

Characterization of Al(III) complexes with hematein in artistic alum logwood inks

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The complexes between Al(III) and hematein, the main coloring matter in alum logwood inks, were characterized by Raman and ²⁷Al NMR (nuclear magnetic resonance) spectroscopies. Raman spectra of the crystallized complexes and of the compounds applied on a paper substrate are presented and assigned based on published data for the parent compounds. These Raman spectra show that the coordination of the hematein to the Al(III) ions takes place in both cases through the carbonyl and hydroxyl groups in the molecule, and that the aromatic rings are also involved in the interaction. The Raman spectra of the pure hematein–Al(III) complexes were found to be consistent with those recorded for a logwood ink prepared following a late 19th century recipe, using logwood chips instead of pure hematein, and applied on a paper substrate. These spectra can be used as references for the noninvasive identification of the compounds in works of art. ²⁷Al solid-state NMR showed that the coordination of the Al(III) atoms in the crystallized powder is predominantly octahedral, while when applied on a paper substrate the colorant is present mainly as a tetrahedral complex, with an octahedral coordination also present in a smaller proportion. The fact that the predominant coordinations for the complexes in the crystallized material and for the ones present on the paper substrate are different is relevant for the study of the lightfastness and thermal stability of works of art bearing these media. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: logwood; hematein; ink; Raman spectroscopy; NMR

Introduction

Logwood inks are prepared basically by boiling heartwood chips from the tree *Haematoxylon campechianum*, a species indigenous to Mexico, Central America, and the West Indies, mixing the decoction with a variety of inorganic salts such as AlK(SO₄)₂·12H₂O or other alums, FeSO₄·7H₂O, Fe(NO₃)₂, CuSO₄·5H₂O, or K₂CrO₄, and adding a solution of dextrine or a gum as binding medium.^[1–3]

Even though it is known that the dyestuff from the logwood tree was already used by the Maya in pre-Columbian times for dyeing textiles and body painting, and its value as a dye for textiles was later discovered by the Europeans in the 16th century,^[4] it is still uncertain when the first logwood ink formulations were developed. The presence of a logwood ink has been reported on an 18th century manuscript^[5] and, in manuals from second half of the 18th century, some recipes call for the addition of logwood extract to improve the coloring properties of iron gall inks^[2] that had been, for more than a thousand years, the material of choice for writing, along with carbon-based black inks. Iron gall inks do not assume their full color intensity when freshly applied, and depending on the relative concentrations of the basic ingredients, gallotannic or gallic acids and an iron salt, usually FeSO₄·7H₂O,^[6,7] it may take several hours, or even days until they became a deep brown or bluish black. This was an important shortcoming of iron gall inks; therefore colorants, such as logwood and indigo, were recommended in order to increase their chromatic intensity.^[2] But rather than just improving the properties of iron gall inks, logwood inks found a place of their own among the artists' materials and writing inks. In a study of a group of drawings by Van Gogh, it was discovered that he did not use a 'traditional' iron gall ink as initially suspected based in the visual appearance of these works of art, but rather relatively new formulations of logwood.^[8,9]

The coloring matter of logwood in its native state is mainly in the form of the colorless compound hematoxilin (Htx, Fig. 1), which rapidly oxidizes to the red hematein (Hm, Fig. 1) when exposed to oxygen.^[10,11] The crude logwood extract has been reported to contain, in addition to the main colorant, small amounts of a derivative of brazilin, and rather larger quantities of five other, still unidentified, colorants, and large amounts of tannins.^[4] Different inorganic salts are added to the logwood extract solutions to impart them certain hues. When combined with alum salts, the deep red Hm solution changes to a deep violet-black; when FeSO₄·7H₂O is used it acquires a greenish shade that gradually changes to brownish-black or black upon drying; the hue is blacker when CuSO₄·5H₂O is used instead of an iron salt; and K₂CrO₄ is

