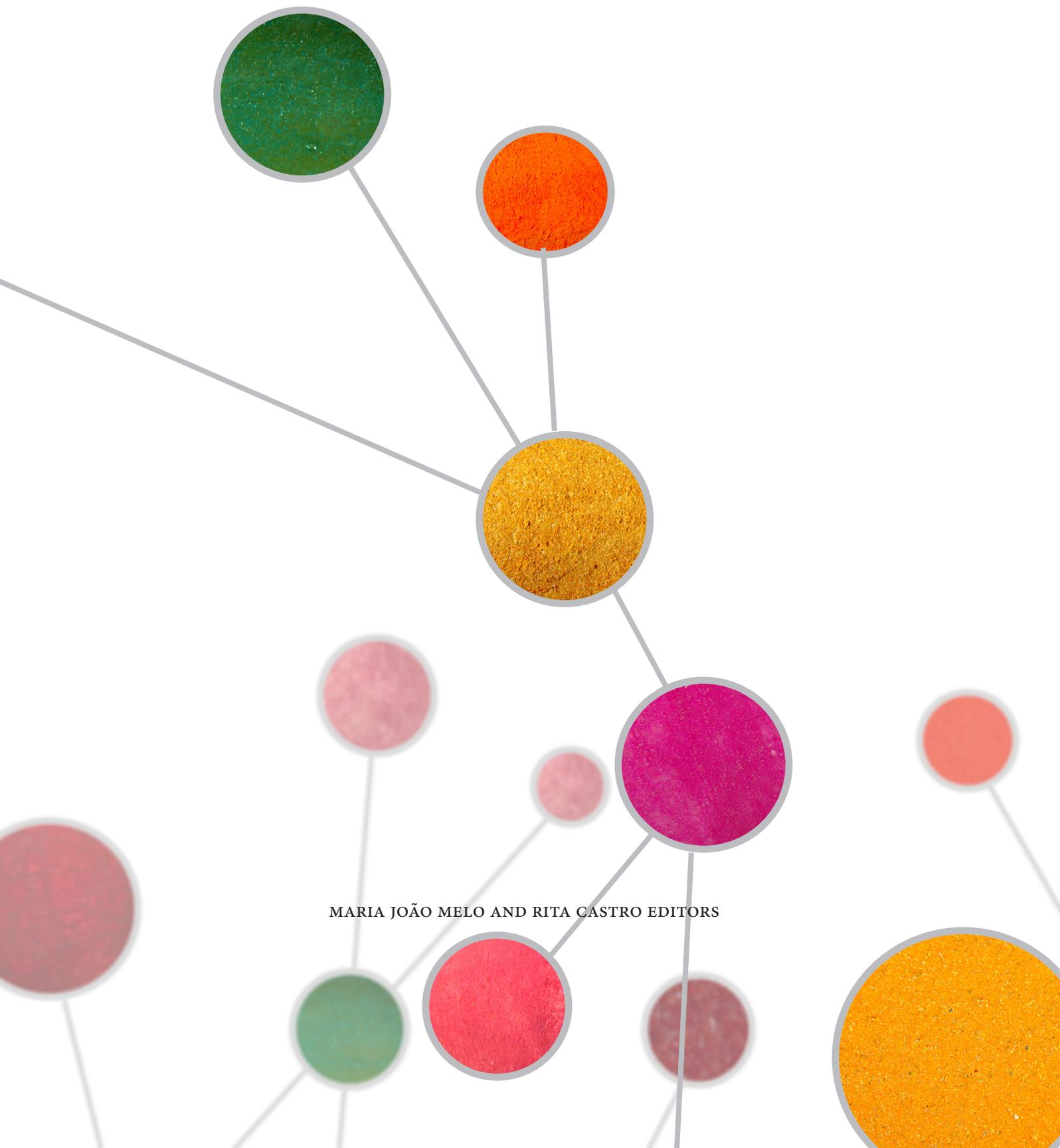


# THE “BOOK ON HOW TO MAKE COLOURS”

*O livro de como se fazem as cores das tintas todas*

medieval colours for practitioners



MARIA JOÃO MELO AND RITA CASTRO EDITORS

# Index

## Introduction

Introdução

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## The 'Book on How to Make Colours'

### Chapter

### Title

- |    |  |
|----|--|
| 1  | Making and tempering mosaic gold         |
| 5  | Making silver blue                       |
| 8  | Making and tempering brazil              |
| 9  | Making another brazil                    |
| 10 | Making red lead from lead white          |
| 11 | Making verdigris (from copper)           |
| 12 | Making verdigris (from brass)            |
| 13 | Making carmine (lac)                     |
| 15 | Making vermilion                         |
| 24 | Making and tempering catassol (turnsole) |
| 27 | Making and tempering another brazil      |
| 40 | Making glue from parchment               |
| 44 | Making and tempering another brazil      |
| 45 | Making green lake from lily              |

## Appendices

- |                   |   |
|-------------------|---|
| <b>Appendix 1</b> | Bibliography                              |
| <b>Appendix 2</b> | Conversion table for weights and measures |
| <b>Appendix 3</b> | Medieval raw materials (in progress)      |
| <b>Appendix 4</b> | Recipes in Portuguese (in progress)       |

# Introdução ao Livro de como se fazem as cores das tintas todas

Convidamos o leitor a entrar no atelier do iluminador, no séc. XV em Portugal. Este iluminador, talvez também alquimista, é herdeiro de uma tradição de saber fazer as cores "com que possas iluminar ou pintar ou escrever" que remontará, pelo menos, ao século XIII. Este saber fazer foi cuidadosamente preservado na língua portuguesa, escrita em caracteres hebraicos, numa coletânea de textos, Ms. Parma 1959, que possivelmente tinha como objetivo final o de produzir Bíblias hebraicas, onde o rigor do texto se iluminava com as cores descritas neste "livro das tintas todas".

Os trabalhos de investigação recente que suportam o resumo acima foram conduzidos no projecto "As Matérias da Imagem", no seio de uma equipa multidisciplinar, e poderão ser consultados no livro homónimo, editado por Luís Afonso, bem como na extraordinária tese de mestrado de Débora Marques, orientada por L. Afonso e, ainda, noutras publicações destes autores descritas no anexo "Bibliografia".

Esta nova edição crítica traz para o laboratório do séc. XXI a ciência e a tecnologia usadas para produzir as tintas da iluminura medieval. A experimentação que permitiu fazer vir até nós essas "cores perdidas no tempo" é levada a cabo por alunos do mestrado em conservação e restauro bem como por investigadores com formação em química e ciências da conservação. O nosso primeiro contacto com este pequeno livro data possivelmente de 2000, na edição de Moreira de Sá, mas a experimentação no laboratório iniciou-se em 2001, com a primeira de uma série de experiências mal sucedidas em redor da produção do vermelhão, HgS, tal como é descrita no capítulo 15. Que não nos desencorajando, pois em cada insucesso racionalizávamos o que tinha corrido mal, nos foram aproximando da experiência em que pela primeira vez se viu a "cinza" transformar-se de novo em "fogo". Ainda que este processo de preparar vermelhão tenha sido investigado no âmbito da tese de doutoramento de Catarina Miguel, ficaram aspectos por esclarecer, e a eficácia do processo continua para nós tão misterioso como quando iniciámos a sua experimentação; faltará algum catalisador, óbvio na altura, e que ainda não descobrimos? Não sabemos, mas no vermelhão

como nas outras cores, mesmo naquelas que nos pareceram mais simples de reproduzir, a investigação que hoje partilhamos, é um trabalho em curso. Um trabalho que desejamos partilhar para que possa ser criticado e melhorado por outros com mais saber, ou com outros saberes. Apresentamos aqui um dos núcleos do "livro das tintas todas", dedicado aos pigmentos (de base orgânica ou inorgânica), descritos na tabela no final desta introdução.

