CHAPTER 44 Making and tempering brazil

Si kiseres fazer boah roseta

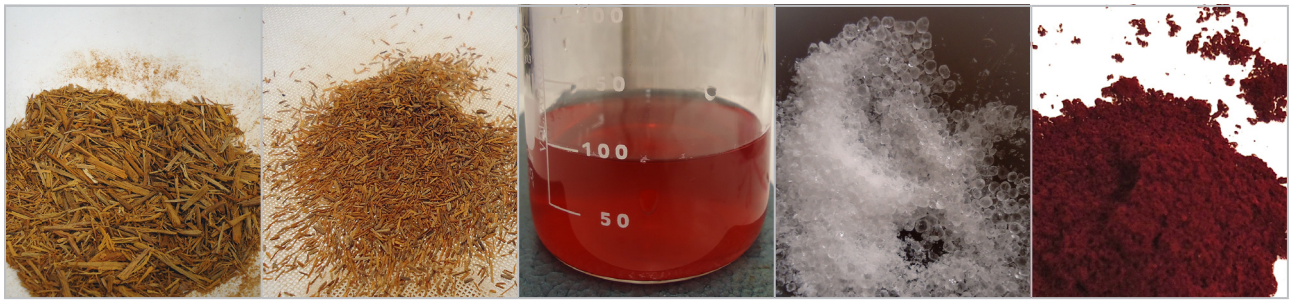

Figure 1 *Reproduction of the making of brazilwood lake pigment*

'If you wish to make good rose-colour, take brazilwood and grind it in a mortar, until it is well ground. Sift it, and take a little virgin lime and place it in a glazed earthenware bowl with water until the water becomes clear, and with this water grind the brazilwood, and put in it a little alum, temper it with gum, and write with it.' [1].

Reproduction

5.0 g of brazilwood are ground on a mortar with a pestle, as indicated in the recipe, to reduce the scrapings size. However, since this normally has little result due to the hardness of the wood, an electric coffee grinder machine is used (instead of the mortar) to effectively reduce the brazilwood scrapings into small particles.

Meanwhile, a lime solution is prepared by adding calcium oxide (CaO) to water until reaching a saturated solution with a very basic pH value (12); if necessary the solution is filtrated.

Afterwards, the fine brazilwood is placed in a glass container, which is filled with 100 mL of the lime solution.

The extraction solution is left to stand for approximately 3 hours, after which it is filtrated into another beaker.

0.5 g of alum are ground, and added to the filtrated solution. (Since there are no precise quantities in this recipe, alum's quantity was weighted in order to obtain a pH value adequate for precipitation.)

Finally, after precipitation, the solution is centrifuged (to separate the solid from the supernatant that is poured) and the pigment is left to dry.

Rationalisation / Chemical reactions

It is described in the literature that in the brazilwood heartwood a yellowish flavonoid is found, named brazilin, which when in contact with oxygen in the air and to light is quickly photo-oxidised and converted into the deep-red flavonoid brazilein [2-5], Figure 2. Thus, brazilein is the main chromophore extracted from brazilwood.

Moreover, brazilein is a weak organic acid, and the protonated and deprotonated forms display different colours [2,5], ranging from orange-red to purple, Figure 2.

In this case, extraction was carried out at very basic pH values due to the lime solution (pH 12). When the lime is poured into the brazilwood, the solution stays immediately red and starts to turn to dark purple as a consequence of the basic environment (pH 10).

The precipitation of the lake pigment is then caused by the addition of alum.

Alum, $(AlK(SO_4)_2.12H_2O)$, a source for aluminium ions (Al^{3+}), is an inorganic salt which while acting as a Lewis acid and forming a metal-dye complex, converts the water-soluble dye into an insoluble pigment, commonly known as lake pigment. In solution, alum is hydrolysed, releasing protons, which contributes to the acidification of the solution.

After the addition of alum, a pH value of 6 was obtained and pigment precipitation occurred.

Key aspects

Colourant extraction: Extracting the colour in basic conditions with lime, turned to be a good approach to improve the colourant extraction. In this case, the extracted colour presented a very deep purple hue.