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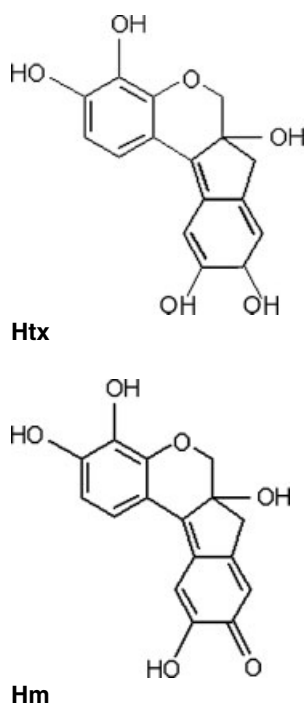


Figure 1. Structural formulae for hematoxylin (Htx) and hematein (Hm).

reported to impart a black color.^[2] These hues may be modified by changing the proportions of the ingredients mentioned above, or by adding others, such as acids and/or other metal salts. For example, a red ink can be obtained by mixing a solution of the logwood extract with alum, copper acetate, dextrine, and small amounts of H_2SO_4 .^[1,2]

The complexes that Hm forms with Al(III) in solution under different conditions have been characterized by UV-vis spectroscopy regarding their properties as stains for use in histology and cytology.^[11,12] Surface-enhanced Raman scattering (SERS) spectra of Htx and Hm have been published,^[13] and Raman spectra of Cr and Fe logwood inks in works of art and those of Cr, Cu, and Fe logwood ink samples prepared in the laboratory have been previously reported^[5,14]; however, to our knowledge, no studies have been published on alum logwood inks or on the structure of the colorants in the inks containing Cr, Cu, or Fe. It has been reported that the metal complexing a particular dye is more important than the dye itself in determining its lightfastness. For example, in a study of a group of natural dyes it was found that of the use of tin and alum mordants results in significantly more fading than when chrome, iron, or copper ones are used.^[15] Therefore, a thorough characterization of the compounds formed is crucial for the conservation and preservation of objects bearing these media.

^{27}Al NMR (nuclear magnetic resonance) has been employed extensively in the investigation of Al complexes in aqueous and nonaqueous solutions.^[16,17] In addition, solid-state NMR has been proved to be a powerful technique for the study of the coordination state of Al species in solid crystalline and amorphous states, such as zeolites and glasses.^[18] The ^{27}Al NMR chemical shift depends on the ^{27}Al chemical environment and is particularly sensitive to the coordination state of the Al(III) species. The chemical shift ranges of ^{27}Al NMR signals are well known to vary in complexes with octahedral (10 to -10 ppm), with respect to a 1 M solution of $\text{Al}(\text{H}_2\text{O})_6(\text{NO}_3)_3$ used as an

external chemical shift reference), tetrahedral (70–50 ppm), and pentahedral (40–20 ppm) coordinations. Within these ranges, ligand substitutions will give significant changes as well.^[17,19]

For the present study, the complexes that Hm forms with Al(III) under the conditions encountered during the preparation of a typical logwood alum ink, as crystallized solids and as applied on a paper substrate, were characterized by Raman spectroscopy and ^{27}Al NMR. The Raman spectra constitute suitable references for the unambiguous identification of these complexes in works of art, and the NMR data provides complementary information on the coordination of the Al(III) species in the aqueous ink, in the crystalline powder and in the ink applied on paper. To our knowledge, this is the first application of solid-state NMR to the elucidation of the state of coordination of an Al complex in a cellulose matrix with relevance to the field of art conservation.

Experimental

Hm (Fluka), logwood shavings (Aurora Silk), logwood extract (Aurora Silk), and $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (alum, Fisher Scientific) reagents were used without further purification. The dry Hm powder was stored in a sealed bag in an Ar atmosphere with oxygen scavengers to avoid oxidation. Solutions of Hm and alum (1.0×10^{-3} M) were prepared with water purified using a Millipore Simplicity 185 system, mixed in a 1:1 proportion, stirred, and used immediately to avoid decomposition. The color of the 1:1 Hm:alum solutions changed from red-yellow to the deep violet characteristic of the ink in less than a minute after mixing. Absorption spectra in the visible and near-UV regions of the Hm and Hm–Al(III) complex solutions were measured immediately after preparation to check for the possible presence of Hm oxidation products.^[11,12] These measurements were carried out in quartz cells using a Varian Cary 50 Bio spectrophotometer.

