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Spectroscopic insights into the formation of alizarin–aluminium lake pigments under variable synthesis conditions

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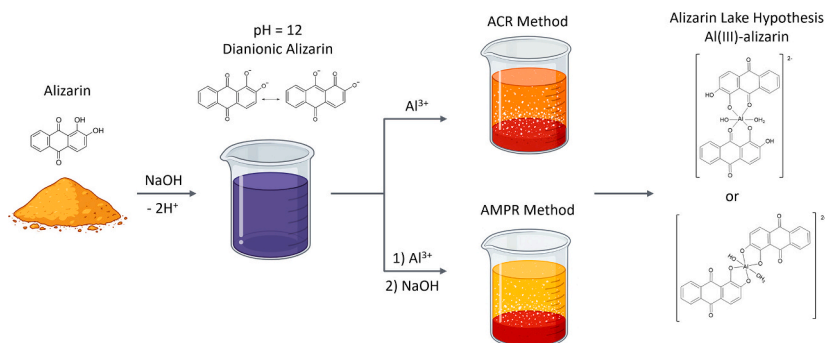
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HIGHLIGHTS

- FTIR was used to study the structure and composition of alizarin lake pigments.
- Reagent addition order affects precipitation behaviour and pigment yield.
- Pigment formation is governed by the interplay of pH and dye-to-metal ratio.
- Co-precipitation of $\text{Al}(\text{OH})_3$ controls lake pigment purity and colour.
- Unprotonated alizarin can remain as an impurity in lake pigments.

GRAPHICAL ABSTRACT



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ABSTRACT

Alizarin (1,2-dihydroxyanthraquinone) forms coloured coordination complexes with metal ions; however, the molecular structure and formation mechanisms of aluminium-based lake pigments remain incompletely defined. In this work, Fourier Transform Infrared (FTIR) spectroscopy was employed to investigate the coordination environment and phase composition of alizarin–aluminium pigments synthesised via two distinct approaches: an alkaline complexation route and an acid-mediated precipitation route. Within each method, pH was systematically varied to evaluate its influence on complex formation and precipitation processes. FTIR spectra display significant modifications in the carbonyl and phenolic stretching regions, reflecting changes in alizarin deprotonation and metal–ligand coordination modes as a function of synthesis pathway. Shifts in $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ bands, together with variations in band profiles, indicate differences in binding geometry and degree of complexation. The synthetic route markedly affects nucleation and precipitation behaviour, altering the relative contributions of coordinated alizarin species and amorphous $\text{Al}(\text{OH})_3$ substrate. Furthermore, pH governs ligand

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deprotonation equilibria and co-precipitation processes, ultimately determining pigment composition and structural homogeneity.

These findings highlight the critical importance of each synthesis stage in directing coordination structure, phase development, and ultimately the properties of the resulting lake pigments.

1. Introduction

Alizarin (1,2-dihydroxyanthraquinone) is the main compound of madder dye, which is extracted from the madder root (*Rubia tinctorum*) and has been used for dyeing textiles for centuries [1–3]. Alizarin is capable of forming complexes with metallic elements, which are exploited in a wide range of fields, including medicine [4,5] the production of dye sensitised solar cells [6,7], the detection of specific compounds [8] or as pigments used in artworks [2]. The latter, historically known as madder or alizarin lakes, are based on complexes made with Al^{3+} ions (Az-Al). They have been used in historical objects since antiquity [9,10], from ancient Egypt [1] to European paintings, and remained part of the artists' palette through the Impressionist and Post-impressionist periods even after the introduction of synthetic alizarin [11–13].

Generally, the preparation of Az-Al complexes takes place in aqueous solutions at alkaline pH, to induce the deprotonation of the hydroxyl groups that act as binding sites for the metal ions, located at C1 and C2 (Fig. 1a). The first deprotonation takes place at the hydroxyl group attached to C2 (2-OH) (Fig. 1b). This preference is explained by the strong stabilisation of the proton attached to C1 (1-OH) through an intramolecular hydrogen bond with the adjacent carbonyl group attached to C9 (9-C=O) [14]. The second deprotonation induces a delocalisation of the added charge, leading to the equilibrium between different tautomers such as the 9,10-keto (Fig. 1c) or the 1,10-keto (Fig. 1d) [14–16]. The pKa of each species has been detailed in previous studies [15,17].

According to publications and the literature, depending on how and at which level alizarin deprotonates, different complexes can be formed [18–24]. Kiel and Heertjes proposed that the complex forms with the 2,10-keto tautomer, resulting in a six-membered chelate ring with a 2:1 ligand-to-metal stoichiometry (Fig. 2a) [18]. Conversely, Wunderlich and Bergerhoff suggested that Al^{3+} preferentially coordinates via the 9,10-keto tautomer to form a five-membered chelate ring (Fig. 2b) [20]. A similar coordination was observed for purpurin- Al^{3+} complexes, where the 4-hydroxy and 10-keto groups remained non-coordinating. More recently, multi-analytical studies, including NMR, have moved beyond these simple 2:1 structures, proposing additional intermolecular interactions that include Al-O-Al linkages and cross-linking via aromatic interactions [21,22]; however, the coordinating sites of the main complexes formed are the ones previously described.

Knowing the precise structure of alizarin complexes is essential for

understanding their reactivity, which is needed to optimise its application in different fields, particularly for their use as lake pigments. However, previous reports do not agree on the type of complex that forms [23,24].

Nonetheless, it should be noted that the alizarin species present during synthesis vary depending on the pH of the solution. Consequently, different pH conditions may be expected to result in variations in the composition of the resulting pigment. Indeed, historical records describe a wide range of synthesis methods, which are likely to influence the nature of the pigment obtained [3,11,25,26]. However, no systematic study has yet investigated the influence of synthesis conditions on alizarin-metal coordination, and this may account for the discrepancies observed in the published data.

In this work, the influence of synthesis conditions on the final composition and solid-state structure of alizarin lake pigments is systematically investigated, with particular emphasis on how the chosen synthetic pathway governs phase development and coordination equilibria. Two chemically distinct preparation protocols were examined (Fig. 3): an alkaline complexation route (ACR) [2], in which Al^{3+} ions are introduced into a pre-alkalised alizarin solution where the ligand is predominantly deprotonated, and an acid-mediated precipitation route (AMPR) [27], in which alizarin and aluminium ions are first combined under acidic conditions, followed by basification to induce precipitation.