Se a motivação para a descoberta deste livro precioso foi a cadeira do mestrado em conservação e restauro História e Técnicas de Produção Artística (HTPA), a oportunidade para sistematizar o seu estudo foi conseguida no âmbito do projecto "A cor da iluminura medieval portuguesa no contexto Europeu: partilha e singularidade", prosseguida no "Colour in medieval illuminated manuscripts: between beauty and meaning". Tendo ainda agregado investigação de duas teses de mestrado, de Tatiana Victorino e Rita Araújo na temática lacas de pau brasil, bem como a tese de doutoramento de Rita Castro dedicada ao vermelho de goma laca (carmim). Os principais autores são, como na época medieval a que reporta o tratado, anónimos que descrevemos como alunos de HTPA. Não significa isso que tenham sido menos importantes, e prevemos que no futuro lhes seja possível mais vezes assinar trabalhos na plataforma digital em que se instalará o "livro das tintas todas"; como o do ouro musivo descrito no capítulo 1, que logo na primeira experiência de 2006 Inês Coutinho assinou com sucesso.

Apresentados os experimentalistas, podemos perguntar o que aprendemos com o "livro das tintas todas"? Se me fosse permitido escreveria, muitíssimo, pois foi um instrumento precioso na investigação fundamental. Em particular, na reconstrução dos materiais e técnicas usadas no passado para a criação de objetos artísticos e culturais. As tintas obtidas foram comparadas, a nível molecular, com as existentes em manuscritos medievais em coleções portuguesas. Destas, destacamos os manuscritos produzidos pelo mundo monástico português nos sécs. XII-XIII e os Livros de Horas de produção francesa e flamenga dos sécs. XIV-XV. Esta comparação permitiu validar as cores e tintas obtidas e como tal propô-las como material de referência, que

poderemos usar na nossa investigação futura; por exemplo, nos estudos dos mecanismos de degradação destas belíssimas tintas medievais, para a sua estabilização e descoberta de novos tratamentos.

Pudemos ainda avaliar sistematicamente, ao longo dos últimos 10 anos, que as descrições dos processos de produção destas cores e tintas são sintéticas e rigorosas e, em muitos casos, nos passos mais críticos trazem informação extra que é preciosa para o praticante. Assim, no caso da produção do vermelhão, no moroso e essencial passo de moagem do mercúrio com o enxofre, temos duas instruções preciosas: sabemos que terminamos a moagem (e obtivemos a forma preta  $\alpha'$ -HgS) no momento em "que se torne o fogo como cinza"; e, também nos é aconselhado que esta moagem se faça "mexendo-o com pé de cão com a sua pele", o que permite capturar o muito fugidio mercúrio e, só quem trabalhou com o "fugitivo", um dos muitos nomes do mercúrio, poderá imaginar esta vantagem. Quando, na reprodução de uma receita, falhamos ou sentimos que ainda não estamos lá, estamos em crer que é porque ainda não interpretámos corretamente a ciência e a tecnologia do processo descrito. Ainda que seja possível apreciar a clareza e rigor da descrição, são

muitos os séculos que nos separam do praticante medieval; e houve e haverá coisas, muito óbvias porque integravam invisivelmente o quotidiano daqueles tempos, que nos escapam. Demorámos muitos anos a perceber o que era a "piah" de gesso ou pedra cré descrita para a preparação das lacas de pau brasil, mas quando o percebemos e as reproduzimos, foi óbvia a sua vantagem e função. O termo "asado" na preparação do carmim de goma laca também é, agora, para nós claro que seria um tacho ou pote com asas (pegas); no entanto chegamos a experimentar com carne assada e os seus sucos, seguindo a proposta de "assado" que Devon Strolovitch propõe na sua transliteração.

Claro, conciso e rigoroso, um livro para praticantes da arte agora como no tempo em que foi escrito. Para um praticante um livro belo. Precioso para nós porque na linguagem da química conseguimos comunicar com os nossos antepassados (quase) sem barreiras, produzindo cores belas e duradouras que nos encantam e maravilham. Um livro precioso para partilhar, esperando que o possam apreciar tanto como nós.

Maria João Melo

**Tabela das tintas reproduzidas, com os nomes adaptados das 10 cores elencadas no livro, ouropigmento e vermelhão, azarcão, verde, azul, carmim, brasil, catasol, açafração, alvaiade**

No índice apresentamos as cores com a ordem dos capítulos do "livro das tintas todas". Aqui optamos por as agrupar como nos parece fazer sentido em termos químicos

tinta	produto final	ingredientes*	capítulo§
	vermelhão HgS	Mercúrio, enxofre	15
	azarcão Pb <sub>3</sub> O <sub>4</sub>	Branco de chumbo	10
	ouro musivo SnS <sub>2</sub>	Estanho, enxofre Cloreto de amónio mercúrio	1
	azinhafre Cu(CH <sub>3</sub> COO) <sub>2</sub> .H <sub>2</sub> O	Placa de cobre, vinagre Mel, estrume de animais	11
	nobre azul Cu(CH <sub>3</sub> COO) <sub>2</sub> .H <sub>2</sub> O		5
	carmim de goma laca	Goma laca Urina, cal e cinzas	13
	rosa	Pau brasil, alúmen Urina, branco de chumbo, taça (pia) em gesso ou carbonato de cálcio	8
	roseta	Pau brasil, alúmen Urina, carbonato de cálcio	44
	boa rosa	Pau brasil, alúmen Água de cinzas, carbonato de cálcio	27
	outra rosa	Pau brasil, alúmen Água, cal	9
	catasol		24
	verde iris		45

\*principais na primeira linha

§ a preto receitas disponíveis; a azul, experiências concluídas, em fase de escrita; a rosa, experiências em curso

# Introduction to *The book on how to make all the colour paints for illuminating books*

This book invites readers to step inside the workshop of a fifteenth century illuminator in Portugal. This illuminator, possibly an alchemist as well, was the carrier of a tradition on how to make colours 'which you can illuminate or paint or capitalize or write' that dates back, at least, to the thirteenth century. This unique knowledge and know-how was carefully preserved in Portuguese language in Hebrew characters, in a collection of texts, now known as Ms. Parma 1959. Its ultimate purpose was to possibly assist on the production of Hebrew Bibles, where the precision of the text would have been illuminated by the colours described in this 'book of all colour paints'.

This summary feeds from the research carried out, by a multidisciplinary team, in the project 'The Materials of the Image', and may be assessed in the homonymous book, edited by Luís Afonso as well as in the master thesis by Débora Marques supervised by L. Afonso and also in other publications from these authors (appendix 'Bibliography').

This new critical edition brings to the 21st century laboratory, the science and the technology used to produce the colour paints for medieval illuminations. The experimentation that has allowed us to recapture those 'lost colours' is carried out by students from the master's degree program in Conservation and Restoration as well as by researchers with a formal background in chemistry and conservation science. Our first contact with this book dates back to around 2000, through the edition of Moreira de Sá, but experimentation in the lab started in 2001 with the first of a series of unsuccessful experiments around vermilion production, HgS, as it is described in chapter 15. Which did not discouraged us, since each single failure allowed to understand what had gone wrong, leading us closer to the experience in which, for the first time, we saw the 'ash' transformed into 'fire'. Despite the making of vermilion has been investigated under Catarina Miguel's doctoral thesis, some aspects remain to be clarified, and the efficiency of the process continues to be as mysterious as when we began its experimentation; is it missing a catalyst, obvious at the time, that we may have not yet discovered? We do not know, but in vermilion as in other colours, even in those that seem easy to reproduce, the research we share today is a work in

progress. A work that we wish to share so that it may be criticised and improved by others more knowledgeable, or with different know-how. Here we will focus on the pigments (organic and inorganic based) that are described in the table at the end of this introduction.

If the motivation to discover this precious book was the course in History of Art Technology and Materials (HTPA) from the Master's in Conservation and Restoration, the opportunity to systematise its study was achieved in the project 'A cor da iluminura medieval portuguesa no contexto Europeu: partilha e singularidade', and followed in "Colour in medieval illuminated manuscripts: between beauty and meaning". This investigation was also deepened with two master theses, by Tatiana Vitorino and Rita Araújo on brazilwood lake pigments (the pink colours), as well as with the doctoral thesis of Rita Castro, dedicated to the study of lac dye (the carmine colour). The main authors are anonymous, as was usual in medieval technical texts, and these are the students enrolled in the HTPA course. This does not mean that they are less important, and we foresee that, on the digital platform where the 'book of all colour paints' will be installed, it will be possible for them to more often sign works; as it is the case of the mosaic gold described in chapter 1, which was successfully achieved by Inês Coutinho in her first experiment that dates back to 2006.

