CHAPTER 9 Making brazil
Making another rose colour

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

'In order to make another rose colour, take brazil wood, as much as you need, and scrape it very fine and place it in a small new pot. And place in the pot lye of vine branches, so that the brazil wood is covered with it. Put it on the fire and heat it enough for the lye to take up the substance of the brazil wood. And take two part alum and at least a half a part of chalk and grind each one well by itself. And then mix it and grind it together, and make, as you already know, rose out of alum.' [1].

Reproduction

Since there are no precise quantities in this recipe (only indications such as 'as much as you need'), ingredients are weighted considering the information presented in chapter 8 and according to the experimental pH values obtained.

5.0 g of brazilwood are ground using an electric coffee grinder machine to effectively reduce the brazilwood scrapings into a fine powder.

Meanwhile, a lye solution is prepared by heating at 100ºC wood ashes in water until reaching a very basic pH value (≈11), and then the solution is filtrated.

Afterwards, the fine brazilwood is placed in a glass container, which is filled with 100 mL of the lye solution ('so that the brazil wood is covered with it').

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

1.0 g of alum and 0.75 g of chalk are ground, first individually, then together, and added to the filtrated solution.

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 the recipes, brazilwood extraction is carried out in acidic, basic or neutral solutions.

In this case, extraction was carried out at very basic pH values due to the lye solution. When the lye 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 is then caused by the addition of both alum and chalk, at neutral pH.

Alum, ($AlK(SO_4)_2.12H_2O$), a source for aluminium ions (Al^{3+}), is an inorganic salt that, 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.

Chalk is added to help controlling the pH, by preventing the alum to change the solution into too acidic conditions and enabling to reach a pH value adequate for precipitation. It acts therefore as a buffer on the process. It also contributes to produce a pigment with more body and lighter colour.

After the addition of alum and chalk, a pH value of 7 was obtained and pigment precipitation occurred.

Key aspects

Colourant extraction: Extracting colour in basic conditions with lye and heating the solution, turned to be a good approach to improve the colourant extraction. Heating helps to extract the colour, although there is no precise indication for how long should it take (it is only advised to 'heat it enough for the lye to take up the substance of the brazil-wood'). 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 value of precipitation was lowered by the addition of alum and controlled by the addition of chalk in order to reach the appropriate value for lake precipitation.

Calcium carbonate: The addition of chalk was important to help precipitation, by increasing the pH to optimal precipitation values. Moreover, since it was not added in high amounts, it allowed producing a pigment with more body and opacity without turning it too clear. However, if the amount of chalk added is changed, different results can be obtained (higher quantities of chalk produce colours with lower b* values, while lower quantities produce darker hues).

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, it is possible to get better insight on the supposed pigment.

Brazilwood grinding: The recipe indicates that brazilwood is to be very finely scraped. Since this is a subjective indication, it is not clear if brazilwood was used as very small scrapings or in the form of actual powder.

Filtration: The recipe does not refer the filtration step after heating brazilwood with lye 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 powder, 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. 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 unless the bigger wood particles 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 together with the extender (chalk) indicating the presence of the wood itself (see Infrared spectrum in Appendix).

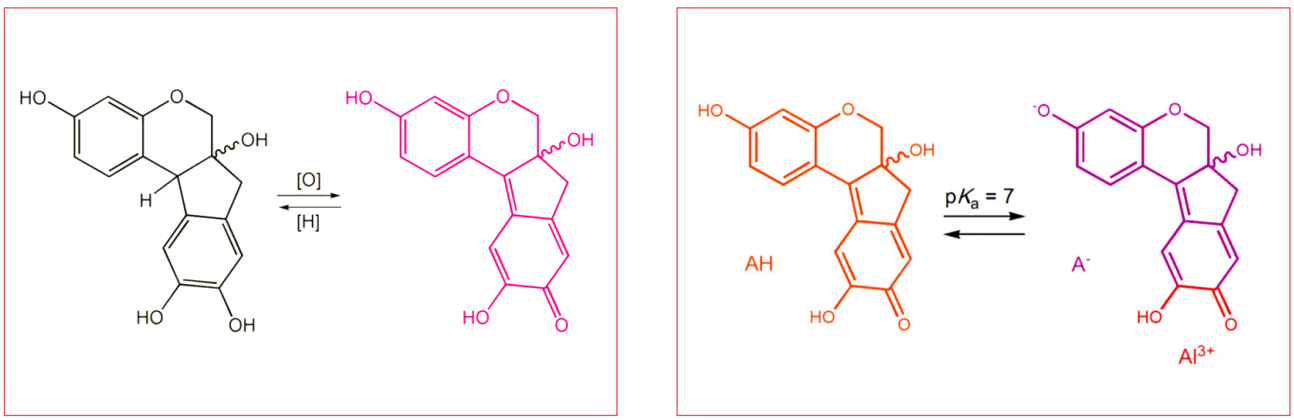

Figure 2 Brazilin (reduced form) and brazilein (oxidised form), left. *Acid-base equilibrium for brazilein,* right

