE-Lab 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).

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

For HPLC-DAD analysis, *Reseda luteola* plant was extracted by placing 1 g of the dry plant material (as collected from nature) with 100 mL of methanol:water (70:30, *v*:*v*) and heating in a water bath at 60 °C for one hour, as described in [26]. The dye from lake pigments was extracted by placing in an eppendorf, 10 mg of powder with a 1 mL solution of oxalic acid (0.2 M):methanol:acetone:water (0.1:3:3:4, *v*:*v*), as described in [27].

Prior to HPLC-DAD analysis, all extracts were centrifuged at 12,000 rpm for about 10 min. The supernatant liquid was gently removed and filtered through a 0.45 µm filter. Before analysis, the solution was diluted with methanol:water (70:30, *v*:*v*) if necessary.

The analysis was carried out in a Thermofinnigan Surveyor® HPLC-DAD system with a Thermofinnigan Surveyor PDA (Thermofinnigan, San Jose, CA, USA), an autosampler, and a gradient pump. The sample separations were performed in a reversed-phase column, RP-18 Nucleosil column (Macherey-Nagel) with 5 µm particle size column (250 mm × 4.6 mm), with a flow rate of 1.7 mL/min with the column at a constant temperature of 35 °C. The samples were injected via a Rheodyne injector with a 25 µL loop. The elution gradient consisted of two solvents, A: methanol and B: 0.1% (*v*/*v*) perchloric acid aqueous solution. A gradient elution program was used of 0–2 min isocratic 7% A, 2–8 min linear gradient to 15% A, 8–25 min linear gradient to 75% A, 25–27 min linear gradient to 80% A, 27–29 min linear gradient to 100% A, and 29–30 min isocratic 100% A (10 min re-equilibration time). The eluted peaks were monitored at 350 nm.

The peaks were integrated and the area of each peak was recorded as well as the percentage. Peak area calculation was done by defining the time intervals for each peak. The area below the peak was integrated within this interval is measured and the percentage of each area is calculated by dividing by the sum of all the peak areas. For this analysis, it was considered the area of the nine peaks visible at λ = 350 nm, between 14 and 24 min, as shown in Figure 2.

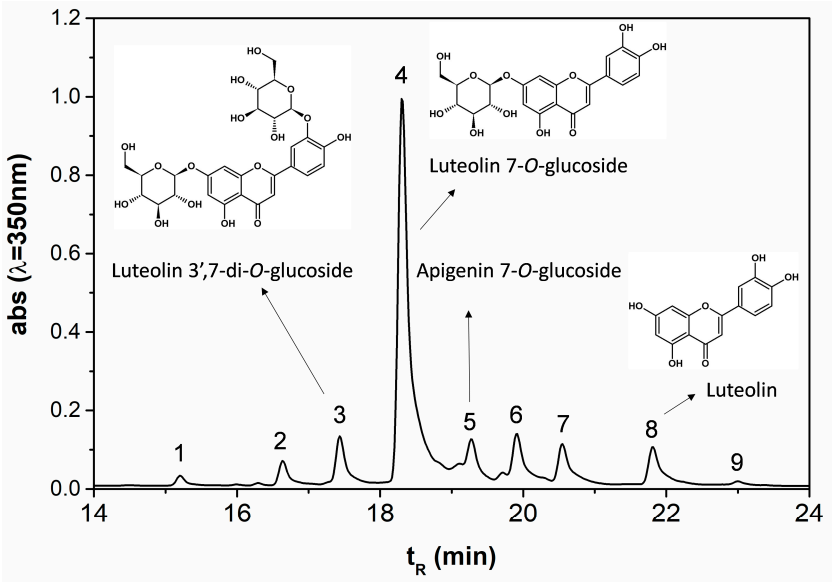


Figure 2. Chromatogram of an extract in MeOH:H_2O (70:30, *v*:*v*) of *Reseda luteola*, λ=350 nm: (1) apigenin-6,8-di-*C*-glucoside, (2) luteolin di-*O*-glucoside; (3) luteolin 3′,7-*O*-glucoside; (4) luteolin 7-*O*-glucoside, (5) apigenin 7-*O*-glucoside, (6) chrysoeriol glycoside, (7) luteolin 4′-*O*-glucoside, (8) luteolin, (9) apigenin.