Having presented the experimentalists, we may ask what have we learned from the 'book of all colour paints'? Enormously, I would like to write, as it has been a unique resource in our fundamental research. as it has been a unique resource in our fundamental research. Particularly on the reconstruction of the materials and techniques used in the past to create artistic and cultural objects. The paints obtained from this treatise have been systematically compared, at the molecular level, with the ones used in medieval manuscripts in Portuguese collections. In particular, the manuscripts produced in Portuguese monasteries in the 12th and 13th centuries and the French and Flemish Books of Hours from the 14th-15th centuries. This comparison has allowed us to validate the colours and paints obtained, and therefore, to propose them as reference materials to be used in

future research; for example, in the study of the degradation mechanisms taking place in these beautiful medieval paints, for their stabilisation and discovery of new treatments.

In these 15 years of experimentation we conclude that the descriptions of the making of colours and paints are brief and precise, and in many cases, they include additional information on the most critical steps, which can be crucial to the practitioner. Thus, in the making of vermilion, there are two valuable instructions in the time-consuming and essential step of grinding mercury with sulphur: i) we know that the grinding is finished (and that we have obtained the black form of  $\alpha$ -HgS) the moment we see 'the fire turns to ashes'; and, ii) it is advised to 'always stirring it with a dog's foot that has its hair and wool', which allows to capture the much fugacious mercury. Those who have not worked with the 'fugitive' – one of the many names for mercury – cannot imagine the advantage of this information. So, whenever we fail or feel that we are not quite there yet, we believe that it is because we have not yet correctly interpreted the science and technology of the process. Although

it is possible to appreciate the clarity and precision of the instructions, many centuries separate us from the medieval practitioner; there were, and there will be obvious things that were invisibly integrated in their daily lives, which will elude us. We took many years to understand what was a 'piah' of gypsum or chalk, described in the preparation of the brazilwood lake pigments, however when we understood and reproduced it, it became obvious what was its benefit and purpose. It is also now clear for us that the word 'asado' in the preparation of lac dye means a vessel or pot with handles; however, we have come to experiment the 'fried meat' and its juices, by following Devon Strolovitch's transliteration.

Clear, concise and precise, a book for art practitioners, as valuable now as it was then. A beautiful book for a practitioner. A little key to the world of medieval technique as in the language of chemistry we communicate with our medieval ancestors (almost) without barriers, producing beautiful and lasting colours. A precious book to share, hoping you can enjoy it as much as we do.

Maria João Melo

**Table of the paint colours reproduced; names adapted from the 10 colours listed in the book, orpiment and vermilion, red lead, green, blue, lac dye (carmine), brasil (rose colour), catasol, saffron and lead white**

In the index, we present the colours according to the chapters of the 'book of all colour paints'. Here we choose to group them according to their chemical composition.

colour paint	final product	ingredients*	chapter <sup>§</sup>
	vermilion HgS	Mercury, sulphur	15
	red lead Pb <sub>3</sub> O <sub>4</sub>	Lead white	10
	gold (mosaic gold) SnS <sub>2</sub>	tin, sulphur Amonium chloride, mercury	1
	verdigris Cu(CH <sub>3</sub> COO) <sub>2</sub> .H <sub>2</sub> O	Copper foil, vinager Honey, animal manure	11
	fine blue Cu(CH <sub>3</sub> COO) <sub>2</sub> .H <sub>2</sub> O		5
	fine carmine	Lac dye Urine, quicklime and ashes	13
	rose	Brazilwood, alum Urine, lead white, bowl (trough) in gypsum or calcium carbonate	8
	good rose colour	Brazilwood, alum Urine, calcium carbonate	44
	good rose colour	Brazilwood, alum Water ashes, calcium carbonate	27
	Another rose colour	Brazilwood, alum Water, calcium oxide	9
	catasol		24
	green lily		45

the main ingredients are in the first line.

; in black, available recipes; in blue, completed experiments, writing stage; in pink, on-going experiments.

## CHAPTER 1 Making and tempering mosaic gold

*Se quisieres fazer o oro*



Figure 1 Main steps in the reproduction of the process of making mosaic gold.

'First of all take ten ounces of *Jupiter*, that is, tin, clear and pure, and take five ounces of *fugitive*, that is, quicksilver, and first melt the Jupiter and place the fugitive into a mortar. And the melted tin, place it in the mortar with the quicksilver. And mix with it five ounces of sulphur and 2 ounces of sal ammoniac, that is, anoxtar, and let this be well ground and sifted, and that which cannot be sifted, grind it again until it is all sifted, and then put it all together in a well-cleaned basin and then place it in a glass bottle. And cover it with pitch and good strong clay four or five times so that it can withstand the fire, and then put it in a pot full of ashes from the hearth and give it moderate heat until you see the fire becoming red, and then cover the mouth of the bottle with some clay and let [the pan] stand over the fire together with the bottle on a tripod. And from time to time uncover the mouth of the bottle, and when you see that it gives forth no smoke remove the pot along with the bottle from the fire and let [it] stand waiting one more day. And then break the bottle and take out an ingot of fine gold, and grind it very fine when you want to work with it, and temper it with gum-water, and do with it as you wish. And this gold is called *aurum musicum*.' [1,2].

### Reproduction

The first step consists on melting 0.5g of tin in an iron spoon beneath an oil lamp. At the same time, 0.25g of mercury, 0.25g of sulphur and 0.1g of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) are placed in a mortar and well mixed with a pestle. Then, gradually, the mixture of mercury, sulphur and ammonium chloride is added to the melted tin (preferably still under heat) in order to ease the process of grinding (Attention: be cautious for the possible sulphur evaporation due

to high heat; if it starts reacting, take the spoon from the fire). After a short period, the amalgam turns into a black and homogeneous powder.

The black powder is then placed on a glass tube (Schlenk) and heated on a sand bath. The temperature is followed with a thermocouple, and kept between 270–370°C, for 4-5 hours.

The Schlenk tube is linked to a flask containing sulphur powder, to keep all the gases that are getting off during the heating procedure.

### Rationalisation / Chemical reactions

Butler and co-workers examined a Chinese recipe for the production of mosaic gold based on the reaction of tin with alum (ca 300 AD) [3] as well as the medieval European process in 'De Arte Illuminandi' (similar to the one in the 'Book on How to Make Colours'), which they describe as 'the oldest known European account is in an anonymous, untitled manuscript of the 14th century'). A complete mechanism for the formation of mosaic gold is discussed and the role of ammonium chloride disclosed.  $\text{NH}_4\text{Cl}$  is presented as the key ingredient that enables the transformation of  $\text{SnS}$  into  $\text{SnS}_2$ , *i.e.*, the oxidation of tin (+2 to +4 state). This may be viewed as the critical step in the European process for mosaic gold, being the other to obtain it crystalline and glistening; indeed, tin (IV) sulphide, when crystalline (lamellar, flakes, pure hexagonal phase  $\text{SnS}_2$ ), looks very much like gold. The authors also conclude that the amalgam of tin and mercury is not necessary to produce tin (IV) sulphide, in agreement with previous published results [4-6], and also with our experiments. They also tested with other ammonium salts and concluded that 'the only salt that could bring about such reac-

tions is an ammonium salt of a strong acid', ruling out  $\text{NH}_4\text{NCS}$  or  $\text{KCl}$ , which was found to not produce any effect [3]. According to our experiments, the same results have been obtained regarding the use of thiourea (instead of  $\text{NH}_4\text{Cl}$ ), confirming the inefficiency of this compound in the production of mosaic gold from tin and sulphur.

In the medieval recipe, the two main ingredients, Sn and S, are brought into contact within a Hg-Sn amalgam to which sulphur and ammonium chloride are subsequently added and thoroughly mixed by grinding. The mixture is then gently heated (more details on the heating procedure are found below).

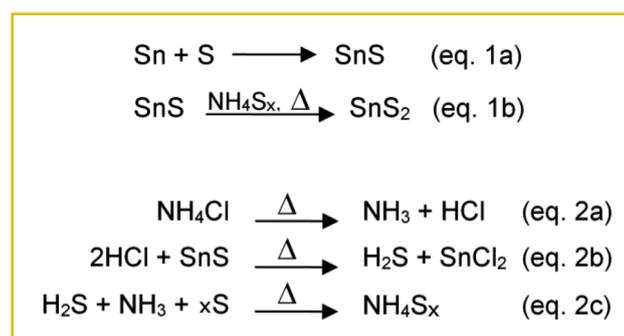


Figure 2 Reaction scheme for mosaic gold synthesis. [3]

As shown in Figure 2, the grinding will lead to the formation of SnS, and the heating to the decomposition of  $\text{NH}_4\text{Cl}$  into  $\text{NH}_3$  plus HCl (eq.2a). The latter will further react with SnS, producing  $\text{H}_2\text{S}$  plus  $\text{SnCl}_2$  (eq. 2b). Brought into contact,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$  and S react, forming ammonium polysulphide ( $\text{NH}_4\text{S}_x$ ), which, finally, will promote the oxidation of SnS to  $\text{SnS}_2$ , mosaic gold (eq. 2c).