The historical ink was prepared by boiling 10 g of logwood shavings (Aurora Silk) in 40 ml of water for 1 h. The decoction was then filtered, and 1.5 g of gum arabic (Sigma-Aldrich) dissolved in 5 ml of water were added to the filtrate. Finally, 0.5 g of $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ dissolved in 5 ml of hot water were added. The ink was then applied on Whatman filter paper and dried. In order to mimic the materials present in real works of art, the samples on paper were aged under different conditions. One set of the ink samples on paper was left to age at 20 °C and 55% RH in the dark for 36 months. Another set was subject to accelerated aging in an Atlas ci35 fadometer with a Xe lamp source. The irradiance was set at 0.9 W/m^2 at 420 nm, with about 100 000 lux on the samples. The black panel temperature was 50 °C, the wet and dry bulb temperatures were 32 and 22 °C, respectively, and the RH was set at 41%. A portion of the samples placed in the fadometer were covered with aluminum foil to keep them from exposure to the Xe lamp.

Color measurements on the ink samples on paper were carried out in a Minolta CR-241 Colorimeter in the CIE $L^* a^* b^*$ color space. The changes CIE $L^* a^* b^*$ parameters calculated as the difference of the values measured for the sample exposed to light minus the values obtained for the sample aged in the dark for 36 months were as follows: $\Delta E_{ab^*} = 14.57$, $\Delta a^* = -3.37$, $\Delta b^* = 8.72$, $\Delta C^* = -5.39$, and $\Delta L^* = 11.18$. The sample protected from light in the fadometer by aluminum foil gave similar CIE $L^* a^* b^*$ parameters as the sample aged in the dark for 36 months.

Raman spectroscopy measurements were carried out using the 488.014 nm laser excitation line in a Horiba Jobin Yvon LabRAM

HR800 Raman spectrometer coupled to an Olympus BXM optical microscope. The spectra were recorded using a 50 \times objective lens and a 1800 grooves/mm grating, with a 0.65 cm⁻¹/pixel spectral resolution. The power at the samples was set to 0.7 or 1.7 mW using neutral density filters. A multichannel air-cooled CCD detector was used, with integration times between 30 and 50 s. Raman spectra were recorded in dry powder samples of Hm and logwood extract as received from the manufacturers without further purification; on dried samples of the Hm–Al(III) complex by applying a drop of the solution in a microscope slide and letting it dry; and *in situ* on the paper substrates for both the Hm–Al(III) complex prepared by mixing Hm and alum solutions and for the ink prepared following the historic recipes.

NMR spectroscopy measurements were performed on a Bruker AV-400 MHz NMR spectrometer (9.4 T) using a 4 mm magic-angle spinning (MAS) rotor for the aqueous samples and on a Bruker AV-750 spectrometer (17.6 T) for the crystallized Hm–Al(III) complexes and for the paper samples. The solid samples were prepared by grinding them in a mortar and pestle. The finely ground samples were then packed into 4 mm zirconia solid-state NMR rotors. For the ²⁷Al MAS experiments, a 1 M solution of Al(H₂O)₆(NO₃)₃ was used as an external chemical shift reference. The ²⁷Al spectrum of the aqueous complex between Hm and Al(III) was acquired with 4048 scans, a 90° pulse duration of 3 μ s, and a repetition delay of 15 s, without spinning, and was processed using an exponential multiplication window function with 50 Hz line broadening. The ²⁷Al spectra of the solids were acquired with 32 scans, a 90° pulse duration of 2.3 μ s, and a repetition delay of 2 s, spinning at 10 kHz, and were processed using an exponential multiplication window function with 100 Hz line broadening. Deconvolution of the NMR spectra was carried out using the Bruker Topspin 2.1 software.