These protocols differ fundamentally in the pH environment at which complexation and nucleation occur, thereby altering the sequence of coordination, hydrolysis, and precipitation events. Such differences are expected to leave a distinct chemical “fingerprint” on the resulting solid phases, influencing metal-ligand equilibria, the formation of amorphous aluminium hydroxide, and the overall structural organisation of the lakes. In both approaches, the initial and final pH values were systematically varied to evaluate their impact on phase composition. The resulting pigments were characterised by Fourier Transform Infrared (FTIR) spectroscopy to probe coordination modes and solid-state equilibria.

2. Materials and methods

2.1. Alizarin solutions

First, the changes in the FTIR spectra of alizarin as a function on the deprotonation state were studied. This was done using aqueous solutions

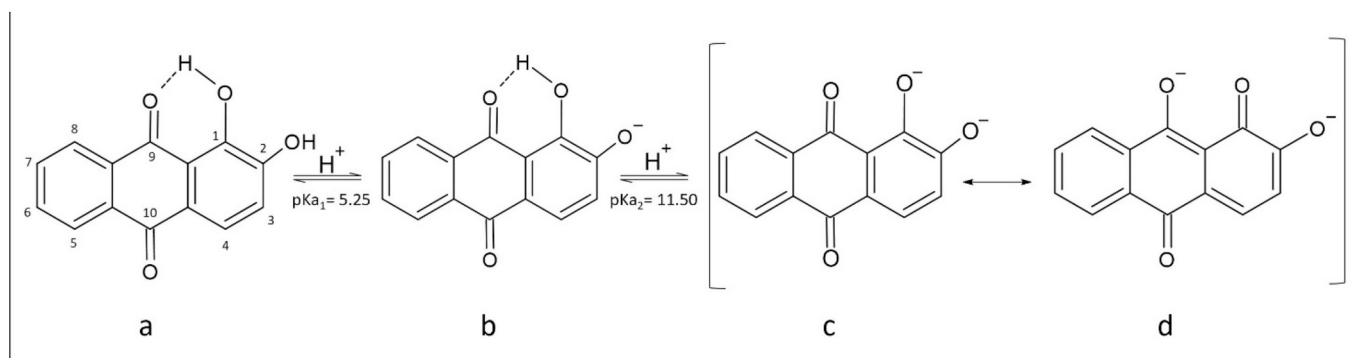


Fig. 1. Deprotonation of alizarin in aqueous solution with increasing pH: (a) neutral form, (b) monoanionic form, (c and d) dianionic forms, showing the equilibrium between the 9,10-keto and the 1,10-keto tautomers. The acidic dissociation constants ($\text{pK}_{\text{a}1}$ and $\text{pK}_{\text{a}2}$) were determined in a DMSO–water mixture (1:1000, v/v) [15].

of alizarin (Sigma-Aldrich, dye content 97%) at increasing pH (5, 7, 10, 11 and 12). These pH values were selected because they lie below and above the pK_a values reported in the literature; although determined in DMSO–water mixtures (1:1000, v/v), they are expected to be comparable in pure water [15]. The pH was adjusted by the addition of variable amounts of a 1 M NaOH (E. Merck, Darmstadt) solution. The pH of the solutions was measured with a calibrated pH meter (CyberScan pH 510 Meter). A few drops of each solution were placed on glass slides, dried at room temperature, and the resulting powders were analysed by FTIR spectroscopy.

2.2. Alizarin lake pigments synthesis

Alizarin lake pigments were synthesised following two protocols originally applied to madder dye. Both procedures were adapted by using alizarin instead of the madder dye to allow clearer observation of the changes in the spectra, AlCl₃·6H₂O (Thermo Fisher GmbH, 99%) in place of alum (KAl(SO₄)₂·12H₂O) to avoid sulphate precipitation [24,28,29], and NaOH instead of potassium carbonate (K₂CO₃) to prevent carbonate formation. A 0.005 M alizarin solution was prepared by dissolving the solid dye in deionised water and adjusting the pH by adding 1 M NaOH under magnetic stirring to ensure the formation of the deprotonated species. For each synthesis, 40 mL of alizarin solution was used. In both approaches, the solutions were filtered, the precipitates washed and then dried at room temperature for 4–5 days. Finally, the lakes were weighed on the filters to determine their yields (Tables 1 and 2) and analysed by FTIR spectroscopy.

2.2.1. Alkaline complexation route

In ACR method, the aluminium solution is added gradually to the basified alizarin solution. Two sets of experiments were carried out. The first set investigated the effect of aluminium ratio at a constant initial pH (pH_i = 12). Aluminium salt was added in small increments to the alizarin solution (pH_i = 12), until reaching a specific Az/Al³⁺ molar ratio. The molar ratio was calculated as:

$$\text{Az} / \text{Al}^{3+} = \frac{n_{\text{Az}}}{n_{\text{Al}^{3+}}}$$

The second set of experiments explored the effect of pH_i at constant Az/Al³⁺ molar ratio. The syntheses were performed at pH_i = 7, 10, 11, and 12. In this configuration, the resulting pH_f depends on both pH_i and the amount of aluminium added and therefore cannot be independently controlled.

2.2.2. Acid-mediated precipitation route

In AMPR method, the aluminium solution (0.5 M) is first mixed with the alizarin solution, forming an acidic mixture (pH ~3.5), after which pigment precipitation is induced by gradual basification. Syntheses were carried out at different Az/Al³⁺ molar ratios (0.005, 0.02, and 0.2). After mixing the dye and aluminium solutions and stirring for 10 min, NaOH was added dropwise under continuous agitation until reaching pH_f values of 5.5, 7, or 10, to evaluate the effect of the final pH on the lake pigment. This configuration enables the controlled adjustment of both stoichiometry and pH_f.

2.3. Fourier transform infrared (FTIR) spectroscopy

FTIR analysis was conducted using a Bruker Alpha II spectrometer equipped with a DTGS detector. Measurements were performed in transmission mode with KBr (Sigma Aldrich, FTIR grade) pellets. A total of 128 scans were accumulated in each sample, using a resolution of 4 cm⁻¹ and a wavenumber range between 4000 and 400 cm⁻¹. To ensure the reproducibility of the results, three spectra were acquired for each sample. Automatic baseline correction and normalisation were applied. FTIR spectra were plotted using OriginPro 8.5 software.