The authors do not discuss the evolution of  $\text{SnCl}_2$ , one of the products formed (eq. 2b); it is possible that it will act as a source of tin ions, but this must be further checked.

### Key aspects

**Reaction stoichiometry:** The amount of sulphur and tin given in the recipe is stoichiometric, as for each mole of tin, two moles of sulphur are being used. However, when reproducing the recipe, whenever the temperature was raised more than it should (leading to some loss of sulphur), more sulphur was introduced by grinding it with the reactional mixture.

**Ammonium chloride (salt ammoniac):**  $\text{NH}_4\text{Cl}$ , salt ammoniac, initiates the reaction between sulphur and tin, favouring the production of  $\text{SnS}_2$ , instead of SnS. On another hand, it reduces the loss of tin and sulfur

by sublimation. Moreover, the  $\text{NH}_3$  and HCl gases produced during the heating process seem to protect  $\text{SnS}_2$  [4].

**Temperature and time of reaction:** There are no specific instructions on this. According to Xiao and Zhang, the best reaction yield is in the range of temperature between 250–300°C and a reaction time of *circa* 10h [4].

**Cooling process:** It is important to allow sufficient time for a complete cooling of the mixture; during the cooling to room temperature, the orange yellow colour solid that is obtained during the heating will be transformed into the yellow glistening mosaic gold.

### Missing / Obscure indications

**Tin-mercury amalgam:** The amalgam used in the mosaic gold production almost certainly will increase the contact area between the reactants, an important parameter for improving the rate, and therefore the yield, of a solid state reaction. As it has already been stated, the presence of mercury is not necessary; however, our reproduction evidenced that the presence of mercury turned to be crucial on the grinding process: pure tin is extremely difficult to grind with sulfur and salt ammoniac, but when melted with mercury, the grinding is faster and easier.

### Comments

**heating temperature:** after a few minutes of heating the mixture it is possible to see the sublimation of sulphur. It is important to close the system at once. The temperature must be stable and controlled to allow the fusion of Sn with S (melting points 232°C and 113–119°C, respectively), and according to some authors it should be under 445°C, to avoid sulphur sublimation [4,6].

**modern synthesis:** It is necessary to refer that recent publications described the synthesis of  $\text{SnS}_2$  nanoplates, in a melt of tin dichloride and thiourea in air at 250–280°C for 0–5 h; the products obtained were phase pure hexagonal  $\text{SnS}_2$  nanoplates, of 20–70 nm thickness [5]. The working temperatures will decompose thiourea into ammonium isocyanate, which Butler *et al.* claim was ineffective in transforming SnS into  $\text{SnS}_2$ , when the reactants were tin and sulfur. The authors were also able to synthesize  $\text{SnS}_2$  'on heating the mixture of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and excess S powders in air at 200–240°C or 0–10h' [5]. Products obtained were subsequently washed 'with carbon disulphide, deionized water and ethanol to remove the impurities (e.g., the residual S),

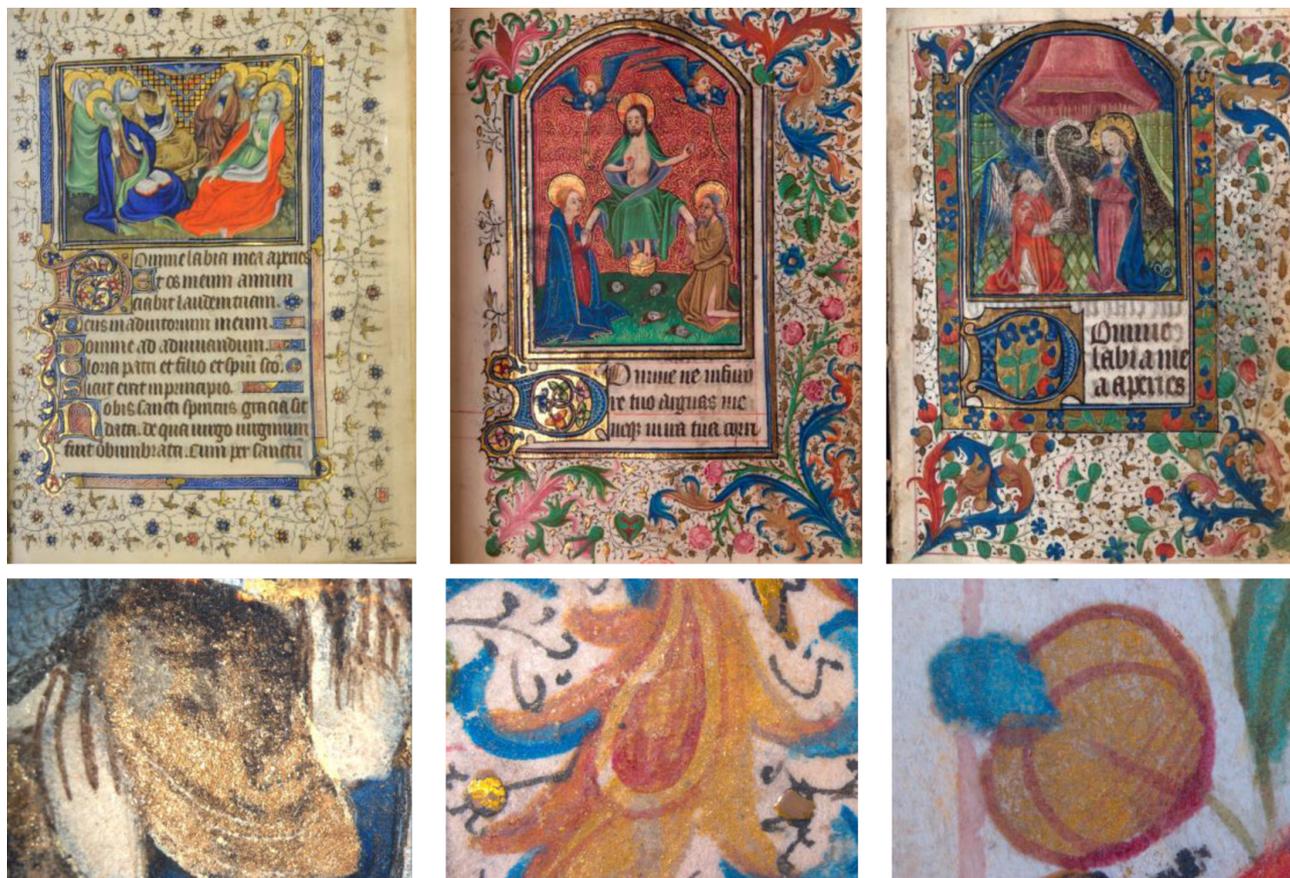


Figure 3 Examples of mosaic gold in Books of Hours. From left to right, Ms. 22, f.74 (PNM); IL.15, f.66 (BNP); IL.21, f.17 (BNP); with details on the bottom row.

dried in air at 80°C, and finally yellow SnS<sub>2</sub> products were obtained'. They offer the following rationale for the efficiency of the novel process: 'the Sn source (SnCl<sub>2</sub>·2H<sub>2</sub>O) we use, it melts (that is, SnCl<sub>2</sub> dissolves in its own crystal water) at temperature above 38°C; (...) the S powder (whose amount is in excess) also becomes molten and participates in the reaction just like a liquid, which certainly increases the interface and contact surface areas between the reactants, and so accelerates the reaction rate'. The same arguments may be applied to the reaction of tin dichloride and thiourea.

**Comparison with the process described in *De Arte Illuminandi*:** Whereas the *BHMC colours* approaches the stoichiometric proportion of Sn:S (1:2), *De Arte Illuminandi* applies Sn in excess (1:1). It seems that this is not the best way for the synthesis since tin is the most expensive reagent and easy to purify.