Results and Discussion

The solution ²⁷Al NMR spectrum of an Hm–Al(III) sample is shown in Fig. 2. In this spectrum, the sharp peak at 0.9 ppm indicates that in the aqueous solution the coordination of the Al(III) is octahedral. A predominant octahedral coordination (–3.2 ppm) is also observed for the Al(III) in the powder sample (Fig. 3, spectrum b), with a very small amount present in a

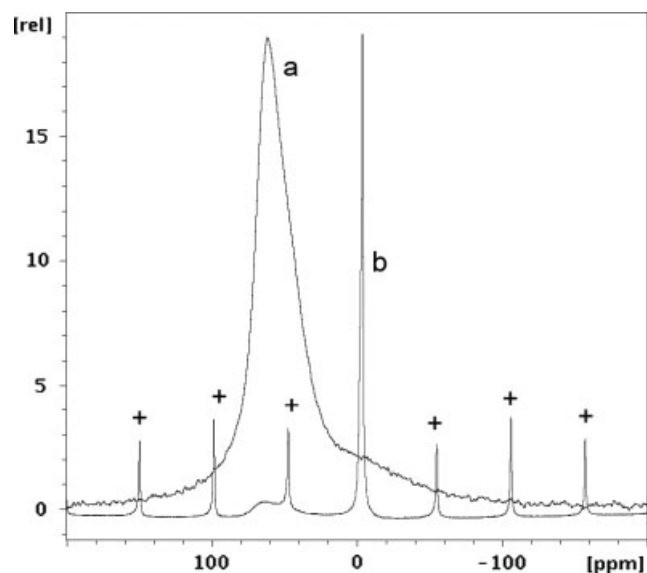


Figure 3. ²⁷Al MAS solid-state NMR spectra of the hematein–Al(III) sample on paper (a), and of the hematein–Al(III) powder sample (b). + stand for spinning side bands.

tetrahedral configuration (~67 ppm). For the sample applied on a paper substrate, a broad peak with a maximum at 63 ppm is observed indicating a predominant tetrahedral configuration (Fig. 3, spectrum a). Although the broad line shapes in this spectrum make it difficult to quantify the results, a deconvolution with three Lorentzian lineshapes provided a good fit with peaks at 63, 40, and 0 ppm. The lines at 63 and 0 ppm can be interpreted as arising from the tetrahedral and octahedral components, respectively. The middle line should be interpreted with caution, as there is a considerable degree of uncertainty due to its position within a relative broad spectral shape and possible broadening mechanisms due to chemical shift dispersion.^[17,20–22]

The fact that the coordinations of the complexes in the powder and as applied on paper are different is relevant for the conservation and preservation of works of art bearing this medium. The fastness of a mordant dye depends, among other

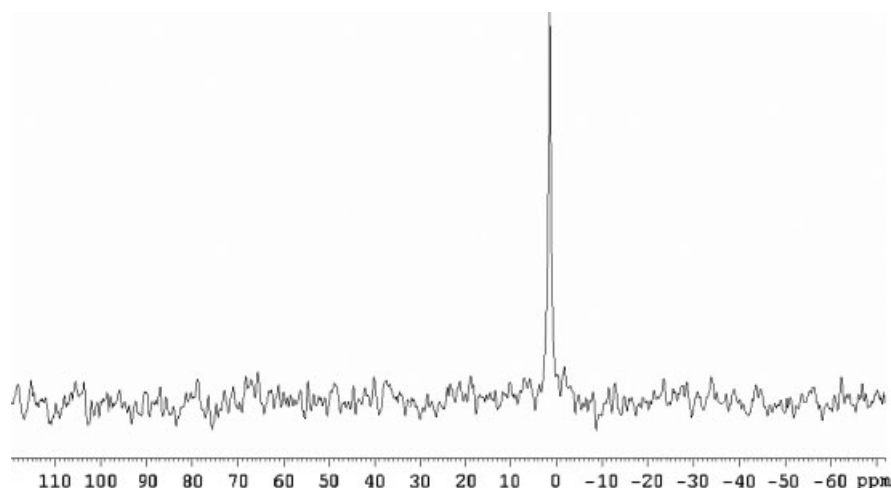


Figure 2. ²⁷Al NMR spectra of an hematein–Al(III) solution prepared by mixing equal volumes of aqueous 1.0 $\times 10^{-3}$ M hematein and alum solutions (pH ~3.9). The peak at 0.9 ppm indicates that the coordination of the Al(III) in the complex is octahedral.