2.4.3. Ultra-High Performance Liquid Chromatography-High Resolution Mass Spectrometry (UHPLC-DAD-HRMS)

Aliquots of 3 µL of plant material were analyzed on a UHPLC Elute system coupled on-line with a quadrupole time-of-flight Impact II mass spectrometer equipped with an ESI source (Bruker Daltoniks, Bremen, Germany). Chromatographic separation was carried out on an RF-C18 Halo column (150 mm × 2.1 mm, 2.7 µm particle size, Advanced Material Technology). The mobile phase consisted of water (A) and acetonitrile (B), containing 0.1% formic acid, at a flow rate of 600 µL/min. The elution conditions were as follows: 0–18 min, linear gradient to 50% B; 18–20 min, linear gradient to 90% B; 20–23 min, isocratic 90% B; and 23–24 min, linear gradient to 0% B (followed by 11 min re-equilibration time). The column and the autosampler were maintained at 45 °C and 8 °C, respectively. High-resolution mass spectra were acquired in the ESI negative mode. Internal calibration was achieved with an ammonium formate 10 mM solution introduced to the ion source via a 20 µL loop at the beginning of each analysis, using a six-port valve. The mass spectrometric parameters were set as follows: end-plate offset: 500 V; capillary voltage: −2.5 kV; nebulizer: 4 bars; dry gas: 8 L/min; heater temperature: 200 °C; m/z range 100–1000 Da; acquisition mode: data-dependent analysis (Auto MS/MS), acquisition rate of 3 Hz, and using a dynamic method with a fixed cycle time of 3, and an isolation window of 0.03 Da. Data acquisition and processing were performed using Data Analysis 4.2 software.

2.4.4. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared analyses were carried out with a Nicolet Nexus spectrophotometer. The pigments were prepared as KBr pellets, and spectra were collected in transmission mode between 4000 cm^{-1} and 650 cm^{-1}, with a resolution of 8 cm^{-1} and 64 scans. The spectra are shown here as acquired, without corrections or any further manipulations.

3. Results and Discussion

3.1. Weld Lake Pigment Recipes in the Winsor & Newton 19th Century Archive Database

From a total of 1511 database records for yellow pigments, 42% pertains to yellow lakes. Although the majority of these records pertain to quercitron-based products, 12 of these mention weld, as referred above. Interestingly, the five recipes to prepared weld lake pigments were discovered in manuscript books belonging to the founder Henry Charles Newton and his son Arthur Henry Newton. The recipes were found under the names: "Yellow from weld", "Yellow Lake. Cool tint." and "Weld Yellow", as described in Tables 1 and 2. It is important to note that the pigments prepared from the first three recipes (*WL1*, *WL2* and *WL3*) were originally produced with 12.7 kgs of weld plants, whereas those from the last recipes ((*WL4* and *WL5*) were produced with 0.9 kg, which suggests the latter were experiments. Nonetheless, all recipes were reproduced, and the pHs of the extraction solution and after precipitation of the weld lake pigments obtained are also presented in Table 2.

As Table 1 shows, W&N was extracting weld in a neutral media for most recipes, excluding *WL3* recipe, which involved a basic media. This was accomplished by the addition of carbonate compounds (($KHCO_3$ and K_2CO_3) that "assist the extraction of the colouring matter" as stated in the recipe *Yellow from Weld (WL1* and *WL2*). The latter recipe also includes the preparation of what W&N called the "body" of the pigment formulation, which involves mixing calcium carbonate ($CaCO_3$) and alum ($KAl(SO_4)_2 \cdot 12H_2O$. *WL1* and *WL2* differ in the order of addition of these ingredients. According to W&N, the pigment resulting from *WL1* was "rather pale because the body was not thoroughly homogeneous" and the improved process *WL2* resulted in a color "deeper & looked brighter". Experimentally, we observe a yellow with a stronger red component, see Table 3. Curiously, they also refer "the quantity of yellow was less" for the *WL2*, however, we did not obtain this result as the yields are very similar, as presented in Table 2. In fact, those that experimentally presented the best yield of all five recipes were *WL1* and *WL2*, while *WL4* had the worst yield. Regarding recipe *WL3*, the yield experimentally obtained was very similar to W&N.

According to them, this recipe produced "a lively kind of yellow lake for sale &c. Greenish in hue, bright in the drop & full coloured" and when "tried in oil it produces a very beautiful yellow lake_very cool_bright & strong". Although the resulting pigment presents one of the lowest red component values (a* ≈ 2), it did not show a greenish hue. This may be related to incomplete precipitation of all coloring matter as in the original recipe (see Table S1) is claimed that the quantity of alum used by W&N "was found to precipitate the colour entirely, leaving only a very faint tinge of yellow in the supernatant". This was not observed in our experiment and will also be addressed in future work.

Table 2. Production name, ingredients, synthesis methods, final pHs and yields for W&N's weld lake pigments.