Most of the instructions are similar, except in the details of the addition of salt or the washing of the amalgam in *De Arte Illuminandi*. They also share identical descriptions on the use of a glass recipient, on the

application of clay, the use of ashes, and the recommendation to use gentle heat. The final product is obtained after breaking the glass recipient, which is described, has an 'ingot of fine gold'. Moreover, they also diverge in the indication of time for the heating. *De Arte Illuminandi* indicates 9h, whereas the *BHMC colours* does not specify any hour. But at the same time, the *BHMC colours* is more detailed in the description on the observation of different smoke colours during the procedure.

#### Mosaic gold in Portuguese medieval illuminations

Mosaic gold has been found in the Galician-Portuguese medieval *Ajuda Songbook*, from the 13th-14th century [7]. We have also identified this pigment in French *Books of Hours* from the 15th century, combined with gold powder (ms. 22, PNM), with lead-tin yellow (ms. 24, PNM) [8], and also pure (IL. 21, BNP). Mosaic gold has been also detected pure in a Flemish *Book of Hours*, IL.15, BNP.

There have been other studies, reporting the use of mosaic gold in substitution of gold, in several Ital-

ian manuscripts dating from the end of the 13th-14th and 15th centuries [9,10] as well as in the German *Göttingen Model Book* from the 15th century [11].

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**Main collaboration:** Inês Coutinho  
**Reviewer:** António Pires de Matos

## Appendix

### Mosaic gold characterisation: synthesised following 'The book on how to make colours'

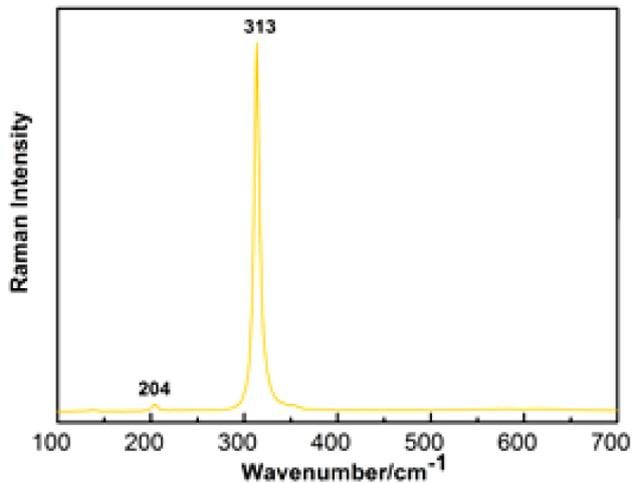


#### Colour

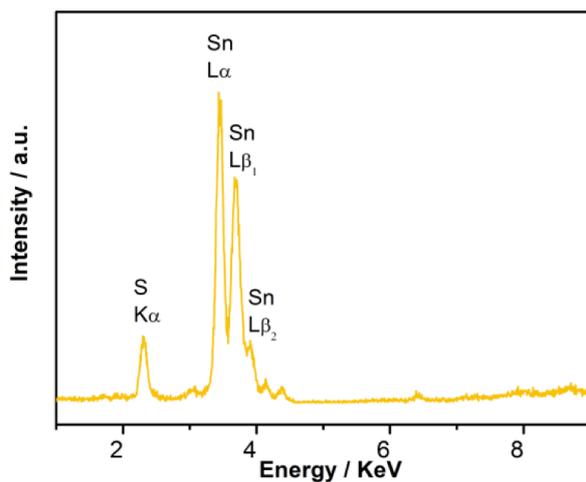
*Table 1* Colour coordinates, Lab\*, for mosaic gold paint reconstructions using two different binders (arabic gum and egg white) applied over filter paper and parchment.

Support	Binder	L	a*	b*
Filter paper	Egg white	60.12	13.54	34.39
	Arabic gum	62.77	13.18	32.01
Parchment	Egg white	59.66	14.59	38.87
	Arabic gum	58.04	14.61	38.41

#### Spectroscopic characterisation



*Raman spectrum acquired with a Labram 300 Jobin Yvon spectrometer. Laser excitation, 632.8 nm; 100x objective ULWD; laser power 1.7mW (characteristic bands at 313 cm<sup>-1</sup> and weaker band at 204 cm<sup>-1</sup>).*



*EDXRF spectrum ArtTAX spectrometer of Intax GmbH, with a molybdenum (Mo) anode, Xflash detector refrigerated by the Peltier effect (Sidrift), with a mobile arm. Experimental parameters: 40 kV of voltage, 300 μA of intensity, for 200 s, under Helium gas flux.*

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

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.

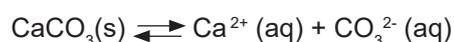
It is described in the literature that in the brazilwood heartwood a yellowish flavonoid is found, named brazilin, which when in contact with oxygen in the air and to light is quickly photo-oxidised and converted into the deep-red flavonoid brazilein [2-5], Figure 2. Thus, brazilein is the main chromophore 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 ( $\text{CO}(\text{NH}_2)_2$ ), 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 ( $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ), a source for aluminium ions ( $\text{Al}^{3+}$ ). 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  $\text{CO}_2$  formation and release, turning the solution to an orange/brown colour, getting redder with time. The  $\text{CO}_2$  release may be explained by the acid-base equation established by  $\text{CO}_3^{2-}$  [2b]:



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

The presence of lead white ( $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ ) 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  $\text{CO}_2$  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.

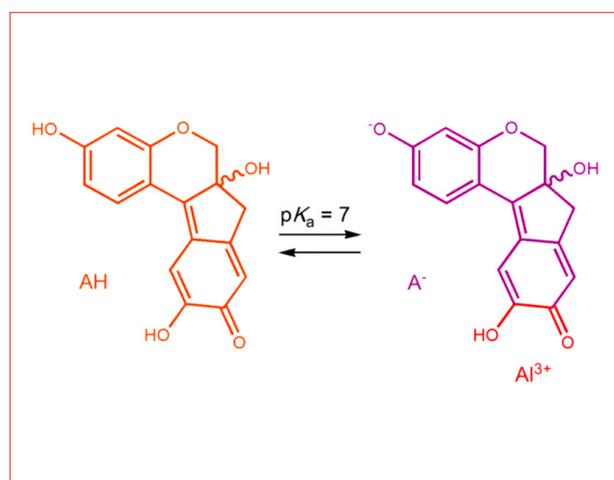
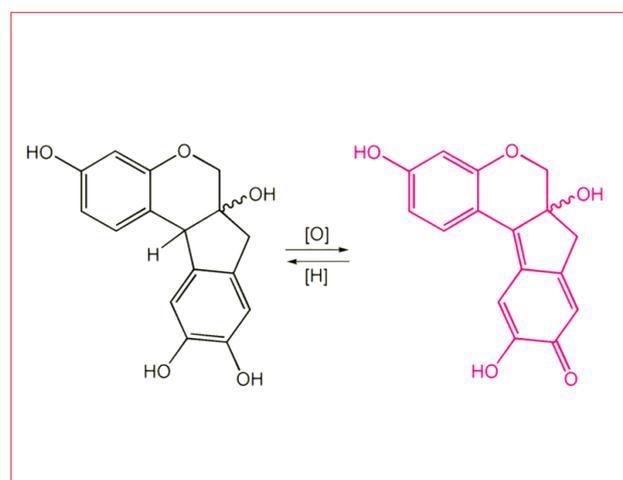


Figure 2 Brazilin (reduced form) and brazilein (oxidised form), left. Acid-base equilibrium for brazilein, right

