CHAPTER 8 Making and tempering brazil
Pera fazer rosah

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

'In order to make rose, take one ounce of fine brazilwood, and scrape it very fine, and set it aside. And then take a quarter ounce of alum and take two pennyweights of white lead and grind it with the alum in a mortar and set it aside. And then take the brazilwood and place it in a cup [*malega*], and put in the other powders with the brazilwood, and pour urine over them until they are covered. And let them stand thus three whole days, always stirring them with a stick 5 or 6 times each day. And then pass it and strain it through a linen cloth above a trough made of gypsum or chalk-stone. And let it soak in the trough, and when it is dry, scrape it very well with a spatula, and keep it carefully from the air. And when you want to work with it grind it with gum water.' [1].

Reproduction

Taking into account the proportions presented in the recipe, 5.0 g of brazilwood are ground using an electric coffee grinder machine to effectively reduce the brazilwood scrapings into small particles.

Afterwards, 1.25 g of alum were ground together with 0.55 g of lead white [taking into account that a pennyweight is equivalent to 1.555 g].

The fine brazilwood and the alum with lead white are placed together in a glass container. The beaker is then filled with 100 ml of urine 'until they are covered').

The mixture is left to stand for three days, stirring 5-6 times a day with a glass rod. The beaker is covered with aluminium foil to prevent evaporation.

After those three days, the solution is filtered through a linen cloth on top of a gypsum or chalk bowl/stone.

Finally, the filtered solution is left to dry and scraped very well with a spatula from the stone.

Rationalisation / Chemical reactions

Chapter 8 is the first of four brazilwood recipes in the *Livro de como se fazem as cores*. Each recipe results in four different brazilwood lakes, displaying different reddish to pinkish hues. The different procedures used for the extraction of the dye (urine for chapters 8 and 27; lye for chapter 9; and lime for chapter 44) and variation of extenders (lead white for chapter 8, and chalk for chapters 9 and 27) produce either pinkish (chapters 8 and 27) or reddish (chapters 9 and 44) colours.

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.

This recipe uses urine as the dye extraction solution. Human urine has in its constitution high concentrations of nitrogen (N), from urea ($CO(NH_2)_2$), phosphorous (P), potassium (K), sodium (Na) and chloride (Cl) [6]. The pH values of fresh urine are within the normal physiological range of 5.6 and 6.8 [6]. This indicates that if fresh urine was used, the extraction solution should not be basic but neutral or slightly acidic. In this case, the fresh urine used presented pH around 7.

Furthermore, the extraction step from this recipe includes another acid: alum ($AlK(SO_4)_2.12H_2O$), a source for aluminium ions (Al^{3+}). This ingredient 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, in neutral to basic solutions, commonly known as lake pigment. In solution, alum is hydrolysed, releasing protons, which contributes to the acidification of the solution.

When urine was added to brazilwood with alum and lead white, effervescence occurred, indicating CO_2 formation and release, turning the solution to an orange/brown colour, getting redder with time. The CO_2 release may be explained by the acid-base equation established by CO_3^{2-} [2b]:

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$

$$CO_3^{2-}(aq) + H_3O \rightleftharpoons HCO_{3-}(aq) + H_2O$$

$$HCO_{3-}(aq) + H_3O+ \rightleftharpoons H_2CO_3(aq) + H_2O$$

$$H_2CO_3(aq) \rightleftharpoons CO_2(g) + H_2O$$

Overall, after the three days, the extracting solution with urine and alum presented a pH around 4.5.

The presence of lead white ($2PbCO_3 \cdot Pb(OH)_2$) might have helped controlling the pH, by preventing alum to change the solution into conditions too acidic, acting therefore as a buffer on the process. As a matter of fact, lead white was never detected in the infrared analysis acquired in the final product, possibly due to its consumption evidenced by the CO_2 escape [2b].

As for gypsum or chalk stone, either one of them were used to receive the filtrated red solution and incorporate the colorant, changing it into a more pink hue and conferring more body to the pigment (which will make it easier to paint with).

Key aspects

Colourant extraction: Since extraction is carried out at slightly acidic pH values, without heating, the solution is left for three days to help extracting more colour. In this case, the final solution presented a red colour. 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: The urine used had a neutral pH and the pH of the solution went to more acidic values due to the presence of alum and to the brazilwood itself. The final pH could not be measured since the filtrated solution was poured directly to the gypsum or chalk stone, where it was left to dry.