3. Results and discussion

3.1. The FTIR fingerprint of alizarin at different pHs

Given the well-known pH-dependent speciation of alizarin solid equilibria [14,16,30], it is hypothesised that the composition of the resulting alizarin lake pigments depends on the pH conditions. Therefore, the study of alizarin's spectral changes as a function of pH will serve as the starting point of this work.

Fig. 4 presents the spectra of alizarin in neutral form and its deprotonation products at different pH values. The spectrum of neutral alizarin (AH₂) is characterised by two distinct absorption bands in the carbonyl region, at 1661 and 1634 cm⁻¹, corresponding to the 10-C=O and 9-C=O stretching vibrations, respectively [15,24]. Other characteristic spectral features are observed at 1588 and 1454 cm⁻¹, ascribed mainly to the aromatic C=C stretching vibrations of the benzene ring [15,31].

At pH 5, the spectrum closely resembles that of neutral alizarin, suggesting that the main form is the fully protonated alizarin (AH₂), as this pH is below or close to the first dissociation constant (Fig. 1a). At pH 7, the FTIR spectrum exhibits pronounced changes relative to the

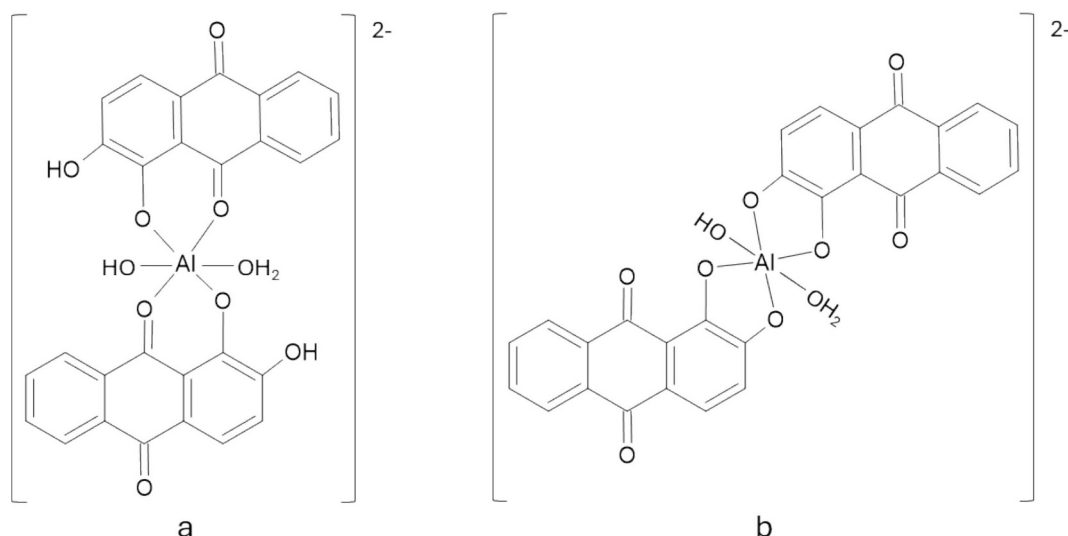


Fig. 2. Reported structures of the Az-Al complex: (a) Kiel and Heertjes' model; (b) Wunderlich and Bergerhoff's model.

neutral form, suggesting the start of the first deprotonation (Fig. 1b). The main variation is the decrease in intensity of the 1661 cm^{-1} band. According to previous reports, this is explained by the delocalisation of the charge across the molecules, leading to the formation of tautomers. This first deprotonation preferentially occurs at the 2-OH position because the protons at C1 is strongly stabilised by the intramolecular hydrogen bond with the C9 [24]. Moreover, new bands appear at 1557 , 1489 , 1382 , and 1362 cm^{-1} , which can be associated with modifications in the resonance of the aromatic system due to the added charge. Consequently, these spectral changes suggest that the first deprotonation has begun. However, since pH 7 is close to the first dissociation constant of alizarin ($\text{pK}_{\text{a}1} = 5.25$), both the neutral (AH_2) and monoanionic (AH^-) forms (Fig. 1b) are expected to coexist at this pH, in agreement with speciation diagrams [17].

The spectrum obtained at pH 10 follows this established trend, showing a more pronounced decrease in the 1661 cm^{-1} band, accompanied by an increased intensity of the 1557 , 1489 , 1382 , and 1362 cm^{-1} bands. Together, these spectral changes suggest a clear progression towards deprotonation. Under this condition, the monoanionic species (AH^-) (Fig. 1b) is expected to be the predominant form, as the pH lies well above the dissociation constant ($\text{pK}_{\text{a}1} = 5.25$) but remains below the second dissociation constant of alizarin ($\text{pK}_{\text{a}2} = 11.50$) [15].

At pH 12, the second deprotonation occurs ($\text{pK}_{\text{a}2} = 11.50$) and a new band appears at 1735 cm^{-1} , likely associated with the carbonyl group, next to the shift of the carbonyl groups downward to 1627 cm^{-1} . At such high pH values, all -OH groups are deprotonated, causing an increase in the charge and its delocalisation across the molecules, which may cause the $\text{C}=\text{O}$ band to shift to higher wavenumbers.

3.2. Influence of synthesis conditions on the composition of alizarin lake pigments

Before focusing on the two specific methods, it is essential to characterise the independent contribution of the Al salts to the pigment's composition across different pH conditions. Since alizarin lake pigments are essentially organic-inorganic hybrids, the structural nature of the Al hydroxides—formed via the precipitation of Al^{3+} ions—is as fundamental to the pigment's identity as the dye-metal complex itself. To isolate these inorganic effects, aqueous solutions containing only the aluminium precursor were processed at different pH levels, allowing the clear differentiation of Al-based vibrational bands from those of the alizarin complexes. All resulting precipitates are white, and their spectra are compared in Fig. S1. Samples obtained at pH 4, 5.5, and 7 show similar features, consistent with amorphous hydrated alumina, evidenced by broad bands at ~ 964 (Al-O-Al stretching vibration) and 570 cm^{-1} (octahedral coordination band) [32]. Another diagnostic feature is the band at 1640 cm^{-1} , which is attributed to the bending vibration of

Table 1

Synthesis conditions, mass, digital pictures and CIE $L^*a^*b^*$ parameters (see Supplementary Materials Section S2 for instrumental details) of alizarin lakes prepared using the ACR method.