Dye Source	Extraction Method		Complexing Agent			Additives
Weld	Potassium bicarbonate $KHCO_3$	Potassium carbonate K_2CO_3	Alum $KAl(SO_4)_2$	Hydrated alumina $Al(OH)_3$	Calcium carbonate $CaCO_3$	Sodium Borate $Na_2B_4O_7$
	Ext	Ext	C	C	C	A

Production name	Code	Synthesis	pH extraction [1]	pH final	η (%) [2]
Yellow from Weld	WL1	Ext + Filtration → C + C	6.18	4.05	$\eta_{W\&N}$ = 25% η_{EXP} = 31%
	WL2	Ext + Filtration → C + C	6.27	3.36	$\eta_{W\&N}$ = 18% η_{EXP} = 32%
Yellow Lake. Cool tint.	WL3	Ext + Filtration → C	9.46	3.63	$\eta_{W\&N}$ = 12.5% η_{EXP} = 12%
Weld Yellow	WL4	Ext + Filtration → C + A	6.02	5.07	$\eta_{W\&N}$ = n.a. η_{EXP} = 6%
	WL5	Ext + Filtration → C	6.35	6.15	$\eta_{W\&N}$ = n.a. η_{EXP} = 9%

[1] The pH extraction is related to the pH after extracting the plant material and subsequent filtration. [2] The observed yield (η) was calculated as follows: (*final lake amount*) ÷ (*weld amount*) × 100. $\eta_{W\&N}$–observed yield calculated by the quantities given by W&N, see Table S1; η_{EXP}–observed yield calculated by the quantities obtained experimentally.

Table 3. Colorimetry, HPLC chromatograms and infrared spectra of the weld lake pigments synthesized applied over filter paper, with gum arabic media. HPLC chromatograms were obtained from the extracts of the lake pigments. For more details, please see text.