Gypsum or chalk bowl: It was observed that whenever the dye solution was filtered directly to a bowl made of gypsum, it was perfectly absorbed forming a reddish solid layer on top of the gypsum, making it easy to scrap. When it was filtered above a bowl made of chalk, the solution was not easily absorbed. The final colour of the pigment will depend on the amount of gypsum/chalk scraped together with the layer of precipitate.

Missing / Obscure indications

Brazilwood grinding: The recipe refers the use of 'fine brazil-wood, and scrape it very fine'. Since this is a subjective indication, it is not clear if brazilwood was used as very small scrapings or as powder.

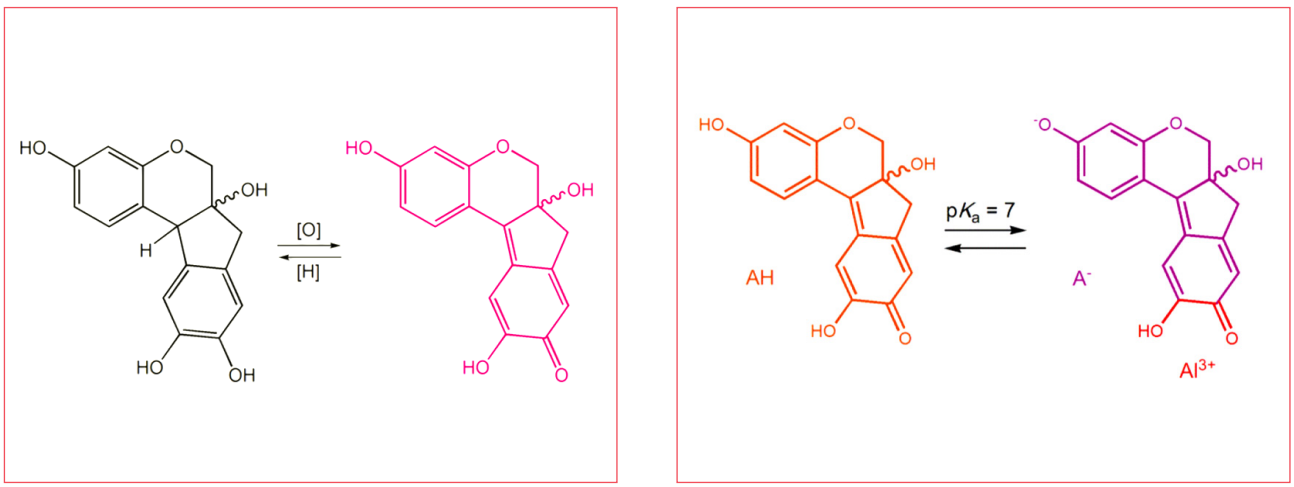

Figure 2 *Brazilin (reduced form) and brazilein (oxidised form),* left. *Acid-base equilibrium for brazilein,* right