Name	Az/ Al^{3+}	pH _i	pH _f	Mass (mg)	Picture	CIE parameters
Az_ACR_1	4	12	10	†		††
Az_ACR_2	1.3	12	7	20.3		$L^*: 11.18$ $a^*: 20.52$ $b^*: 6.81$
Az_ACR_3	1	12	5.5	41.8		$L^*: 24.66$ $a^*: 39.12$ $b^*: 21.37$
Az_ACR_4	1	7	3.5	6.3		$L^*: 49.65$ $a^*: 48.88$ $b^*: 32.35$
Az_ACR_5	1	10	3.9	13.9		$L^*: 44.73$ $a^*: 52.46$ $b^*: 25.82$
Az_ACR_6	1	11	3.9	27.6		$L^*: 45.63$ $a^*: 54.29$ $b^*: 27.16$

† No precipitate had formed, and the mass of the filters were essentially unchanged.

†† CIE $L^*a^*b^*$ values were not determined.

coordinated water [25]. Above pH 10, the bands observed in the $1650\text{--}1400\text{ cm}^{-1}$ region could be attributed to the presence of amorphous aluminium products [33]. At pH 11 and 12, three distinct bands at 3657 , 3549 , and 3467 cm^{-1} become visible, along with the appearance of peaks at 1020 and 775 cm^{-1} , which are typical of bayerite [34,35]. These characteristic bands will be commented in the following paragraphs to emphasise the differences between the two synthetic paths.

3.2.1. ACR method

Fig. 5 compares the FTIR spectra of alizarin and its deprotonated form at pH 10 with those of the lake pigments synthesised via the ACR method. Fig. 5a shows the differences as a function of the molar ratio while keeping the pH_i constant (pH_i = 12). At the highest molar ratio

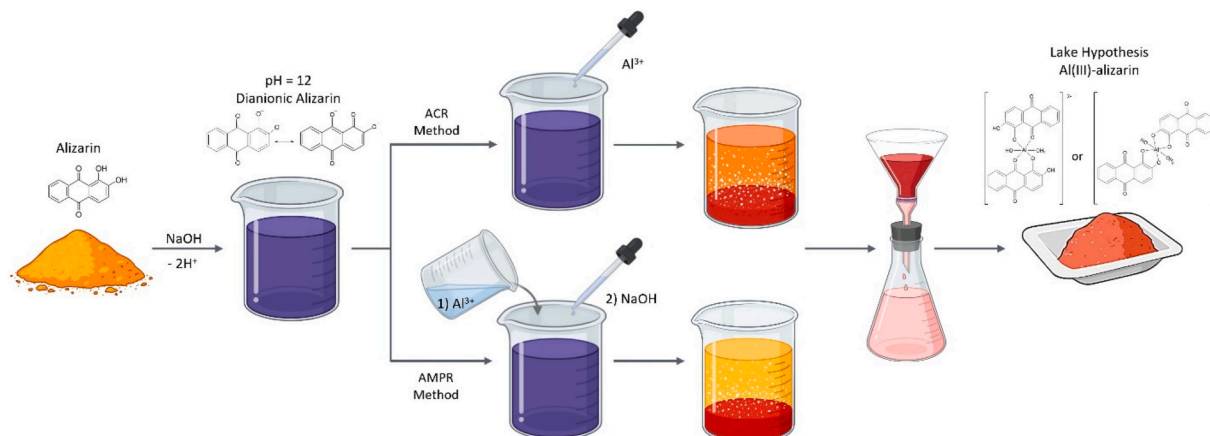


Fig. 3. Schematic representation of the synthesis of lake pigments using the two different methods: the ACR method and the AMPR method.

Table 2

Synthesis conditions, mass, digital pictures and CIE L*a*b* parameters (see Supplementary Materials Section S2 for instrumental details) of alizarin lakes prepared using the AMPR method.

Name	Az/ Al ³⁺	pH _i	pH _f	Mass (mg)	Picture	CIE parameters
Az_AMPR_1	0.2	12	5.5	188.8		L*: 14.52 a*: 24.22 b*: 12.59
Az_AMPR_2	0.2	12	7	181.6		L*: 15.18 a*: 27.52 b*: 7.84
Az_AMPR_3	0.2	12	10	156.0		L*: 11.89 a*: 22.41 b*: -11.17
Az_AMPR_4	0.02	12	5.5	1586.4		L*: 30.35 a*: 38.53 b*: 24.99
Az_AMPR_5	0.02	12	7	1532.9		L*: 28.05 a*: 37.63 b*: 26.33
Az_AMPR_6	0.02	12	10	1493.0		L*: 27.19 a*: 30.55 b*: 15.49
Az_AMPR_7	0.005	12	5.5	6681.6		L*: 48.26 a*: 51.28 b*: 31.55
Az_AMPR_8	0.005	12	7	6856.5		L*: 47.53 a*: 42.91 b*: 27.52
Az_AMPR_9	0.005	12	10	6053.4		L*: 34.82 a*: 48.92 b*: 23.88

(Az/Al³⁺ = 4), the pH_f is 10; thus, under these conditions, alizarin is already deprotonated prior to Al³⁺ addition and remains in its deprotonated form during complexation. Indeed, the spectra show a single band at 1640 cm⁻¹, associated with the coordination of alizarin to the Al³⁺.

It is well established that coordination of alizarin to a metal centre results in only one carbonyl stretching band within the region where the two C=O groups (typically at 1661 and 1633 cm⁻¹) are observed in neutral alizarin [22–24]. This spectral change indicates that the carbonyl groups have either become equivalent through electronic resonance or that the 9-C=O vibration has shifted significantly as a consequence of the direct coordination [24]. Another notable change is the appearance of a new band at 1516 cm⁻¹, which is commonly reported in the literature as a diagnostic feature of complex formation [23,24]. According to previous studies, these bands are consistent with the coordination of the dye to the metal via the 9-C=O and the 1-OH groups, the same coordinating sites as in the Kiel and Heertjies' model (Fig. 2a) [36]. This band is, in fact, commonly associated with acetylacetonate-like complexes, suggesting that the dye is coordinated to aluminium through the 9-C=O and adjacent phenolate groups [24].