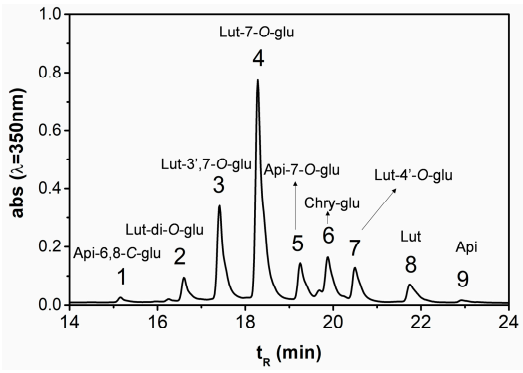
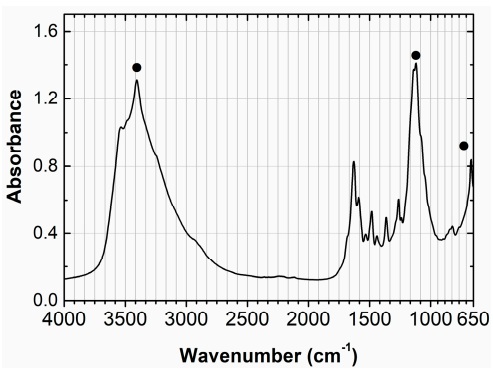
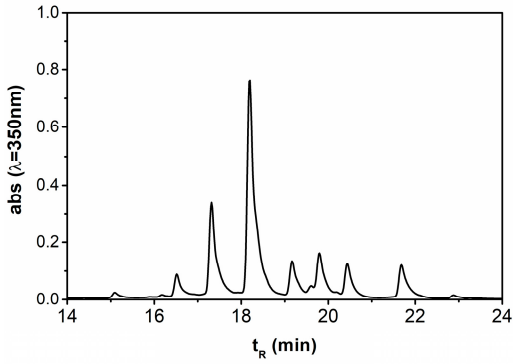
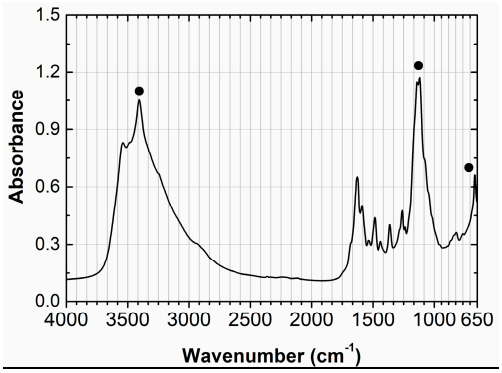
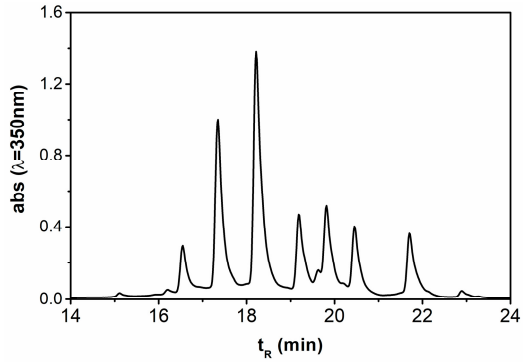
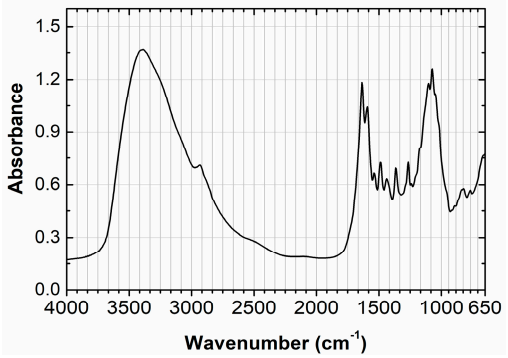
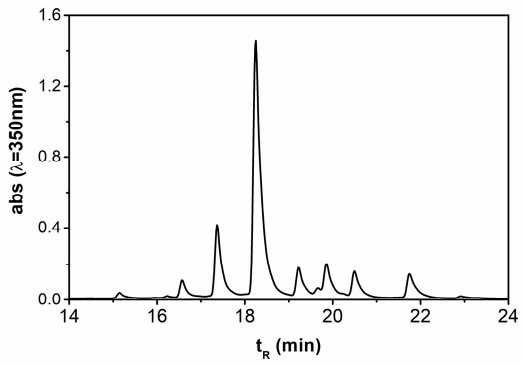
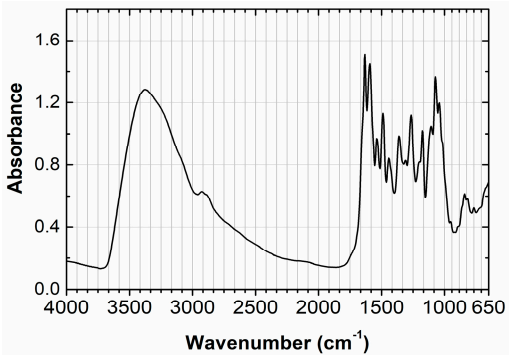
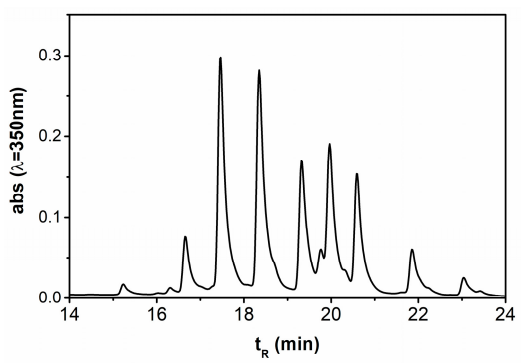
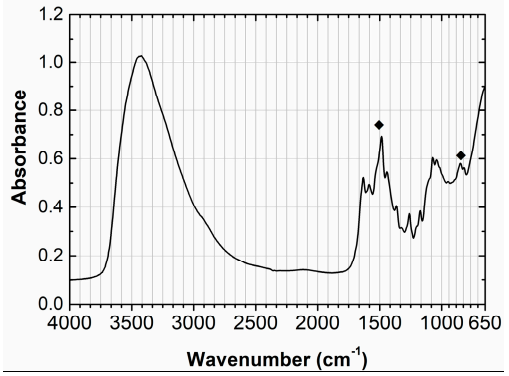
Recipe	HPLC	Infrared
WL1 L* = 86.25 ± 0.06 a* = 1.56 ± 0.19 b* = 81.82 ± 1.00 **gypsum (●)**		

Table 3. *Cont.*

Recipe	HPLC	Infrared
WL2 L* = 82.28 ± 0.21 a* = 5.78 ± 0.29 b* = 82.91 ± 0.57 **gypsum (●)**		
WL3 L* = 86.49 ± 0.27 a* = 2.78 ± 0.27 b* = 80.2 ± 0.24		
WL4 L* = 76.93 ± 0.69 a* = 8.81 ± 0.58 b* = 74.93 ± 0.92		
WL5 L* = 85.66 ± 0.13 a* = 0.96 ± 0.15 b* = 75.75 ± 0.06 **Al(OH)$_3$ (◆)**		

The complexing agent always used was Al^{3+} in the form of alum ($KAl(SO_4)_2 \cdot 12H_2O$) in the majority of the recipes and hydrated alumina ($Al(OH)_3$) in *WL5* recipe; however,

complexation with Ca^{2+} cannot be excluded as this has been observed for W&N 19th century cochineal lake pigments [18]. The addition of borax ($Na_2B_4O_7$) was also experimented with alum in *WL4* recipe. The pH after precipitation was slightly acidic, between 3 and 6, but always resulted in bright yellow lake pigments, as shown in Table 3. The reasoning for the production methods found is discussed below.