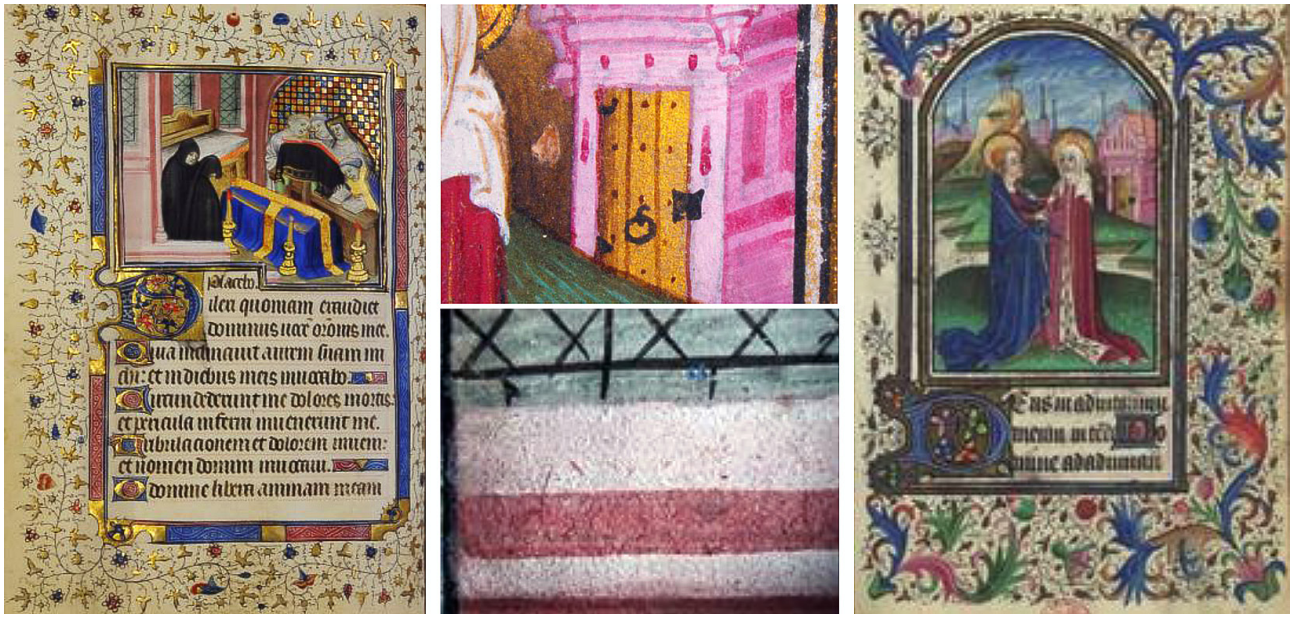

Figure 3 Examples of brazilwood in several Books of Hours*. From left to right, Ms.22, f.76 (PNM); IL.15, f.26 (BNP); with their respective details in the middle.*

Comments

Recipe description: Chapter 8 is the more complete recipe for brazilwood lake manufacture, when comparing to chapters 9, 27 and 44, since it describes precise quantities to use for each ingredient and includes a filtration step. The other recipes, on the other hand, omit significant details.

Malega: It is interesting to find the word *malega* in the recipe. In Portuguese, the world *malega* comes from the word 'malga', which means a bowl where people drink soup or wine (an old tradition from the North of Portugal). But in this case, it is believed that *malega* is used as a name for the wood of which such bowl is made [1,7].

Trough: A chalk stone or gypsum over which the solution is to be filtered and dried. The actual term in the recipe is 'piah feitah de gis o de pedra kri' [1].

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 [8].

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) [9] 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 [8].

Works cited

[1] Strolovitch, D. L. 2010. 'O libro de komo se fazen as kores das tintas todas (Translation)', in L.U. Afonso (ed.), *The Materials of the Image. As Matérias da Imagem*. Lisboa: Campo da Comunicação, p. 227-228.

[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."

[3] Perkin, A., Everest, A. 1918. *The Natural Organic Colouring Matters. Longmans*, Green & Company.

[4] Cardon, D. 2007. Natural Dyes. Sources, Tradition, *Technology and Science*. London: Archetype Publications.

[5] Berger, S., Sicker, D. (Eds.) 2009. 'Dyestuffs and coloured compounds', in Classics in *Spectroscopy – Isolation and Structure Elucidation of Natural Products*, pp. 211-230. Weinheim: Wiley-VCH.

[6] Karak, T., Bhattacharyya, P. 2011. 'Human urine as a source of alternative natural fertilizer in agriculture: a flight of fancy or an achievable reality'. *Resources, Conservation and Recycling*. 55: 400-408.

[7] Matos, D.M. 2011. *The Ms. Parma 1959 in the context of Portuguese Hebrew illumination*. Master thesis, Lisbon: Faculdade de Letras, Universidade de Lisboa.

[8] Melo, M.J., Nabais, P., Guimarães, M., Araújo, R., Castro, R., Oliveira, M.C., Whitworth, I. 2016. 'Organic dyes in illuminated manuscripts: a unique cultural and historic record', *Philosophical Transactions of the Royal Society A*, 374(2082): 20160050-20160069.

Further reading

Written Sources

Blondheim, S. 1928. 'An old Portuguese work on manuscript illumination', *Jewish Quarterly Review*, 19: 97-135.

Clarke, M. 2011. Mediaeval Painters' Materials and Techniques. *The Montpellier Liber diversarum arcium*. London: Archetype Publications.

Nunes, F. 1982 [originally written in 1615]. *Arte da Pintura, Simetria e Perspectiva*. Porto: Editorial Paisagem.

Other

Afonso, L.U. 2010. 'New developments in the study of O livro de como se fazem as cores das tintas', in L.U. Afonso (ed.), *The Materials of the Image*, 3-27. *As Matérias da Imagem*. Lisboa: Campo da Comunicação.