However, after extraction the wood still remains with too much colour and it is possible to use it again to carry out further extractions.

pH control: Although extraction was carried out at very basic pH values, the pH of precipitation was lowered by the addition of alum in order to reach the appropriate neutral pH value for lake precipitation.

Missing / Obscure indications

Quantities: The absence of precise quantities for each ingredient makes it difficult to correctly reproduce the recipe and the result obtained might be different from what was supposed to be. Only through accurate reconstructions and changing ingredients' quantities, following a coherent methodology, is it possible to get better insight on the supposed pigment.

Brazilwood grinding: This recipe indicates that brazilwood is to be ground 'in a mortar, until it is well ground', and sifted. Afterwards, it is again ground with the lime water. However, as previously mentioned, the grinding of brazilwood with a manual mortar proved to have no effect on the wood. As such, extraction was carried out following the general procedure, which is to leave the brazilwood in the extraction solution for some hours.

Filtration: The recipe does not refer the filtration step after extraction with lime, nor after precipitation at the end of the process. However, filtration after the extraction seems to be an essential step to obtain an adequate pigment. If the solution is not filtrated, the pigment will include the brazilwood particles, which – despite being very well ground – will influence the final result. It is also possible to consider that straining the dyestuff solution would be common knowledge and thought to be unnecessary to write down and was therefore omitted on purpose from the procedure. In this case though, the indication to sift the ground brazilwood might mean that there would be no filtration and the sifting would be carried out to guarantee that the bigger scrapings were taken away. Experimentally, the absence of filtration after extraction produces a redder pigment with the ground wood mixed together with the pigment's particles. This proved to be difficult to paint with unless the bigger wood scrapings were removed (at least to some extent) when the pigment is mixed with a binder to be used as a paint. In the respective infrared spectrum the cellulose pattern can be detected, indicating the presence of the wood itself.

Comments

This is the simplest recipe, when comparing with chapter 8, 9 and 27, and the only one without the addition of chalk or any extender. As a consequence of this and of the basic extraction, the colours produced are darker and have higher b* values tending towards red-purple colours. Moreover, in the pigment's infrared spectra, both the pigment's amorphous substrate and dye can be detected (see Infrared spectrum in Appendix). The identification of these bands was possible since no extenders were added; therefore there is no overlapping of their characteristic bands.

Brazilwood in Portuguese medieval illuminations

Brazilwood has been identified in the Galician-Portuguese medieval Ajuda Songbook, from the 13th-14th century. It was admixed with lead white for lighter tones, and shaded with a proteinaceous binder [6].

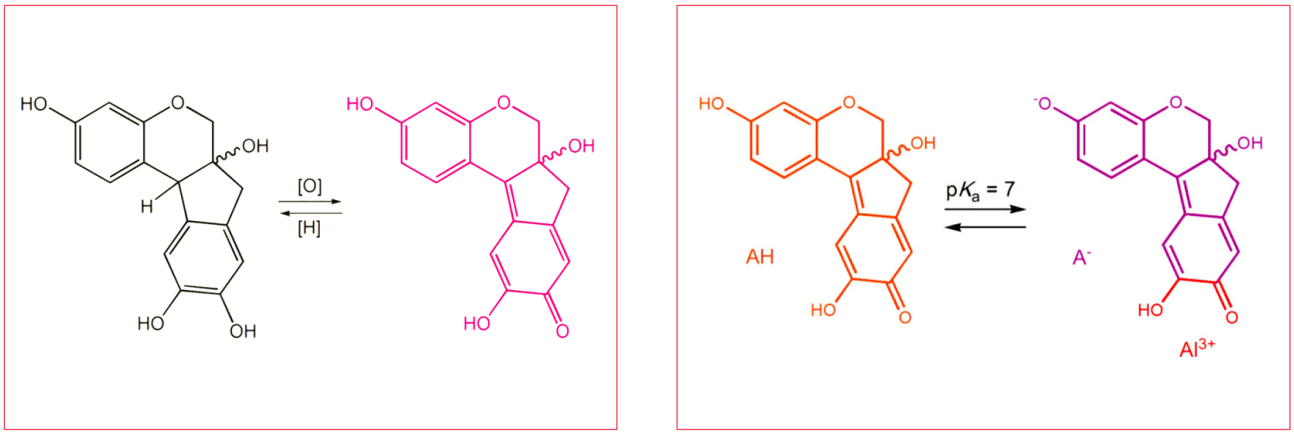

Figure 2 Brazilin (reduced form) and brazilein (oxidised form) left. *Acid-base equilibrium for brazilein,* right.