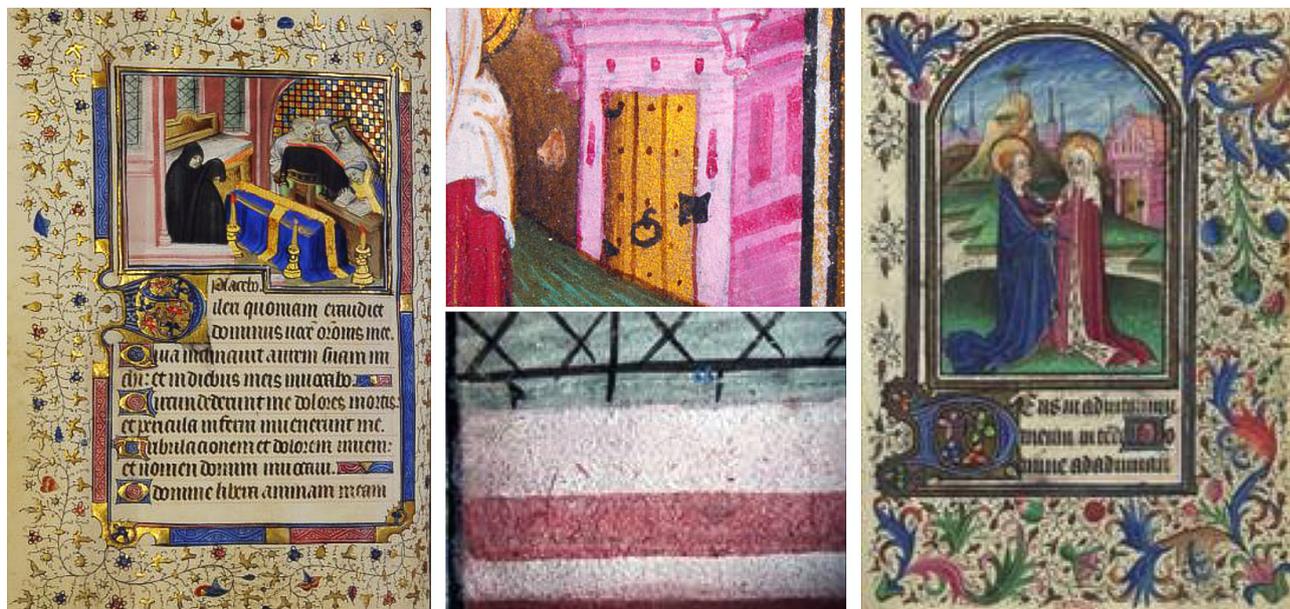


Figure 3 Examples of brazilwood in several Books of Hours. From left to right, Ms.22, f.76 (PNM); IL.15, f.26 (BNP); with their respective details in the middle.

## 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 word *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 feita 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 13<sup>th</sup>-14<sup>th</sup> 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 15<sup>th</sup> 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

16<sup>th</sup> century (ANTT-DGARQ), which was most likely produced in Goa [8].

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- [1] Strolovitch, D. L. 2010. 'O livro de como se fazem as cores 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.
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**Main collaboration:** Tatiana Vitorino

**Reviewer:** Maria João Melo

## Appendix

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

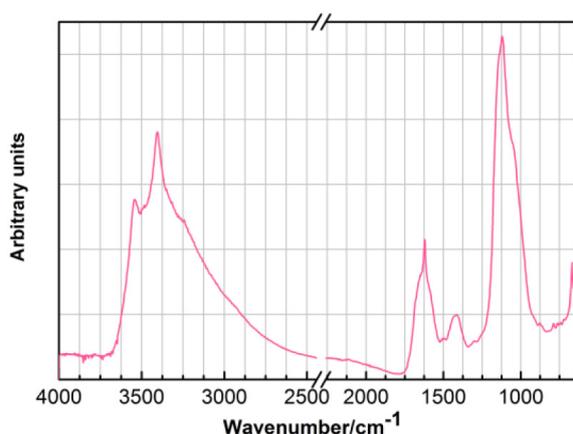


### Colour

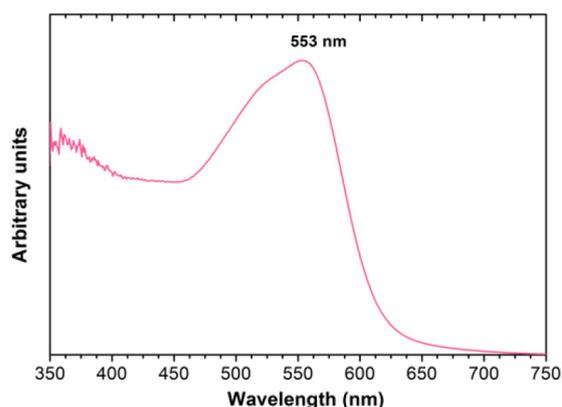
*Table 1* Colour coordinates, Lab\*, for brazilwood paint reconstruction using two different binders (arabic gum and parchment glue) applied over filter paper and parchment.

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

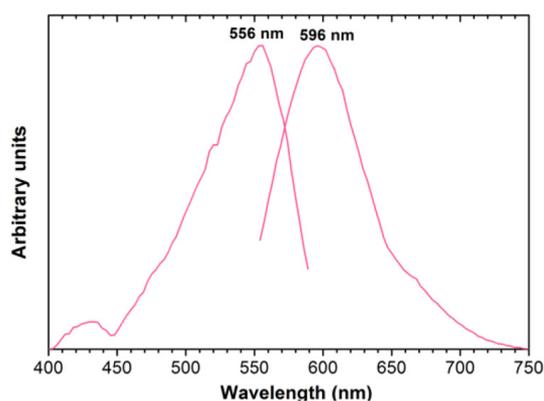
### Spectroscopic characterisation



*Infrared spectrum acquired with a Nicolet Nexus spectrophotometer coupled to a Continuum microscope (15x objective) with a MCT-A detector. Spectra were obtained in transmission mode, with a resolution of 4 cm<sup>-1</sup> 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 hyphenated 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.*

## 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 100°C wood ashes in water until reaching a very basic pH value ( $\approx 11$ ), 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.

1.0g of alum and 0.75g 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,  $(\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O})$ , a source for aluminium ions ( $\text{Al}^{3+}$ ), 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).

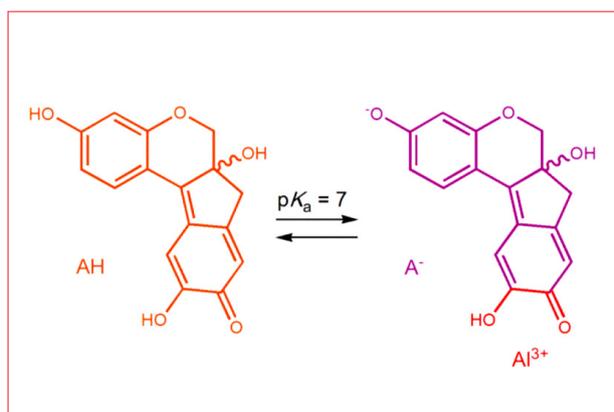
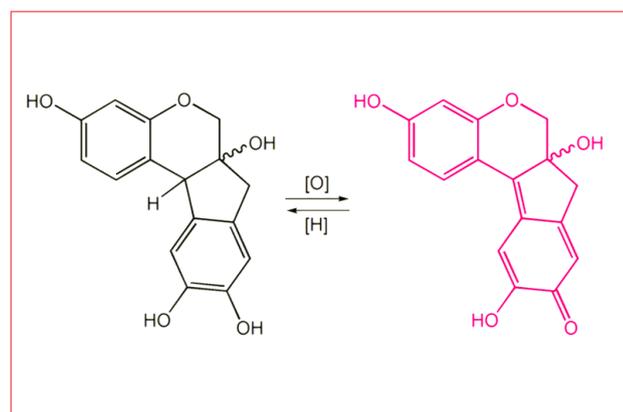


Figure 2 Brazilin (reduced form) and brazilein (oxidised form), left. Acid-base equilibrium for brazilein, right