This protocol results in only negligible amount of dark precipitates (Table 1). This is most likely due to aluminium being strongly limiting relative to alizarin, which leaves excess deprotonated alizarin in solution and restricts the extent of complex formation.

Noticeable changes can be observed when the molar ratio of Az/Al³⁺

decreases to 1.3 and 1. First, the larger amount of Al salt added causes a decrease in pH_f to 7 and 5.5, respectively. This is explained by the equilibrium of Al³⁺ ions at different pH values, which undergo rapid hydrolytic reactions to form soluble species and amorphous solids as the pH shifts [37]. Due to the lower pH_f, it is expected that there will be increasing amounts of protonated neutral alizarin mixed with the alizarin complex. This is not always evident from the spectra since the bands from alizarin are often overlapped with the ones from the complex; however, a broadening of the band centred around 1460 cm⁻¹ can be observed, which would correspond to the increase of the band at 1454 cm⁻¹ from protonated alizarin. Nevertheless, the supernatant remained red (Fig. S2), suggesting that part of the alizarin is still in solution and, hence, remains deprotonated. In these spectra, the diagnostic band associated with complexed alizarin (metal dye chelate) is observed at 1530 cm⁻¹, together with a broadening of the band at 1635 cm⁻¹ [23,24] respect to the one observed in the spectrum at pH_f 10. This broadening may arise from the overlap with the bending vibration of coordinated water in Al-based products (see Fig. S1 for comparison) [11,23]. Further evidence of the presence of an inorganic matrix is provided by the broad features at ≈900 cm⁻¹ (Al-O-Al stretching vibration) and ≈500 cm⁻¹ (octahedral coordination band) (Fig. S1) [11,38]. As indicated in Table 1 and observed in Fig. S2, the yields of the precipitate obtained at pH_f 7 and 5.5 are higher than that obtained at pH_f 10, probably due to the increasing amount of Al within the solution providing more substrate for the precipitation.

Since the highest precipitate yield was obtained at Az/Al³⁺ = 1, this ratio was selected to investigate the influence of pH_i on the formation of the complex, keeping the molar ratio of Az/Al³⁺ constant (Fig. 5b).

The FTIR spectrum of the precipitate obtained at pH_i = 7 (pH_f = 3.5) is dominated by the characteristic spectral features of neutral alizarin, most notably due to the presence of the two distinct carbonyl bands at 1661 and 1632 cm⁻¹. This is consistent with the results shown in Fig. 4, which indicate that at pH_i 7 alizarin is predominantly protonated. The addition of the Al solution further decreases the pH_f to 3.5, and consequently, the proportion of alizarin able to coordinate with the metal is expected to be extremely low. The presence of Al-based products can be ascribed to the minor absorption at about 600 cm⁻¹ (see Fig. S1 for comparison).

Furthermore, the orange-coloured filtrate and the bright red precipitate surrounded by an orange halo (Fig. S3) suggest the presence of residual, non-complexed alizarin, most likely in its protonated form. Collectively, these observations may support the FTIR interpretation, indicating that the synthesis produces a heterogeneous product comprising unreacted alizarin together with a precipitate predominantly composed of aluminium by-products and only a minor fraction of complexed alizarin.

The spectrum of the precipitate obtained at pH_i 10 (pH_f = 3.9) retains several characteristic alizarin features. Two carbonyl bands are still observed at 1662 and 1629 cm⁻¹, however, the intensity of the former decreases, suggesting a higher proportion of deprotonated alizarin compared to pH_i = 7. The interpretation could be further supported by the increased intensity of the band at 1526 cm⁻¹, which is absent in neutral alizarin and is widely recognised as a coordination complexation of Al³⁺ with the dye [23,24]. At the same time, the markers from the Al-based products at ≈850 and 600 cm⁻¹, (see Fig. S1 for comparison) may indicate the presence of these compounds. The increased contribution of these aluminium-containing phases may occur for the higher final yield, as reported and Fig. S3. This latter also shows the presence of an orange filtrate and bright red precipitate with an orange halo possibly due to the presence of unreacted, protonated alizarin.

At higher pH_i, an increase in features associated with the formation of the alizarin complex is observed. These include the appearance of a single band in the carbonyl stretching region and the merging of the two bands in the 1290–1250 cm⁻¹ region. This behaviour is often associated with the coordination of aluminium with the phenolic oxygen atom at C1, which may indicate the formation of the alizarin complex [23].