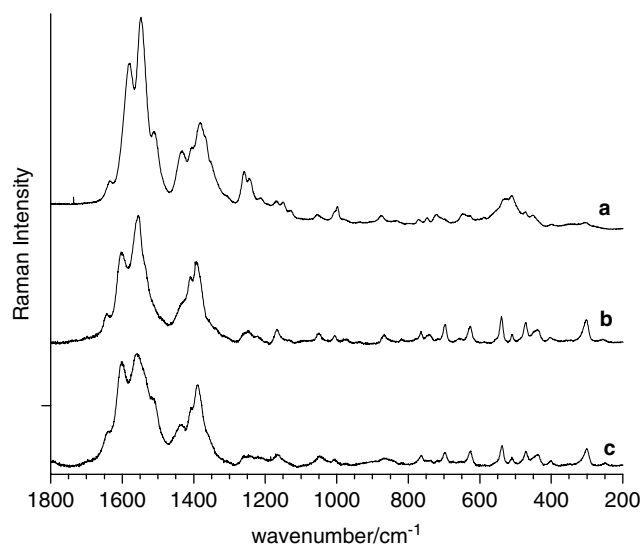


Figure 4. Raman spectra of an hematein–Al(III) powder sample prepared by mixing hematein and alum solutions in a 1 : 1 proportion and letting the mixture dry in air (a), of pure dry hematein (b), and of a dry sample of logwood extract (c). $\lambda_0 = 488$ nm.

factors, on the mordant and mordanting method and, in fact, the type of complexes formed between a dye and a mordant are more important than the dye itself in determining the lightfastness.^[15,23,24] Therefore studies of lightfastness and thermal stability of these artistic materials should be carried out on the compounds applied on the respective substrates rather than on the crystallized powders.

The Raman spectra recorded with 488 nm excitation on a pure dry Hm sample, on a dry logwood extract sample, and on a dried sample of the Hm–Al(III) complex prepared by mixing equal amounts of Hm and $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ 1.0×10^{-3} solutions are shown in Fig. 4 for the 1800–200 cm^{-1} range. The bands observed for the logwood extract appear broader than those of Hm as expected for a less pure compound.

Table 1 shows the Raman wavenumbers for the dry Hm and for the Hm complex with Al(III), together with tentative assignments based on data published for the parent compounds. The most prominent differences between the spectra of both compounds are in the range 1800–1300 cm^{-1} , with smaller differences observed below this range.

The carbonyl stretch $\nu(\text{C}=\text{O})$ in quinones is in the range 1680–1640 cm^{-1} . In substituted quinones, the wavenumber of this group is between 1670 and 1600 cm^{-1} , with electron-withdrawing and electron-donating groups shifting the wavenumbers up or down, respectively, within this range. Hydrogen-bonding OH groups lower the $\nu(\text{C}=\text{O})$ wavenumber.^[25,26] For the model compound 1,4-benzoquinone, the C=O stretch is approximately at 1663, 1640, and 1613 cm^{-1} , coupled to a certain extent with the aromatic C=C stretch.^[27,28] In the case of the substituted 2,5-dihydroxy-1,4-benzoquinone, the C=O appears at ca 1647 cm^{-1} in the Raman and at ca 1630–1625 cm^{-1} in the IR,^[29,30] and modes at ca 1540 and 1380 cm^{-1} are assigned as mixed C=O and C=C.^[29] When 2,5-dihydroxy-1,4-benzoquinone is substituted with two Cl atoms in the 3- and 6-positions, the C=O has a similar wavenumber, 1648 cm^{-1} , with the mixed C=O and C=C at 1540 and 1370 cm^{-1} .^[29] In maltol, which also contains a ketonic oxygen atom *ortho* to a hydroxy group, the C=O band is at ca 1650 cm^{-1} with two other bands tentatively assigned

Table 1. Raman wavenumbers (in cm^{-1} , acquired with 488 nm excitation) and tentative assignments based on data published for parent compounds^[25–35]