3.2. Extraction Method

The analysis of the plant extract was done by HPLC-DAD-HRMS. It was possible to find as a major chromophore Lut-7-*O*-glu, and minor compounds, Api-6,8-*C*-glu, Lut-di-*O*-glu, Lut-3′,7-*O*-glu; Api-7-*O*-glu, Chry-gly, Lut-4′-*O*-glu, Lut and Api, see Figure 2. This is in accordance with what has been reported in the literature [6,8,9]. It was confirmed that the chromophores identified by HPLC-HRMS were the same as observed by HPLC-DAD.

For both *WL1* and *WL2* recipes, potassium bicarbonate is added to the plant material' solution, raising the pH to a neutral media (pH ~6). For the rest of the recipes, potassium carbonate was added previously to the weld, also resulting in a neutral media (pH ~6), except for the *WL3* recipe that remained at a basic media. Although the recipes present two different extraction methods, they do not influence the chromophores extracted as the chromatographic profiles are similar, see Figure 2 and Figure S1.

It is very interesting the use of carbonates ($KHCO_3$ and K_2CO_3) for the extraction of the flavonoids. The use of such extract solutions instead of water was possibly to allow the highest amount of lake pigment. Favaro et al. used fluorimetric titration to characterize the various luteolin species detected within the pH range explored (pH = 2–12) [28]: neutral form (pH < 5), mono-anion (pH ~7), di-anion (pH ~9) and tri-anion (pH ~12), and the successive deprotonations occur in the order 7-OH; 4′-OH; 3′-OH or/and 5-OH [28]. In *WL3*, *WL4* and *WL5* the extraction is carried out in a basic pH, turning neutral after the addition of the plant material. This creates the optimum conditions for the metal chelation through the OH at C^5 and the carbonyl at C^4, since the first is deprotonated only at pH $\approx$ 10.3, as mentioned above.

3.3. Characterization of the Weld Lake Pigments

A summary of the multi-analytical results of Colorimetry, High-Performance Liquid Chromatography-Diode Array Detector (HPLC-DAD) and Fourier Transform Infrared Spectroscopy (FTIR) for the weld lake pigments prepared may be observed in Table 3.

3.3.1. HPLC-DAD Analysis

Other authors have done an extensive analysis of the characterization of weld by HPLC, including quantitation of the chromophores [6,8–10,29,30]. Based on this, in this work, we only compared the chromatographic profiles of the lake pigments using HPLC-DAD, which is preferable to perform a semi-quantification.

When analyzing the HPLC chromatograms of the weld lake pigment extracts, some differences are visible, as shown in Table 3. The two variants of recipe *Yellow from Weld* (*WL1* and *WL2*) present the same chromatographic profile, indicating that the order in which alum and calcium carbonate are added does not affect the chromatographic profile, i.e., the percentage of chromophores present, as seen in Table S2. However, when compared with the extract, in Figure 2, it is possible to see that both lake pigments present a higher percentage of Lut-3′,7-*O*-glu than the plant extract (15.35–17.25% in the lake pigment when compared with 4.92% of the extract). Considering that the extracts in K_2CO_3 and $KHCO_3$ presented the same chromatographic profile as in MeOH:H_2O (see Figure S1), the difference is not due to different extraction methods, but possibly to a higher preference of complexation for the di-glucoside. Interestingly, this difference is even higher in the lake pigment from *WL3* and *WL5*, where the Lut-3′,7-*O*-gluc represents 20.91% and 23,05% of the total peak area, while the Lut-7-*O*-glu represents 30.26% and 18.63%, respectively. *WL3* is the only recipe with the addition of alum to an extraction solution of *Reseda luteola* at a basic pH of around 9. Moreover, *WL5* also has a higher percentage of Api-7-*O*-glu, representing

11.22% of the total peak area. *WL5* is the only recipe where alumina is added. Regarding the recipe *WL4*, it has the closest chromatographic profile to that of the extraction, with 13.17% of luteolin 3′,7-di-*O*-glucoside and 52.551% of luteolin 7-*O*-glucoside.