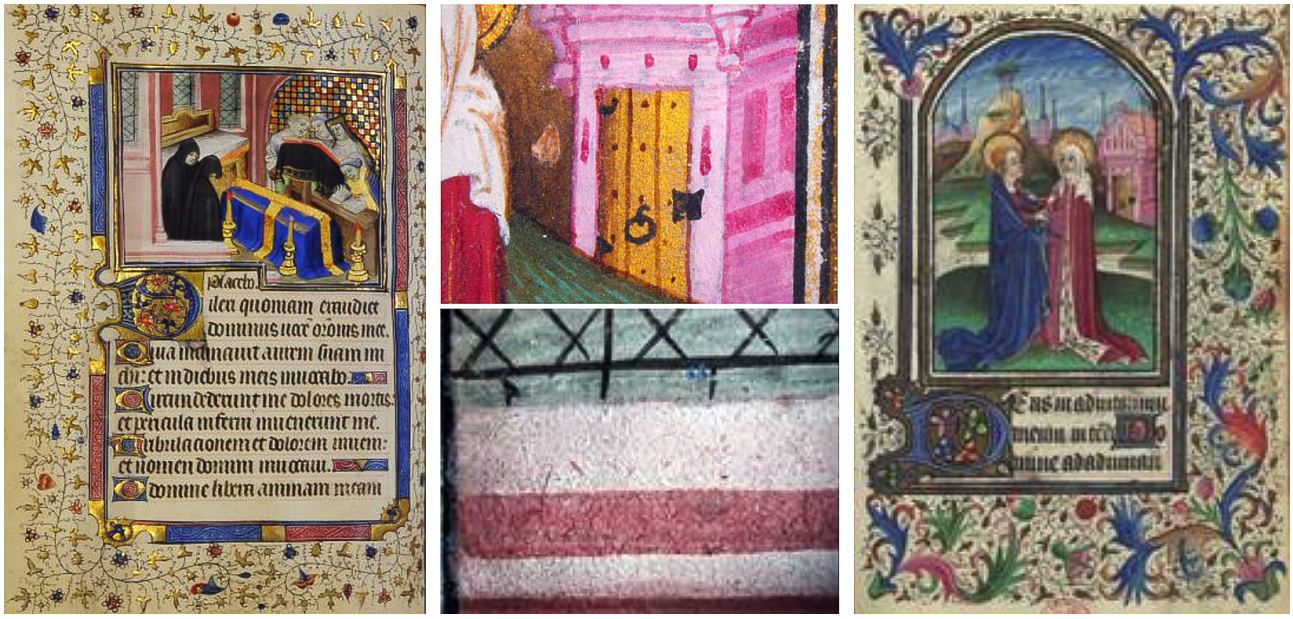

Figure 3 *Examples of brazilwood in several* Books of Hours. *From left to right, Ms.22, f.76 (PNM); IL.15, f.26 (BNP); with their respective details in the middle.*

Comments

The recipe does not indicate the whole procedure. Instead, it ends with 'make, as you already know, rose out of alum'. In this sense, the general procedure for lake precipitation was carried out: filtrating the extraction solution and adding alum and chalk to it until precipitation occurs.

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].

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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Further reading

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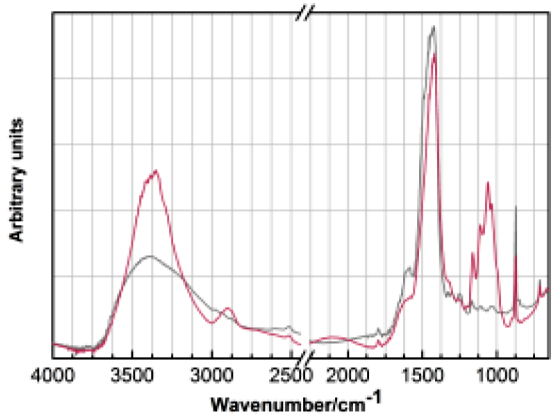
Brazilwood lake pigment characterisation: synthesised following 'The book on how to make colours', Chapter 9

Colour

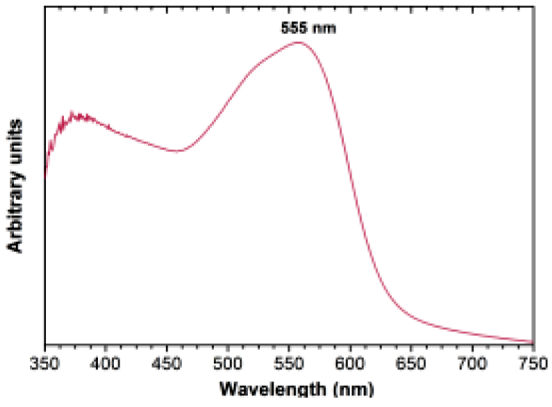
Table 1 Colour coordinates, Lab, for brazilwood paint reconstructions using two different binders (arabic gum and parchment glue) applied over filter paper and parchment.*

Support	Binder	L	a*	b*
Filter paper	Parchment glue	37.2	17.8	-7.86
	Arabic gum	29.7	14.9	-5.29
Parchment	Parchment glue	29.5	23.4	-5.82
	Arabic gum	32.6	21.7	-2.54

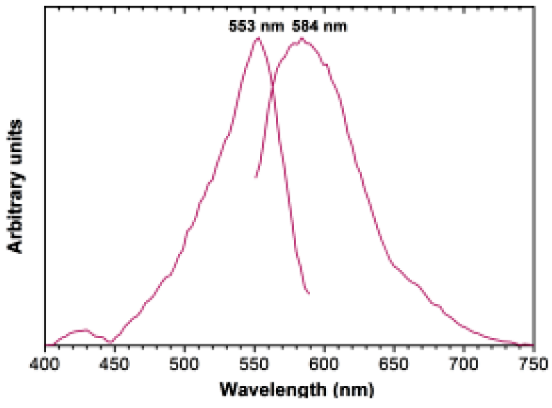
Spectroscopic characterisation



Infrared spectra acquired with a Nicolet Nexus spectrophotometer coupled to a Continuµm microscope (15x objective) with a MCT-A detector. Spectra were obtained in transmission mode, with a resolution of 4 cm^{-1} and 128 scans. The pigment lake 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 BX51 M confocal microscope. Dichroic filters of 540 (exciting at 530 nm) and 600 nm (collecting at 610 nm) were used at 45°. Both 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.