Hematein	Hm : Al (III) 1 : 1	Tentative assignments
1643w	1634w	C=O stretch + aromatic C=C
1601s	1581s	aromatic C=C stretch + C=O stretch
1561vs	1549vs	aromatic C=C stretch
1533w, sh		aromatic C=C stretch
1511vw, sh	1511mw	aromatic C=C stretch
1437mw	1434m	aromatic C=C stretch
1409m	1405mw	COH bend
1390s	1384ms, br	COH bend
	1366w,sh	COH bend
	1351w,sh	COH bend
1307vw, br	1305vw,br	COH bend
1262w, sh	1258mw	Out-of-phase CCO stretch
1244w	1246w	Out-of-phase CCO stretch, asymmetric C ₅ –O–C ₆ stretch
	1216vw	Out-of-phase CCO stretch, CH in-plane deformation
1167w	1167vw	CH in-plane deformation
	1151vw	CH in-plane deformation
	1131vw	CH in-plane deformation
1054 vw,sh	1053vw	CH in-plane deformation, symmetric C ₅ –O–C ₆ stretch
1049w		
1005w	1006w,sh	Mixed in-phase ring stretch and in-plane ring bend, CH in-plane deformation
	999w	Aromatic ring in-plane deformation/ring breathing
973vw, br	973vw,br	CH out-of-plane deformation, CH in-plane deformation
	875w	CH out-of-plane deformation
867w,br		CH out-of-plane deformation
	830vw	CH out-of-plane deformation
814vw		CH out-of-plane deformation
	774vw	CH out-of-plane deformation
764w		CH out-of-plane deformation
747vw	747vw	CH out-of-plane deformation
738vw		CH out-of-plane deformation
718vw	721w	CH out-of-plane deformation
696mw	696vw,sh	Aromatic ring deformation, CH out-of-plane deformation
659vw	659 vw, sh	Aromatic ring deformation, CH out-of-plane deformation
	646w, br	Al–O stretch
627mw	627vw, sh	Aromatic ring deformation
588vw	587vw	Aromatic ring deformation
538m	531w,br	Aromatic ring deformation
509w	507w, br	Aromatic ring deformation
472mw	471vw	Aromatic ring deformation
	452vw	Aromatic ring deformation
439w,br		Aromatic ring deformation
403vw	400vw	Aromatic ring deformation
355vw, br	350 vw, br	
302mw	304vw	
256w		

to mixed C=O and C=C modes at *ca* 1610 and 1550 cm^{-1} .^[31] In all these model compounds, 2,5-dihydroxy-1,4-benzoquinone, its 3,6-dichloro derivative, and maltol, the wavenumber of the C=O stretch shifts to lower wavenumbers upon complexation. Therefore, the band at *ca* 1643 cm^{-1} in the Raman spectrum of Hm (Fig. 4) can be assigned as the C=O stretch. This band is shifted 9 cm^{-1} to lower wavenumbers in the Hm–Al(III) complex, indicating that the carbonyl group is involved in the complexation.

The C=C skeletal in-plane vibrations of aromatic compounds have been assigned in the ranges 1625–1590, 1590–1575, 1525–1470, and 1465–1430 cm^{-1} by Socrates, and in the ranges 1620–1565 and 1525–1400 cm^{-1} by Lin Vien *et al.*^[26,32] The wavenumber at 1533 cm^{-1} is higher than the expected 1525–1470 cm^{-1} but is consistent with data that reports the band shifts to higher wavenumbers in the case of unsymmetrical trisubstitution.^[33] Thus, for Hm the observed wavenumbers at 1601, 1561, 1533, 1511 and 1437 cm^{-1} are assigned as aromatic ring stretch vibrations. Based on published data for model compounds, as discussed above, certain degree of coupling is expected between the C=O and C=C stretch modes. The bands at 1601 and 1561 cm^{-1} in the spectrum of Hm shift to lower wavenumbers in the complex, approximately 20 and 12 cm^{-1} to 1581 and 1549 cm^{-1} , respectively, indicating that these modes are also involved in the bonding to Al(III). Also in the complex, the relative intensity of the band at *ca* 1511 cm^{-1} increases.

The wavenumbers between 1405 and 1305 cm^{-1} are assigned to the COH bends, reported in the literature for phenols in the range 1410–1310 cm^{-1} .^[26]

A 6 cm^{-1} shift to lower wavenumbers is observed for the Hm COH bend at 1390 cm^{-1} ; in addition, two shoulders, also assigned as COH bends, appear in the spectrum of the complex at 1366 and 1351 cm^{-1} .