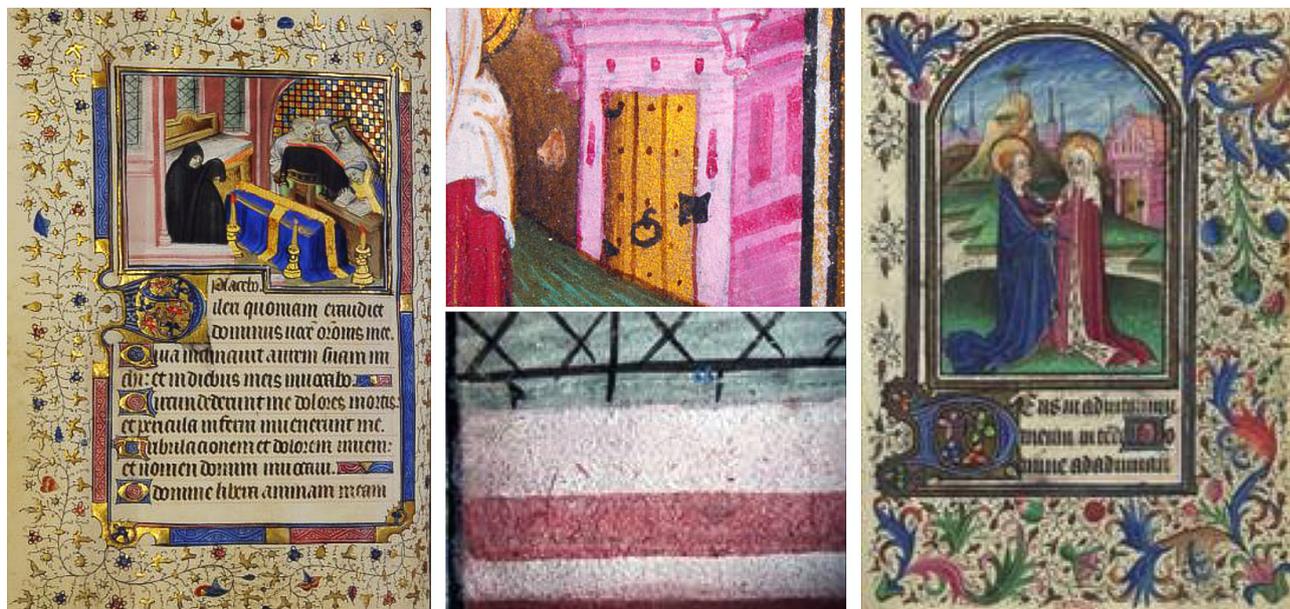


Figure 3 Examples of brazilwood in several Books of Hours. From left to right, Ms.22, f.76 (PNM); IL.15, f.26 (BNP); with their respective details in the middle.

## 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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**Main collaboration:** Tatiana Vitorino

**Reviewer:** Maria João Melo

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

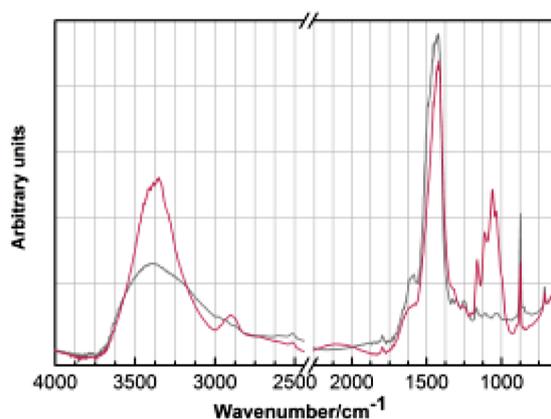


**Colour**

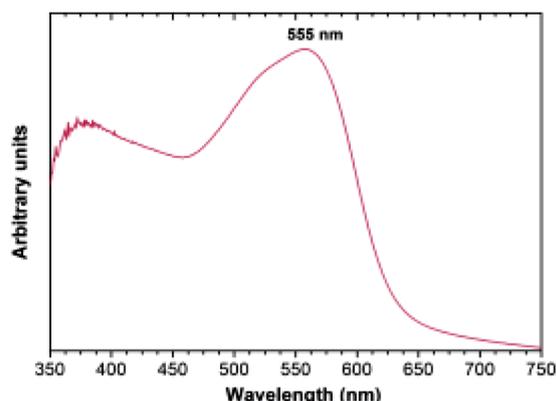
*Table 1 Colour coordinates, Lab\*, for brazilwood paint reconstructions using two different binders (arabic gum and parchment glue) applied over filter paper and parchment.*

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

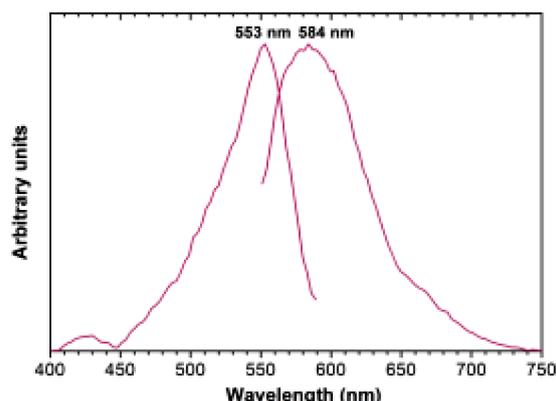
**Spectroscopic characterisation**



*Infrared spectra acquired with a Nicolet Nexus spectrophotometer coupled to a Continuum microscope (15x objective) with a MCT-A detector. Spectra were obtained in transmission mode, with a resolution of 4 cm<sup>-1</sup> 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 hyphenated 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.*

## CHAPTER 10 Making red lead from lead white

*Para fazer mui nobre azarcon*

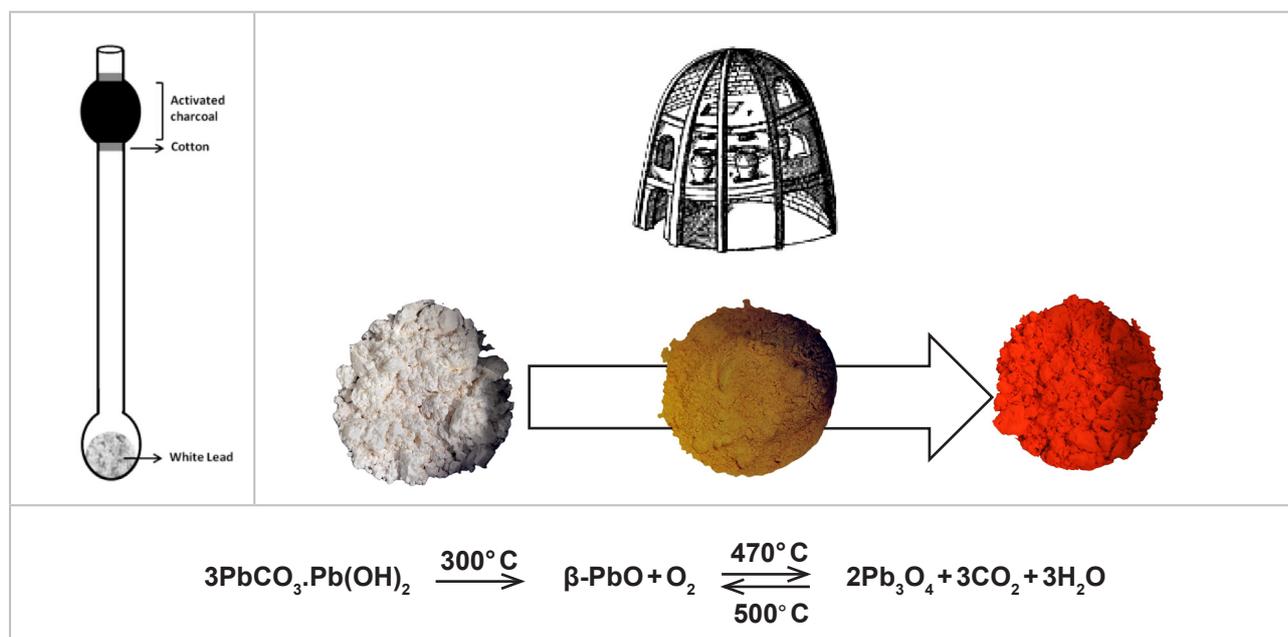


Figure 1 Reaction scheme for red lead synthesis.

‘In order to make very fine red lead, take white lead, as much as you wish, and grind it and sift it, and toss it in a broad bowl or bowls. And take it to a glazed furnace, and leave it stand for twenty-two days. And after these days take it out of the furnace, and you will find very good red lead. In this way you will make as much as you wish.’ [1]

### Reproduction

In a first experiment, 3 g of lead white were placed in a ceramic crucible in a pre-heated furnace at 300°C. The temperature was slowly increased to 475°C.

After 24 hours of heating, the crucible was cooled to room temperature, and the red lead formed was ground.

If we consider the temperatures inside a medieval glass furnace, 700–1100°C, we may conclude that this experimental procedure could not work, because at these high temperatures the reagents and products will volatilize. It is possible that the author meant in contact but outside the furnace and not inside, so we looked for several possibilities in a homemade glazed furnace and selected a place in which temperature was rather constant at around 470°C. An open glass ampoule with two spherical compartments (separated by 9 cm of tube) was specifically

constructed for the purpose. White lead was put in the bottom compartment, whereas activated charcoal placed between cotton layers (to trap released toxic gases) was put on the second compartment. In 1 day lead white was converted into yellow lead, and after 6 days into red lead

### Rationalisation / Chemical reactions

The heating of lead white ( $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ ) produces, on a first stage, the orthorhombic form  $\beta\text{-PbO}$  (designated also as massicot), a pale-yellow compound, unstable above 300°C, Fig. 1 [2-7].