3.3.2. FTIR Analysis

Both yellow lake pigments from the recipe *Yellow from Weld* (*WL1* and *WL2*) have shown similar FTIR results as observed by HPLC-DAD. Notably, the formation of gypsum ($CaSO_4 \cdot 2H_2O$) by FTIR was detected, due to its characteristic absorption bands for νOH at 3405 cm^{-1}, $\nu_{as}(SO_4^{2-})$ at 1132 cm^{-1} and $\delta_{as}(SO_4^{2-})$ at 670 cm^{-1} [31], as observed in Table 3. Gypsum was not directly added but was rather a product of the reaction between alum ($KAl(SO_4)_2$) and calcium carbonate ($CaCO_3$). The reason why W&N chose to create gypsum through a reaction rather than adding it directly is still unclear at the moment. Further experimentation will be performed using gypsum directly in the recipe to understand the role of this reaction.

As may be seen in Table 3, FTIR analysis of all yellow lake pigments shows bands attributed to flavonoids-metal complexes, which is very clear in the infrared spectra of *WL3* and *WL4*, where only alum was added, plus borax in the latter recipe; the role of this ingredient is also still to be investigated. A more thorough analysis of the infrared data of the flavonoids-metal complexes is offered below. Besides identifying gypsum in *WL1* and *WL2* pigments, it was also detected the presence of hydrated alumina in the *WL5* lake pigment, due to its characteristic absorption bands for $\delta(H_2O)$ at 1485 cm^{-1} and the δ(Al-OH) at 852 cm^{-1} [31], as shown in Table 3.

3.4. Infrared Markers of Weld Lake Pigments

Although infrared spectroscopy has rarely been used to characterize flavonoids, several studies have proven its effectiveness in studying flavonoids-metal complexes [12,13]. Machado et al. [32] did DFT calculations of IR and Raman spectroscopies of hydroxyflavones, and their assignments are summarized in Table 4.

As mentioned above, flavonoids-metal complexes are observed in the infrared spectra of *WL3* and *WL4*. Figure 3 compares the two lake pigments and references of luteolin and luteolin 7-*O*-glucoside and shows the similarity between the infrared spectra, namely between *WL4* and luteolin 7-*O*-glucoside. These data are corroborated by the HPLC-DAD analysis, since this recipe has 53.31% of luteolin 7-*O*-glucoside, when compared with the 30.38% of the recipe *WL3*. The presence of a glucoside in position 7-OH shifted the vibrational frequency from 1186 to 1179 cm^{-1}. The fact that both lakes show lower frequencies, at 1178 and 1173 cm^{-1}, corroborates with the HPLC data. The reference of luteolin 3′,7-di-*O*-glucoside will provide more insight into the effect of glucosides in the infrared spectra, and further studies are underway.

Regarding the presence of an organometallic complex, the stretching vibration of C=O of luteolin at 1666 cm^{-1} is shifted to 1632 cm^{-1}. According to Dong, this shift is characteristic of the existence of a complex [12]. It is the co-ordination of carbonyl oxygen with metal ion bonded to 5-OH group of A ring and 4-CO carbonyl group of C ring [12,33,34]. This is also visible in the stretching at 1613 cm^{-1}. Moreover, the OH bending of C^5 shifts from 1509 cm^{-1} to 1484-9 cm^{-1}, probably also due to the metal coordination. Another possible indication of metal complexation in positions OH (C^5) and CO (C^4) is the decrease from 1096 cm^{-1} to 1077-68 cm^{-1} from the stretching of C^3-C^4. In fact, the extraction solution of *WL3* had pH ~9.4, the optimum conditions for the metal chelation in the OH at C^5 and the carbonyl at C^4. The analysis of luteolin, both as aglycone and with glucosides, complexed with Al^{3+} is ongoing.