Bands between 1262 and 1216 cm^{-1} in the spectra of the pure Hm and of the Hm–Al(III) complex are assigned to out-of-phase CCO stretch, consistent with the wavenumbers assigned as such in phenols in the range 1260–1180 cm^{-1} .^[26] For the model compound catechol, 1,2-dihydroxybenzene, this mode appears at 1265 cm^{-1} in the Raman and at 1257 cm^{-1} in the IR, and between 1280 and 1180 cm^{-1} for different catecholato complexes with transition metals.^[34]

An alkoxy group on an aromatic ring usually gives rise to two bands: the asymmetric and symmetric C–O–C stretch vibrations at *ca* 1310–1210 cm^{-1} and 1050–1010 cm^{-1} , respectively. For example, phenyl ethyl ether has bands that appear at 1240 and 1040 cm^{-1} .^[25,26] The C–O–C group in six-membered rings absorbs in about the same region that noncyclic ethers do,^[25] therefore bands at 1244 and 1054/1049 cm^{-1} in the spectrum of Hm and 1246 and 1053 cm^{-1} in the spectrum of the complex can be tentatively assigned to the asymmetric and symmetric stretch vibrations C₅–O–C₆, respectively.

Lin-Vien *et al.*^[26] assign the out-of plane CH deformations of aromatic compounds in the range 935–728 cm^{-1} and the wavenumbers in the region 1200–1145 cm^{-1} as in-plane CH bending modes. Bellamy^[33] assigns the CH in-plane deformations between 1225 and 950 cm^{-1} and places the CH out-of-plane deformations in the range 1000–650 cm^{-1} , depending on the number of substituents and their locations in the ring; these ranges contain those assigned as such by Li Vien *et al.* Therefore, in the spectra of the Hm and the complex, the bands between 1216 and 973 cm^{-1} are assigned to CH in-plane deformations and the bands between 973 and 659 cm^{-1} to CH out-of-plane deformations.

The bands at *ca* 1005 cm^{-1} in the spectrum of Hm and at *ca* 1006 and 999 cm^{-1} in the spectrum of the Hm complex with Al(III) can be assigned as the mixed in-phase ring stretch and in-plane ring bend, reported at 1000 ± 10 cm^{-1} for substituted aromatic rings.^[26]

Lin Vien *et al.*^[26] assign the aromatic ring out-of plane bendings in the range 710–665 cm^{-1} and at *ca* 400 cm^{-1} , and the in-plane ring bendings at 650–605 cm^{-1} , while Socrates^[32] assigns them in the range 625–400 cm^{-1} ; therefore the bands at 696 and 659 cm^{-1} and between 627 and 400 cm^{-1} are assigned as aromatic ring deformations. The Hm bands of medium to weak intensities that appear at *ca* 696 and 627 cm^{-1} become very weak shoulders in the spectrum of the Hm–Al(III) complex. Differences in the range 550–460 cm^{-1} are also observed between the spectra of the Hm and that of the complex: the Hm medium band at 538 cm^{-1} broadens and weakens in the spectrum of the complex, while the medium to weak Hm band at 472 cm^{-1} becomes very weak, pointing to the interaction of the aromatic rings with the Al(III) ions in the complex.

The weak feature at *ca* 646 cm^{-1} in the spectrum of the complex can be assigned to the Al–O stretch, reported as a weak band in the range 612–645 cm^{-1} for Al(III) complexes with flavonoids.^[35]

Therefore, from the Raman analysis it is possible to suggest that the complexation of the Al(III) ions takes place mainly through the C=O and OH groups in the Hm molecule, and that the Hm aromatic rings are also involved in the interaction with the metal atoms. Similar results were obtained for the same type of sample applied on paper (spectrum not shown), indicating that the Hm bonds to the Al(III) ions in a similar manner, despite the complexes in the crystallized powder and in the paper having different coordination numbers. These results are, in fact, not surprising. Bettinger and Zimmermann^[12] in their thorough study by UV–visible spectroscopy of Hm–Al(III) complexes in solution at different pH show that the chromophores are only slightly influenced by their interaction with the aluminum atoms and that these chromophores are similar even for complexes with different stoichiometries.

