CHAPTER 27 Making and tempering brazil Si kiseres fazer boah rosah



Figure 1 Reproduction of the making of brazilwood lake pigment.

'If you wish to make good rose-color, take brazilwood, as much as you want, and scrape it well over a conch or retort, then add alum to it. And once you have done this, take the urine of a chaste man and add pour it over the brazilwood and the alum until they are well-covered, and let them stand thus for three days. And then take a piece of chalk and throw some of its powder over this brazilwood until it seems that there is as much of one as of the other. And then let this concoction stand for a day or two. And then take this rose-color and grind it with gummed eggwhite, and write with it.' [1].

Reproduction

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

5.0g of brazilwood are ground using an electric coffee grinder machine to effectively reduce the brazilwood scrapings into small particles.

Afterwards, 1.5g of alum are ground, and placed together with the fine brazilwood in a glass container. The beaker is then filled with 100 ml of urine ('until they are well covered').

The mixture is left to stand for three days, without stirring. During that time, the beaker is covered with aluminium foil to prevent evaporation.

After those three days, the solution is filtered into another beaker and 2.0 g of chalk are added to the filtered solution. This solution with chalk is then left to stand for two more days. Finally, the solution is centrifuged and the pigment is washed with water and left to dry.

Rationalisation / Chemical reactions

Brazilein is the main chromophore extracted from brazilwood. The brazilwood heartwood has a yellowish flavonoid, named brazilin, which when in contact with oxygen in the air and to light is quickly photooxidised and converted into the deep-red flavonoid brazilein, as a result of the conversion of one hydroxyl group from brazilin into a carbonyl group [2-5], Figure 2.

Moreover, brazilein is a weak organic acid, which protonated and deprotonated forms are of different colours [2,5], Figure 2. Therefore, brazilwood extraction might be developed following acidic, basic or even neutral conditions. This will constrain the colour of the extracted compound: in acidic conditions, brazilein develops red hues whereas in basic conditions the colorant displays deeper purple hues [2,5].

This recipe uses 'urine of a chaste man' 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 (CI) [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(SO₄)₂.12H₂O), a source for aluminium ions (Al³⁺). 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, 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, effervescence occurred, indicating CO_2 release. This CO_2 release may be explained by the acid-base equation established by CO_3^{2-} (see further ahead) [2b]. The solution turned to an orange/brown colour, getting redder with time.

After the three days, the extracting solution with urine and alum presented a pH around 4.5. Urine (pH 7) proved to be ineffective at keeping a neutral pH of extraction.

Pigment precipitation was then caused by the addition of chalk to the filtrated solution. In fact, chalk was added to help controlling the pH, by enabling to reach a pH value adequate for precipitation (a pH value of 6.5 was obtained). It acts therefore as a buffer on the process. It also contributes to change colour to a lighter pink hue and to produce a pigment with more body (which will make it easier to paint with).

Yet, in the recipe, the reference to the quantity of chalk ('take a piece of chalk and throw some of its powder over this brazil-wood until it seems that there is as much of one as of the other') is not totally clear. As such, chalk was weighted in order to obtain the adequate pH for precipitation.

An effervescence effect was again observed when chalk was added to the acidic coloured solution. CO₂

release and chalk's buffering effect may be explained by the acid-base equation established by CO_3^{2} [2b]:

$$CaCO_{3}(s) \longrightarrow Ca^{2+} (aq) + CO_{3}^{2-} (aq)$$

$$CO_{3}^{2-} (aq) + H_{3}O \longrightarrow HCO_{3-} (aq) + H_{2}O$$

$$HCO_{3-} (aq) + H_{3}O + \longrightarrow H_{2}CO_{3} (aq) + H_{2}O$$

$$H_{2}CO_{3} (aq) \longrightarrow CO_{2} (g) + H_{2}O$$

As a matter of fact, infrared analysis of the pigment obtained reveals the presence of gypsum as well as that of chalk (see Infrared spectrum in Appendix) indicating that the former was produced during pigment synthesis. This may be explained by the disappearance of $CO_3^{2^-}$ in the form of CO_2 and the simultaneous presence of $SO_4^{2^-}$ ions from alum and Ca^{2^+} from calcium carbonate in solution, at acidic conditions (when chalk was added the dye solution containing alum was at pH 4.5).

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 extracted colour 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: Urine at neutral pH was not able to keep the extraction pH, which went to more acidic values due to the presence of alum and to the brazilwood itself. The pH value of precipitation was controlled by the addition of chalk in order to reach the appropriate value for lake precipitation (neutral).



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.

Calcium carbonate: The addition of chalk was important to help precipitation, by increasing the pH to optimal precipitation values. In this case, since the quantity of chalk added was relatively high (if comparing with that of recipe 9), not only it created a pigment with more body and opacity, but it also produced a lighter pink colour. In fact, the addition of higher quantities of chalk produces colours with lower b* values. However, if too much chalk is added (for example, to make it the same volume as that of the brazilwood solution), there will be little colour and it will be very difficult to paint with such pigment.

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 the brazilwood is to be well scraped 'over a conch or retort'. It is however not clear if brazilwood was used as small scrapings or if it was scraped to the form of powder.

Filtration: The recipe does not mention the filtration step after the three days of extraction with urine and alum, 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. 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. Curiously, in the respective infrared spectrum - which can be seen in the appendix - the cellulose pattern can be detected together with the extender (chalk) indicating the presence of the wood itself.

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 [7].

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) [8] 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 [7].

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. 232-233.

[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] 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.

[8] 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.

Further reading

Written Sources

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

Cennini, C. 1960. *The Craftsman's Handbook – The Italian 'II libro dell'arte'*, translated by D.V. Thomson. New York: Dover Publications.

Theophilus, Smith, C.S., Hawthorne, J.G. 1979. On Divers Arts: *The foremost medieval treatise on painting, glassmaking, and metalwork*. New York: Dover Publications.

L'Ancien, P. 1985. *Histoire Naturelle, Livre XXXIII*. J.M. Croisille (transl.). Paris: Belles Lettres.

Merrifield, M.P. 1999. *Medieval and Renaissance Treatises on the Art of Painting: original texts with English translations*. London: Dover Publications.

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.

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 27.



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	55.7	39.3	-6.20
	Arabic gum	48.9	38.2	-2.77
Parchment	Parchment glue	49.2	43.9	-3.97
	Arabic gum	44.5	50.8	4.57

Spectroscopic characterisation



Infrared spectrum acquired with a Nicolet Nexus spectrophotometer coupled to a Continuµm 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 BX51 M 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 μ m spot (50x objective) with the following slits set: emission = 3 / 3 / 3 mm; excitation = 5 / 3 / 0.8 mm.