Clarke, M. 2010. 'The context of the O livro de como se fazem as cores: late mediaeval artists' récipes books (14th-15th centuries)', in L.U. Afonso (Ed.), The Materials of the Image, 45-73.. *As Matérias da Imagem*. Lisboa: Campo da Comunicação.

Melo, M.J., Araújo, R., Muralha, V.S.F., Lemos, A. 2013. 'O que nos dizem os materiais da cor sobre os Livros de Horas do Palácio Nacional de Mafra', in A. Lemos (Ed.), *Os livros de Horas Iluminados do Palácio Nacional de Mafra*, Instituto de Estudos Medievais – FCSH/NOVA, Palácio Nacional de Mafra.

Roger, P., Villela-Petit, I., Vandroy, S. 2003. 'Les laques de brésil dans l'enluminure médiévale: reconstitution à partir de recettes anciennes', *Studies in Conservation*, 48(3): 155-170.

Strolovitch, D. 2005. *Old Portuguese in Hebrew Script: convention, contact, and convivência*, pp. 116-184. PhD Dissertation, Cornell University.

Villela-Petit, I. 1996. 'Brésil et autres rouges: dix recettes de laque médiévales', *Technè – Revue du Laboratoire de Recherche des Musées de France*, 4: 68-73.

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Appendix

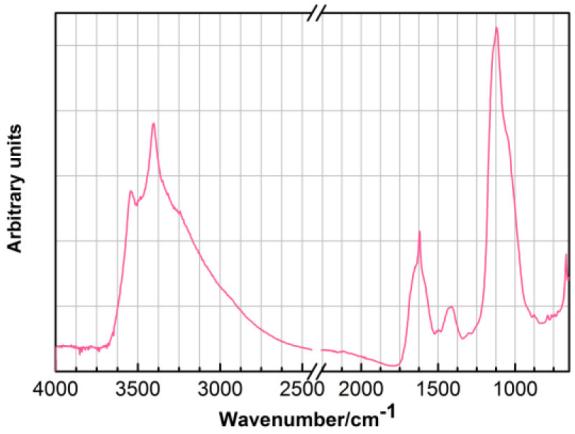
Brazilwood lake pigment characterisation: synthesised following 'The book on how to make colours', chapter 8

Colour

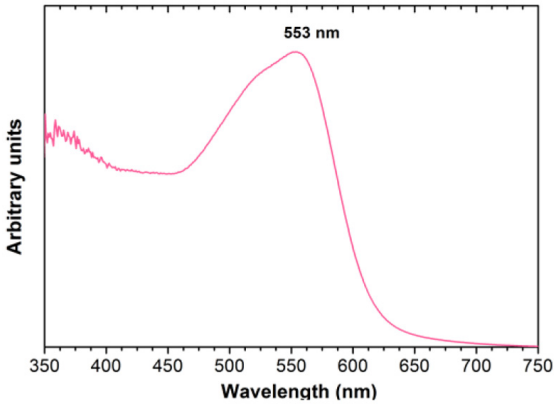
Table 1 Colour coordinates, Lab, for brazilwood paint reconstruction using two different binders (arabic gum and parchment glue) applied over filter paper and parchment.*

Support	Binder	L	a*	b*
Filter paper	Parchment glue	47.0	29.0	-0.27
	Arabic gum	47.8	28.6	4.77
Parchment	Parchment glue	44.7	34.3	4.32
	Arabic gum	61.2	29.2	9.21

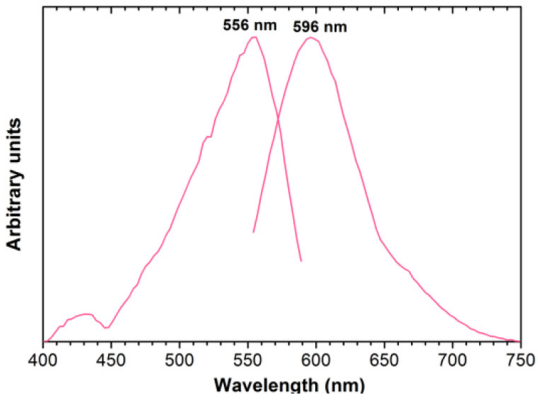
Spectroscopic characterisation



Infrared spectrum 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 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 BX51 M confocal microscope. A continuous 450 W Xenon lamp was used. 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.