The Raman spectrum of the ink prepared following the historic recipe, that is mixing the filtered decoction of logwood chips with the alum solution and adding gum arabic as a binding medium, applied on a paper substrate, dried, and aged in the dark for 36 months presents a fluorescent background (Fig. 5, spectrum a) most likely due to the aging of the binding medium, but it is otherwise similar to the spectrum of the Hm–Al(III) powder sample prepared by mixing Hm and alum in a 1:1 proportion (Fig. 5, spectrum c). As mentioned above, and in order to mimic the materials present in real works of art, the samples on paper were aged under different conditions. The ink sample on paper that was faded by exposing it to a Xe lamp gave a Raman spectrum similar to the historic ink on paper aged in the dark for 36 months (Fig. 5, spectrum b), despite the visible color difference between these two samples. Since the Raman spectra of the aged logwood samples and that of the non-aged powder sample on paper are similar, except for the differences in the fluorescent background, it is not possible to determine whether there are any chemical changes in the chromophore, albeit likely, using this technique. It is possible that part of the color change observed is due to the aging of the binding medium itself, as polysaccharide gums are known to discolor considerably upon accelerated aging under similar conditions to the ones used in this study.^[36]

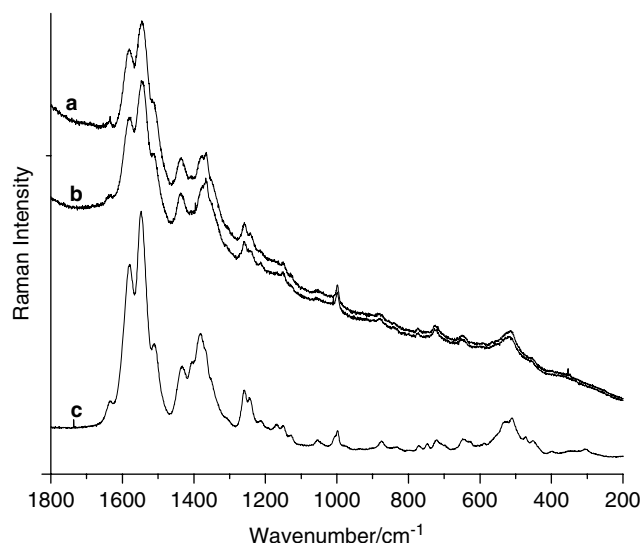


Figure 5. Raman spectra of an alum logwood ink prepared following a 19th century recipe, applied on filter paper, aged in the dark for 36 months (a), same sample as (a) exposed to a Xe lamp in a fadometer (b), respectively, and of a hematein–Al(III) powder sample prepared by mixing hematein and alum in a 1:1 proportion and letting the mixture dry in air (c). $\lambda_0 = 488$ nm.

Conclusions

Despite logwood inks having been used in drawing by artists like Vincent Van Gogh, whose use of other painting materials has been relatively well studied and documented, very little is known about the chemical properties of these inks. For the present study, the complexes between Al(III) and Hm, the main coloring matter in alum logwood inks, were characterized by Raman and ^{27}Al NMR spectroscopies. ^{27}Al NMR results showed that in the aqueous ink the Al(III) ions have an octahedral coordination, and that in the crystallized powder the coordination is predominantly octahedral while when applied on a paper substrate, the colorant is present mainly as a tetrahedral complex, but an octahedral coordination is also present. The fact that the complexes in the crystallized material and the ones present on the paper substrates are different is relevant for the study of the stability of these inks in works of art since the type of complexes formed between a dye and a mordant are among the most important factors in determining the lightfastness, even more important than the dyes themselves.

Raman spectroscopy of the complex powder and of the ink applied on a paper substrate showed that in both cases the coordination of the Hm molecules to the Al(III) ions takes place through the carbonyl and hydroxyl groups in this molecule, and that the aromatic rings are also involved in the interaction. The Raman spectra of the pure Hm–Al(III) complexes were found to be consistent with those recorded for alum logwood inks prepared following late 19th century recipes, using logwood chips instead of pure Hm, and applied on paper substrates. The spectra presented are references for the identification of the compounds in works of art.

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