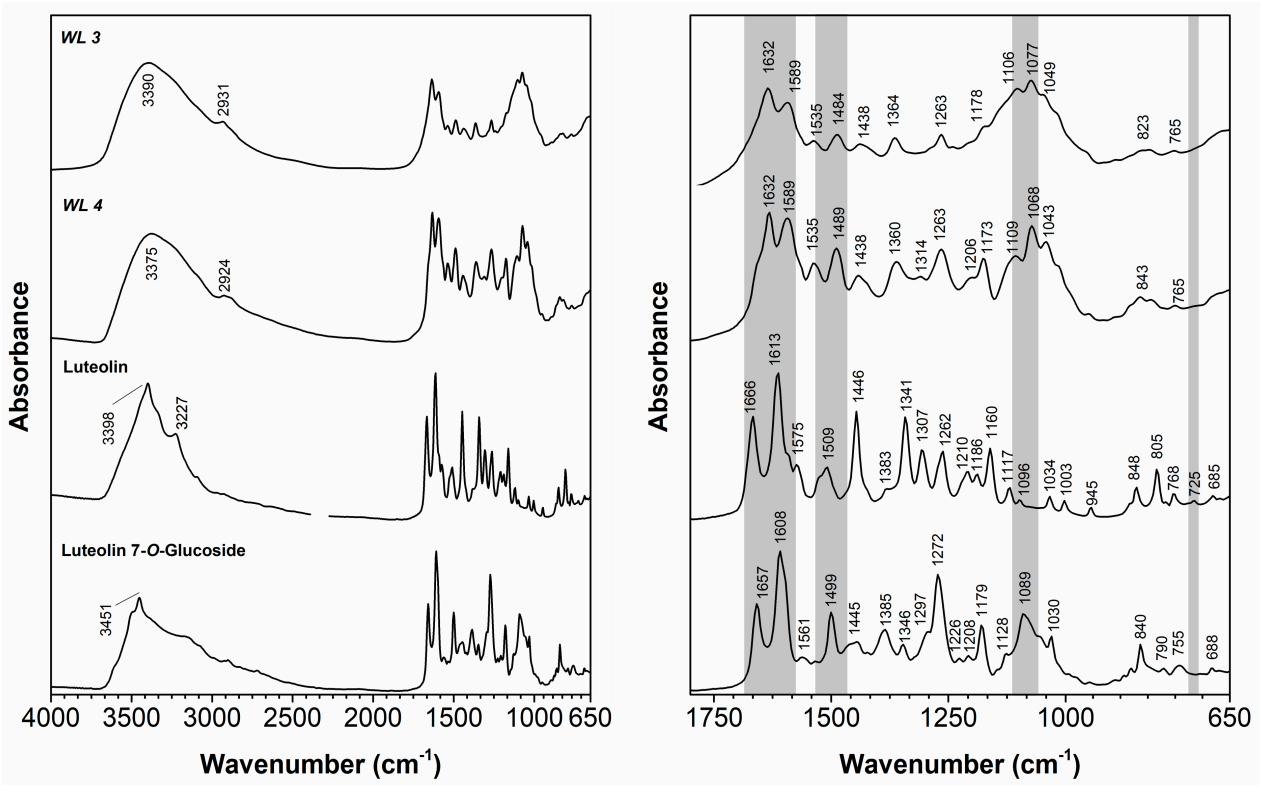


Figure 3. Infrared spectra of weld lake pigments *Yellow Lake. Cool tint.* (*WL3*) and *Weld yellow* (*WL4*), and references of Lut and Lut-7-*O*-glu.

Table 4. Infrared assignments for luteolin, luteolin 7-*O*-glucoside and weld lake pigments *WL3* & *WL4*. Highlighted in grey are the vibrations correlated with the A ring and positions C^5-OH and C^4=O, metal chelating groups.

				Literature [32]	
Lut	**Lut-7-*O*-glu**	**WL3**	**WL4**	**Lut**	**Assignments**
3398	3451	3390	3375	~3400	$\nu(O^{3'}—H)$, $\nu(O^{7}—H)$, $\nu(O^{4'}—H)$
3227	-	-	-		$\nu(O^{5}—H)$
-	-	2931	2924		
1666	1657	1632	1632	1656	$\nu(C=O)$, $\nu(C^2—C^3)$, $\delta(O^3—H)$
1613	1608	1589	1589	1612	$\nu(C=O)$, $\delta(O—H)$, $\delta(O^{4'}—H)$
1575	-	-	-	1575	$\nu(C=O)$, $\delta(O—H)$, $\delta(O—H)$
-	1561	-	-	1561	$\nu(C^2=C^3)$, $\delta(O^5—H)$, $\delta(O^{4'}—H)$, $\delta(O^7—H)$
-	-	1535	1535	1518	$\delta(O^7—H)$, $\delta(O—H)^A$
1509	1499	1484	1489	1507	$\delta(O^5—H)$