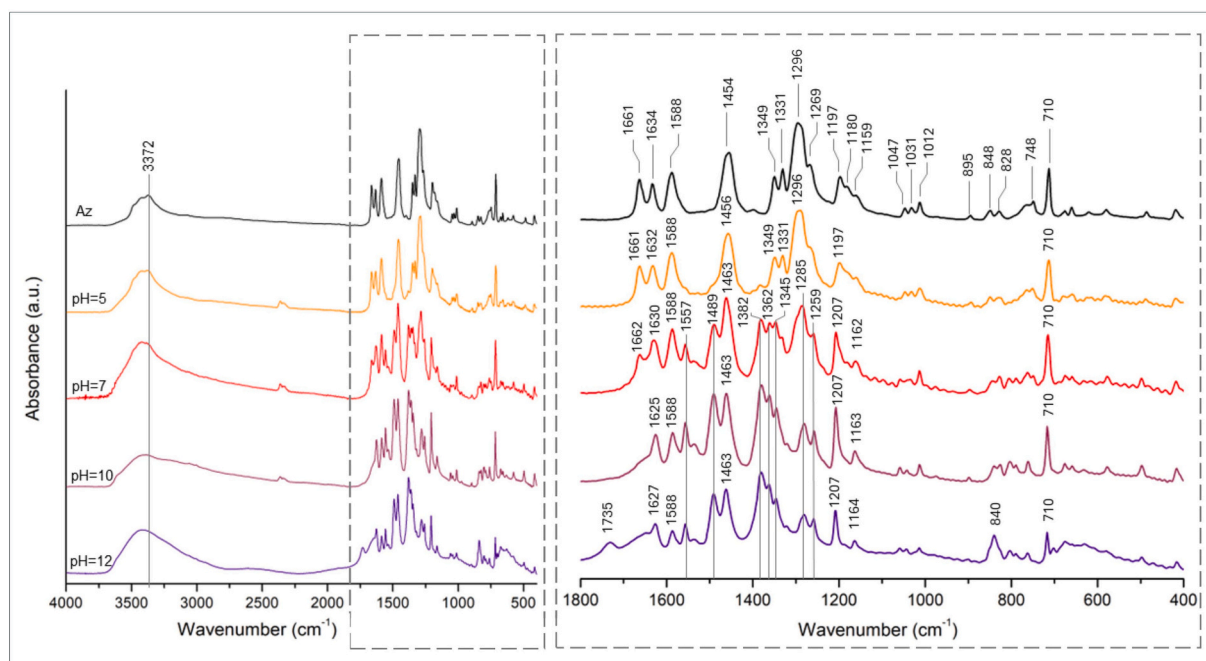


Fig. 4. FTIR spectra of alizarin and the products of its ionisation at pH 5, 7, 10, and 12. The right-hand panel shows a magnified view of the 1800–400 cm^{-1} spectral region.

Concurrently, an increase in markers related to the Al-based products is also evident. The great contribution of these inorganic phases is consistent with the higher yields (Table 1 and Fig. S3). Accordingly, the resulting precipitate can be described as a heterogeneous material containing a higher proportion of Al-by product mixed with alizarin complex. Compared with the synthesis performed at lower pH_i , the filtrate was more transparent, and the precipitate appear darker and more homogeneous, with no visible orange residues (Fig. S3).

Overall, FTIR results suggest that, under these conditions, alizarin-aluminium complexes are formed. Further evidence of the complexation was provided by the UV–Vis study (Fig. S7, Section S2). While the spectrum of neutral alizarin is characterised by an absorption maximum at 430 nm, the precipitates obtained at pH_f 5.5 and 7 exhibit a substantial bathochromic shift to 525 nm. This shift indicates the transition of the ligand from its neutral form to a coordinated, mono-ionised state [28,39]. As the synthesis environment becomes more basic (pH_f 10), the main absorption band shifts further to 540 nm, consistent with the deprotonation of the C2 hydroxyl group [40]. Consequently, pH_f acts as a primary factor for the final electronic state.

Furthermore, the results may indicate that the synthesis conditions significantly influence the composition of the resulting product when using the ACR method. Specifically, lower Az/Al^{3+} molar ratios lead to higher yields, associated with a greater proportion of Al-based compounds. Conversely, variations in the initial pH (pH_i) result in different types of impurities, namely protonated alizarin or Al-based products. As also reported in previous research and case studies, lake pigments are generally described as hybrid materials composed of a dye complex and an aluminium oxide substrate [25].

3.2.2. AMPR method

Fig. 6 compares the FTIR spectra of alizarin and its deprotonated form at pH 10 with those of the lake pigments synthesised via the AMPR procedure. Fig. 6a shows the differences as a function of the molar ratio while keeping the pH_f constant ($\text{pH}_f = 5.5$). According to the results obtained from Fig. 4, at pH = 5.5 alizarin is mainly protonated, hence the formation of the complex is expected to be limited.

At $\text{Az}/\text{Al}^{3+} = 0.2$, the spectrum shows a band at 1527 cm^{-1} , together with a single band in the carbonyl region at 1638 cm^{-1} . These bands are

diagnostic features of the complex formation [23,24], although they may also be assigned to the Al-based products [11,23]. The presence of Al-based products is further supported by the broad features at ≈ 970 and 570 cm^{-1} (see Fig. S1 for comparison). In addition, the presence of bands common to alizarin and the complex can also be observed (1590, 1469, 1287, and 1269 cm^{-1}). This may indicate that the precipitate is a hybrid of the dye complex and the aluminium hydroxide substrate.

As the ratio decreases to $\text{Az}/\text{Al}^{3+} = 0.02$, the spectral features of the Al-based products become progressively more intense, reflecting the greater amount of Al-based products formed. Despite this, bands associated with the alizarin complex can still be detected at 1527, 1471, 1360, and 1290 cm^{-1} suggesting the coexistence of complexed alizarin mixed and aluminium substrate.

At a ratio $\text{Az}/\text{Al}^{3+} = 0.005$, the intensity of the markers of the Al-based products increased further, while those attributed to the dye complex decreased in intensity but are still present. The increasing amount of these Al-based products agrees with the colour of the filtered pigment, which is lighter at lower Az/Al^{3+} ratios (Table 2). It is worth noting that the filtered supernatants of all lake pigments synthesised following the AMPR method, regardless of the Az/Al^{3+} molar ratio and pH_f , were colourless (Fig. S4 and S5).

The influence of pH_f on lake synthesis was also investigated. Fig. 6b shows lake pigments prepared at pH_f 5.5, 7, and 10 at a constant Az/Al^{3+} ratio of 0.2, while Fig. S6 presents spectra of lake pigments synthesised at the same pH_f values but with lower Az/Al^{3+} ratios (0.02 and 0.005).

The spectra displayed in Fig. 6b are very similar regardless of the pH_f values and are comparable to those in Fig. 6a. FTIR spectra indicated that the overall structure of the dye complex remained consistent across pH values, with only minor variations in band intensity and position. Increasing pH_f primarily affected the band at approximately 970 and 570 cm^{-1} . These bands are associated with the amorphous aluminium substrate, influencing the final precipitate's colour and yield. In particular, lake pigments synthesised under neutral pH exhibited lighter red hues, whereas those obtained under alkali conditions appeared darker (Table 2). Fig. S6 may indicate that under all tested conditions, the AMPR method leads to formation of dye complexes mixed with variable amount of amorphous aluminium substrate. The formation of dye complexes is not clearly evident in the FTIR spectra due to the presence