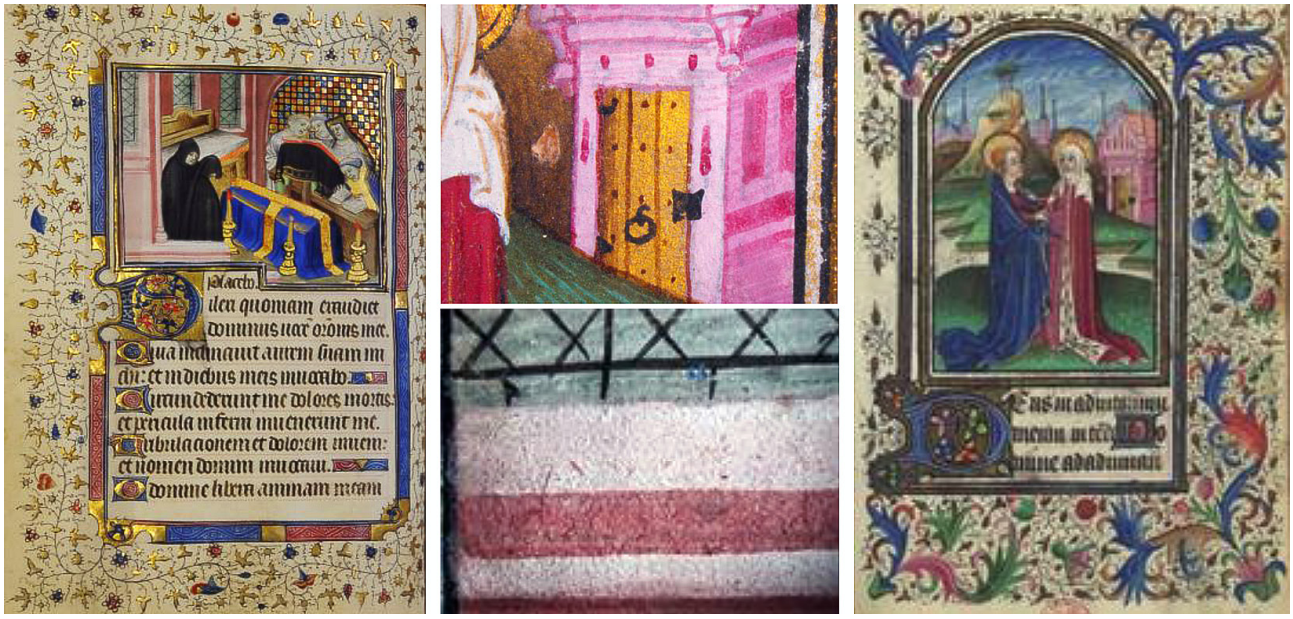

Figure 3 *Examples of brazilwood in several* Books of Hours. *From left to right, Ms.22, f.76 (PNM); IL.15, f.26 (BNP); with their respective details in the middle.*

We have also identified this colourant in pink and red colours of illuminations found in French books of hours from the 15th century, from Palácio Nacional de Mafra (PNM) [7] and from Biblioteca Nacional de Portugal (BNP), Figure 3. Brazilwood was also identified in the Fernão Vaz Dourado's Atlas, from the 16th century (ANTT-DGARQ), which was most likely produced in Goa [6].

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[2] a) Melo, M. J., Otero, V., Vitorino, T., Araújo, R., Muralha, V. S. F., Lemos, A., Picollo, M. 2014. 'A Spectroscopic Study of Brazilwood Paints in Medieval Books of Hours', *Applied Spectroscopy*, 68(4): 434-443. b) Vitorino, T., Melo, M. J., Carlyle, L., Otero, V. 2015. 'New insights into brazilwood manufacture through the use of historically accurate reconstructions', *Studies in Conservation*, 61(5): 255-273.