Table 4. *Cont.*

Lut	Lut-7-*O*-glu	WL3	WL4	Literature [32]	
				Lut	Assignments
1446	1445			1456	δ(O—H)^{B}
-	-	1438	1438	1439	δ(O—H)^{B}, δ(O^{3}—H)
1383	1385	1364	1360	1367	ν_s(C—O^{1}—C^{2}), δ(O$^{4'}$—H)
1341	1346	-	-	-	n.a.
		-	1314	1313	δ(O—H), ν(C$^{4'}$—O)
1307	-	-	-	1303	ν(C$^{4'}$—O)
-	1297	-	-	1284	ν(C$^{4'}$—O)
1262	1272	1263	1263	1263	δ(C^{2}—H), ν(C^{2}—O^{1}), ν(C—C), δ(O^{5}—H)
-	1226	-	-	-	n.a.
1210	1208	-	1206	1210	δ(O—H)^{A}, ν(C^{2}—O^{1})
1186	1179	1178	1173	1194	δ(C^{6}—H), δ(O^{7}—H)
1160	-	–	-	1162	δ(O—H)^{B}, δ(O^{7}—H)
1117	1128	1106	1109	1120	δ(C^{2}—H), δ(O—H)^{B}
1096	1089	1077	1068	1094	ν_s(C—O^{1}—C^{2}), ν(C—O^{1}), ν(C^{3}—C^{4}), $\phi_{ip}{}^{A,B}$, δ(O—H), δ(O^{7}—H)
1034	1030	1049	1043	1031	ν_s(C—O^{1}—C^{2}), $\phi_{ip}{}^{A,B}$, δ(C^{2}—H)
1003	-	-	-	999	ϕ^{A} + $\phi_{ip}{}^{B}$
945	-	-	-	946	$\phi^{A,B}$, Δ(C^{3}—C^{4}=O), ν(O^{1}—C^{2})
848	840	823	843	839	γ(C^{2}—H)
805	790	-	-		n.a.
768	755	765	765	766	ϕ^{A}
725	-	-	-	728	$\phi_{op}{}^{A}$, Γ(C^{3}—C^{4}=O), γ(O^{5}—H)
685	688	-	-		n.a.

Annotations: ν—stretching, ϕ—aromatic ring normal vibrations, δ—in-plane deformation, γ—out-of-plane deformation, Γ—out-of-plane deformation of skeleton atoms, Δ—in-plane deformation of skeleton atoms, ip—in-plane, op—out-of-plane, *s*—symmetric mode.

4. Conclusions

The W&N 19th century Archive Database has proven, once more, to be an exceptional source of information on 19th-century artists' materials and their commercial preparation, enabling the first study of five W&N manufacturing processes for yellow lake pigments from weld.

This investigation showed that W&N 19th-century methods for preparing weld lake pigments involved extracting the dye in neutral-basic media by adding carbonate compounds ($KHCO_3$ and K_2CO_3) and complexation of flavonoid compounds was always achieved by the addition of Al^{3+}. Five bright yellow lake pigments were obtained and characterized by a multi-analytical approach. Their chromatographic profiles display as main yellows, luteolin 7-*O*-glucoside (Lut-7-*O*-glu) or both Lut-7-*O*-glu plus luteolin 3′,7-*O*-glucoside (Lut-3′,7-*O*-glu). In two of the processes, the presence of gypsum ($CaSO_4 \cdot 2H_2O$) was detected by FTIR, being formed as a by-product of the reaction of alum and $CaCO_3$. This work also offers the first identification of weld lake pigments' characteristic infrared bands: the stretching vibration of C=O at 1632 cm^{-1}, the OH of C^5 bending at c. 1484-9 cm^{-1}, the stretching of C^3-C^4 at 1077-68 cm^{-1}, all clear indications of metal complexation in positions OH (C^5) and CO (C^4) of flavonoid compounds.

The five recipes result in two types of lake pigments: yellows in which a filler, such as gypsum, is present (*WL1* and *WL2*) and yellows in which the lake pigment was found in an aluminate matrix (*WL3* as well as *WL4* and *WL5*). In the first type, the paints' mechanical performance is controlled by the filler [35], and the pigments are more opaque when applied as oil paints. On the other hand, the second type allows the preparation of translucent paints that can be applied as glazes.

The yields obtained experimentally were very similar or better than those of W&N, excluding recipes *WL4* and *WL5*, which were considered experiments. In the future, we intend to investigate variants of the processes and explore the full precipitation of the coloring matter as described by W&N in *WL3*. Moreover, since infrared spectroscopy revealed a powerful technique for the characterization of flavonoids-metal chelation, further work is ongoing with the analysis of other luteolin and apigenin "type-chromophores" complexed with Al^{3+}.

The pigment reconstructions will be fundamental to advancing on degradation studies and supporting analytical methodologies useful for identifying weld lake pigments in artworks, contributing to ensuring effective conservation and authentication procedures.

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