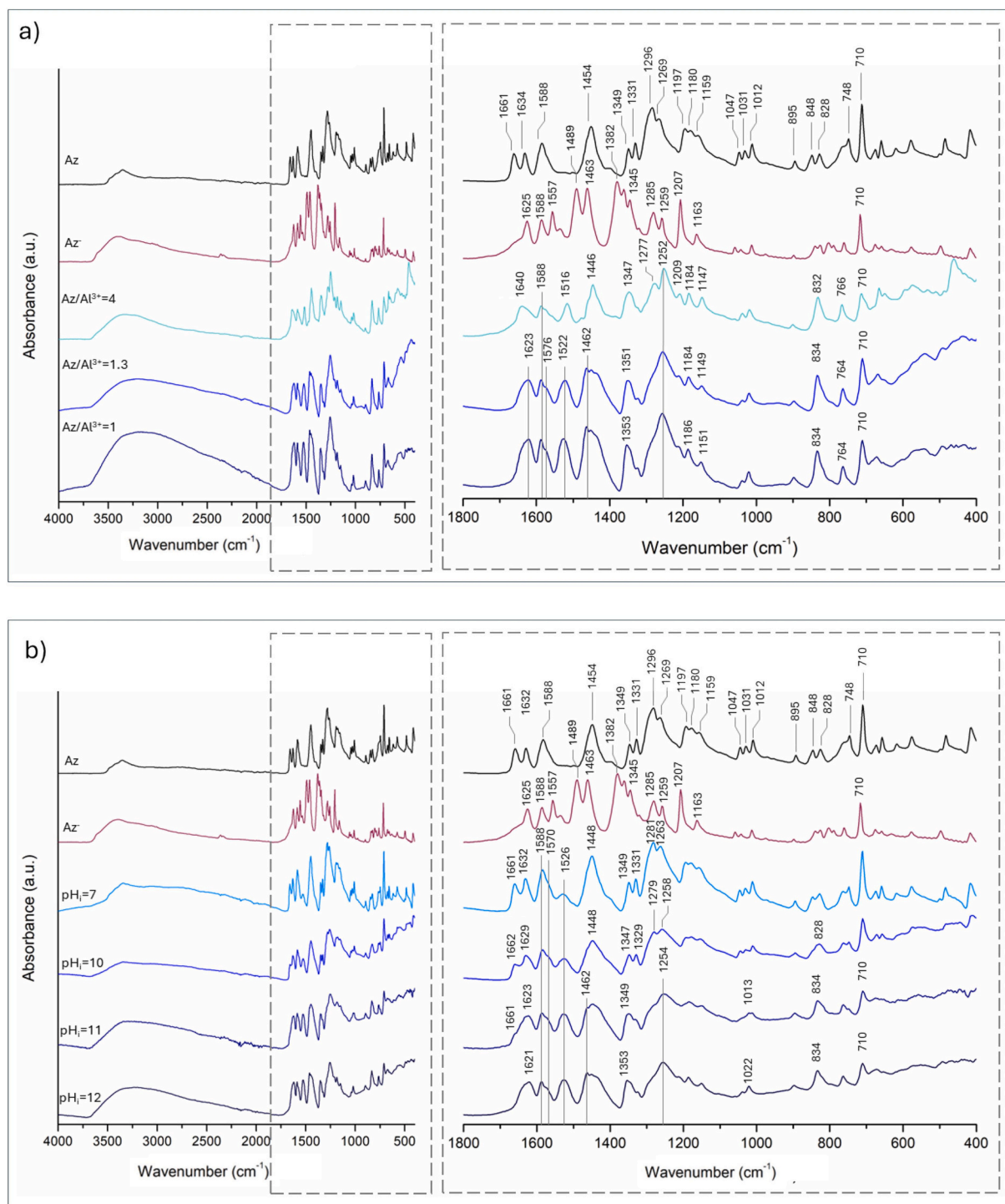


Fig. 5. FTIR spectra of the lakes obtained using the ACR method compared with pure alizarin (Az) and alizarin at pH 10 (Az^-). a) Lakes obtained at different Az/Al^{3+} molar ratios while keeping the pH_i constant ($pH_i = 12$). b) Lakes synthesised at different pH_i values while keeping the Az/Al^{3+} molar ratio constant ($Az/Al^{3+} = 1$).

of the intense bands of the Al-by product but it can be further corroborated by UV-Vis spectra (Fig. S8, Section S2). The lake pigment synthesised at pH_i 5.5 exhibits a shift from 430 to 460 nm compared to alizarin, while the precipitate obtained at pH_i 7 exhibits a substantial bathochromic shift to 520 nm. This latter corresponds to the transition of the ligand from its neutral form to a coordinated mono-ionised state [28,39]. At pH_i 10, the main absorption band shifts further to 535 nm, reflecting the deprotonation of the C2 hydroxyl group [40].

The AMPR method yields to a heterogeneous material composed

predominantly of aluminium hydroxide-based products containing a limited amount of Al-alizarin complexes together with residual non-complexed alizarin. It is worth noting that a high content of Al-salts may adversely affect the stability of the paint layer, as Al can react with carboxylic acids in drying oils to form Al soaps. These soaps are known to cause craquelure and surface protrusions, with significant implications for the long-term conservation of artworks [41,42]. Overall, these observations indicate that complex formation occurs but is less extensive than in the corresponding ACR syntheses.