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Further reading

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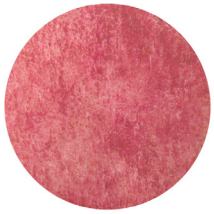
Appendix

Brazilwood lake pigment characterisation: synthesised following 'The book on how to make colours', chapter 44.

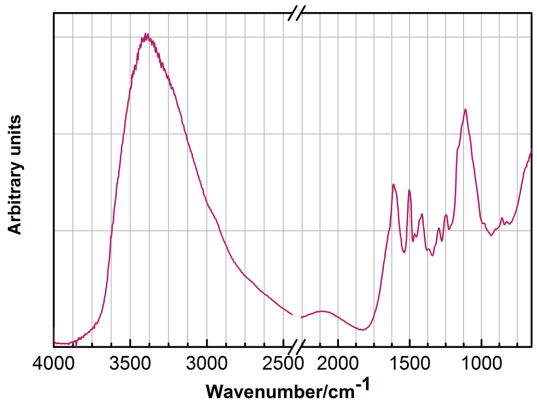


Colour

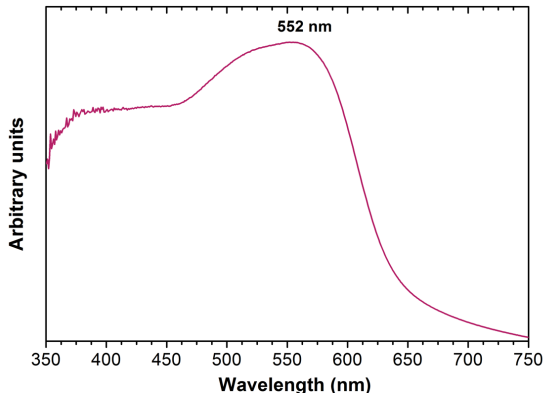
Table 1 Colour coordinates, Lab, for brazilwood paint reconstructions using two different binders (arabic gum and parchment glue) applied over filter paper and parchment.*

Support	Binder	L	a*	b*
Filter paper	Parchment glue	41.6	17.7	2.79
	Arabic gum	49.7	21.2	3.53
Parchment	Parchment glue	48.4	24.3	10.6
	Arabic gum	57.3	24.4	10.1

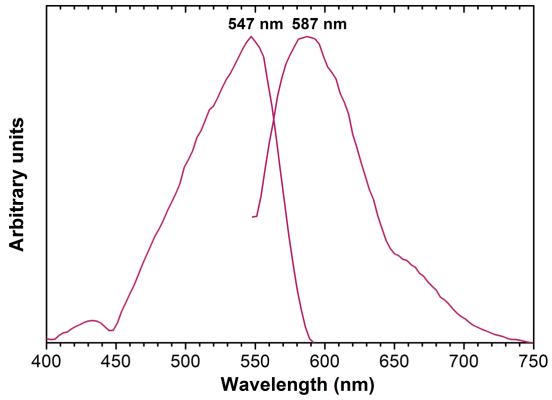
Spectroscopic characterisation



***Infrared** spectrum acquired with a Nicolet Nexus spectrophotometer coupled to a Continuum microscope with a MCT-A detector. Spectra were obtained in transmission mode, with a resolution of 4 cm^{-1} and 128 scans. The lake pigment was previously compressed using a Thermo diamond anvil compression cell.*



***Apparent absorbance** spectrum acquired with a Zeiss spectroanalyser equipped with optical fibres: MCS 601 UV/VIS model (with a 1024 Si photodiode array sensor) operating in the 190-1025 nm range, with a resolution of ~ 0.8 nm/pixel. A tungsten-halogen lamp (Zeiss CLH600) was used. Spectra were acquired in reflectance mode with the 0°/2x45° configuration.*



***Excitation and emission** spectra were acquired with a Jovin-Yvon SPEX Fluorog 3-2.2 spectrofluorometer hyphened to an Olympus BX51M confocal microscope. Dichroic filters of 540 (exciting at 530 nm) and 600 nm (collecting at 610 nm) were used at 45°. Spectra were acquired in a 30 µm spot (50x objective) with the following slits set: emission = 3 / 3 / 3 mm; excitation = 5 / 3 / 0.8 mm.*