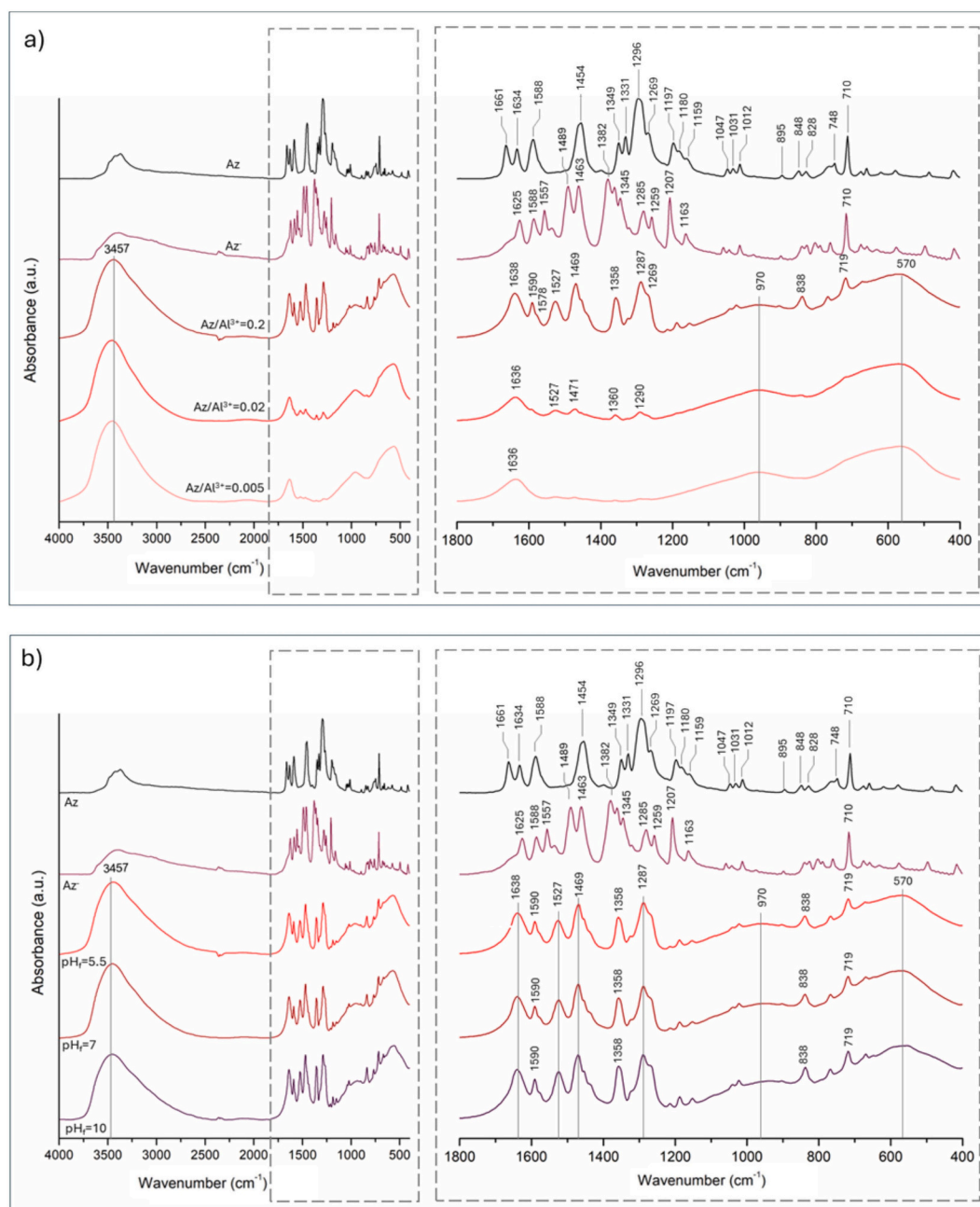


Fig. 6. FTIR spectra of the lakes obtained using the AMPR method, compared with pure alizarin (Az) and alizarin at pH = 10 (Az^-). a) Lakes obtained at different Az/ Al^{3+} molar ratios at a constant $\text{pH}_f = 5.5$. b) Comparison of lakes synthesised at different pH_f (5.5, 7, and 10) while keeping the Az/ Al^{3+} molar ratio constant (Az/ $\text{Al}^{3+} = 0.2$).

4. Conclusion

This study elucidated how critical synthesis parameters, specifically the order of reagent addition, pH, and dye-to-metal molar ratio, affect the formation, composition, and colour of alizarin-Al lake pigments. By comparing two synthetic paths, the results demonstrated that both the dye-to-metal ratio and pH are decisive factors in determining pigment yield, purity, and final hue.

The method involving gradual neutralisation of the dye-metal solution (AMPR Method) generally provided higher pigment yields and superior control of final pH (pH_f). In this approach, pH_f served a dual purpose: it governed the deprotonation state of alizarin, thereby enabling a wider colour variation, and it regulated the precipitation of $\text{Al}(\text{OH})_3$. Furthermore, the possibility of introducing Al in excess closely

mirrors historical practice, aligning with the efficient, large-scale methods used by Winsor & Newton to achieve both high yield and broad colour variation.

Conversely, while the ACR Method theoretically offers finer control over alizarin- Al^{3+} interactions, it proved more challenging to manage in practice. Excess Al tended to lower the pH_f , reverting alizarin to its protonated state, which limited complex formation and partially redissolved the $\text{Al}(\text{OH})_3$ matrix, resulting in lower yields and reduced colour variation. These findings underscore the inherent challenges of replicating historical pigment manufacture at a laboratory scale, where precipitation dynamics may deviate from large-scale processes.

Finally, the challenges associated with reproducing historical pigment manufacture at the laboratory scale should not be forgotten. A simplification of historical recipes was performed to allow controlled

study of alizarin complex formation. Syntheses were carried out using pure alizarin rather than madder root, which contains other hydroxyanthraquinones alongside alizarin. Alum ($KAl(SO_4)_2 \cdot 12H_2O$), reported in historical recipes, was intentionally replaced with $AlCl_3 \cdot 6H_2O$ to avoid sulphate precipitation. Similarly, potassium carbonate (K_2CO_3), commonly used as an alkali reagent in historical procedures, was replaced by NaOH to prevent carbonate precipitates that could obscure FTIR bands associated with the complex. While these substitutions were necessary to isolate and characterise the alizarin-Al coordination chemistry under controlled conditions, they represent a simplification of the historical system. Therefore, the results presented here should be regarded as a model system for understanding the fundamental chemistry of alizarin-aluminium interactions, rather than a direct reproduction of historical lake pigments. Future research should therefore focus on synthesising lake pigments under conditions that more closely replicate traditional practices, to better understand natural colour variation, co-precipitation processes, and the long-term stability of madder lake pigments.

CRediT authorship contribution statement

Beatrice Menegaldo: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Giulia Moro:** Writing – review & editing, Supervision, Data curation, Conceptualization. **Karolien De Wael:** Writing – review & editing, Supervision, Resources, Conceptualization. **Ligia Maria Moretto:** Writing – review & editing, Supervision, Resources, Conceptualization. **Balliana Eleonora:** Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation, Supervision, Conceptualization. **Victoria Beltran:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Supervision, Conceptualization.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.saa.2026.128486>.

Data availability

Data will be made available on request.

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