On a second stage, the temperature increases until circa 470°C, and through a combustion process, massicot ( $\beta\text{-PbO}$ ) reacts with atmospheric oxygen to produce red lead ( $\text{Pb}_3\text{O}_4$ ), carbon dioxide and hydrogen [2-7].

However, the process can be reverted if the temperature increases to 500°C, leading to the formation of the massicot, again [2-7].

### Key aspects

**Reaction stoichiometry:** Not relevant.

**Transformation of lead white into red lead** is strongly dependent on the complete conversion of the inter-

mediate massicot,  $\beta$ -PbO produced in the first heating step of lead white and on the temperature control of this chemical equilibrium.

**Temperature of reaction:** based on what is known about medieval glazed furnace, the place where the pot was placed in the furnace takes, indeed, a crucial role in the temperature control of the process and, therefore, in the success of the reproduction. One of the advantages of a glazed furnace is that it is always on (night and day), and there will be many available places in its outside wall with high and stable temperatures; an experimented professional could take big advantages of this existing energy.

### Missing / Obscure indications

**heating temperature:** In medieval times a glass furnace worked from 700/800°C till 1100°C [2]. Since it is only mentioned 'take it to a glazed furnace'; it is not known if it should be placed inside or outside the furnace. Possibly at the time a glassmaker would know where to put it, such as in some shelf in the outside wall of the furnace.

### Comments

**heating temperatures:** From the 1960s to the present, several authors have been proposing different temperatures for the synthesis of red lead, although with minor differences [3-7]. Buxbaum (1998) and Cabral (2001) are the ones that refer the most appropriate temperatures [4,5], according to our experiments.

**location:** Considering the working temperature of a glazed furnace, it is expected that the pot was put in a shelf in the outside wall of the furnace where the temperature could be around 460°C.

**heating time:** it is clear that if the correct temperature for the reaction is reached and maintained constant, the reaction takes place in hours and not days (the recipe refers 'twenty-two days'). However, this would depend on the temperature at which the pot was placed, if lower than 450–470°C than more time would be necessary. The end point could be easily assessed by the colour change. To an experimented professional it would be possible to determine when the final conversion of lead white would have taken place, or at least if a satisfactory colour had been reached. It is not necessary to have a full conversion of lead white into red lead, as the first can act as a filler.

### Red lead in Portuguese medieval illuminations

Red lead is an important colour in 12-13<sup>th</sup> c. Portuguese medieval manuscripts. Red lead was applied as a pure pigment for orange colours or admixed with vermilion to produce reds; calcium carbonate and lead white were added as extenders (as they did not affect the final colour), although the latter could be the result of an incomplete synthesis. In the Lorvão collection, mixtures of vermilion with variable percentages of red lead (from 5% up to 40% wt) were found in the red colours of big size illuminations, from the Apocalypse manuscript (Lorvão 44, ANTT-DGARQ) [8-11].

Red lead was also found in Fernão Vaz Dourado's Atlas, dated from the 16th century, at ANTT-DGARQ [12].

This particular pigment presents some conservation challenges, because of its alteration into the lead sulphide, galena (PbS), which is a black degradation product [10-12]. This phenomenon is evident in the Apocalypse manuscript as well as in the detail from the Fernão Vaz Dourado's Atlas, Figure 2.

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Figure 2 Examples of red lead in Portuguese medieval manuscripts, from left to right: Alcobaça 446, f.96v; Lorvão 15, f.11; Fernão Vaz Dourado's Atlas, f.18; Lorvão 44 Apocalypse, f.86.

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**Main collaboration:**

**Reviewer:** António Pires de Matos

## Appendix

### Red lead characterisation: synthesised following.

'The book on how to make colours'

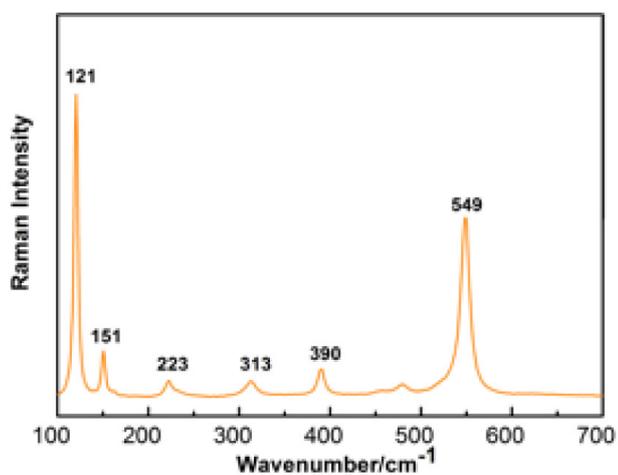


### Colour

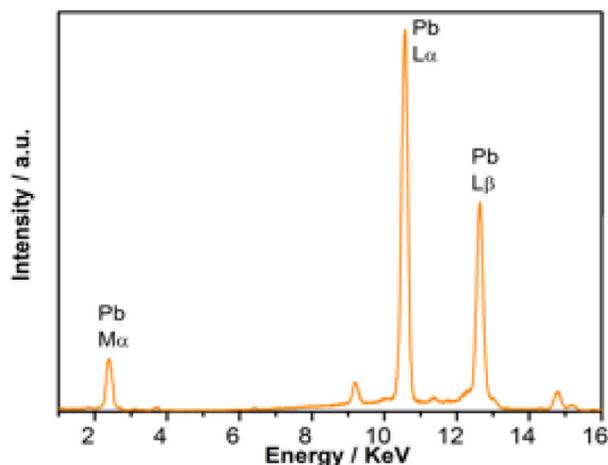
*Table 1* Colour coordinates, Lab\*, for red lead paint reconstructions using two different binders (arabic gum and parchment glue) applied over filter paper and parchment.

Support	Binder	L	a*	b*
Filter paper	Parchment glue	72.25	48.91	63.27
	Arabic gum	72.22	51.07	69.70
Parchment	Parchment glue	71.59	45.72	68.23
	Arabic gum	70.45	47.71	77.31

### Spectroscopic characterisation



*Raman* spectrum acquired with a Labram 300 Jobin Yvon spectrometer. Laser excitation, 632.8nm; 100x objective ULWD; laser power 1.7mW (characteristic bands at 121, 151, 223, 313, 390 and 549  $\text{cm}^{-1}$ ).



*EDXRF* spectrum ArtTAX spectrometer of Intax GmbH, with a molybdenum (Mo) anode, Xflash detector refrigerated by the Peltier effect (Sidrift), with a mobile arm. Experimental parameters: 40 kV of voltage, 300  $\mu\text{A}$  of intensity, for 200 s, under Helium gas flux.

## CHAPTER 11 Making verdigris (from copper)

*Pera fazer azinhafre mui fino*

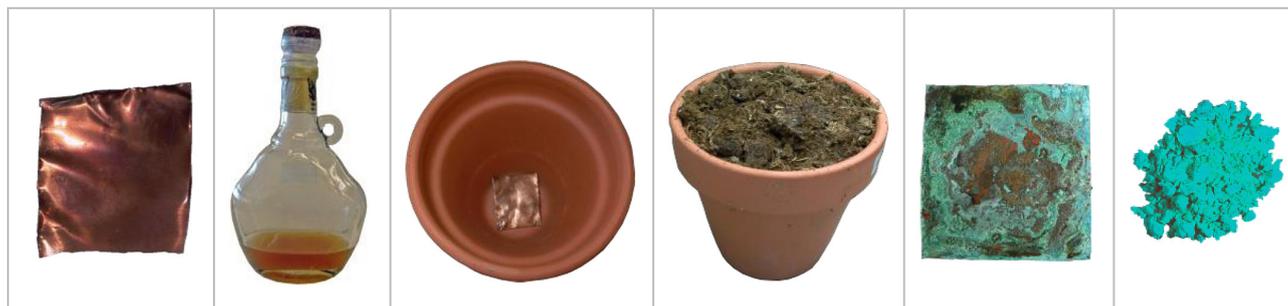


Figure 1 Main steps in the making of verdigris

'In order to make very fine verdigris, take very thin leaves\* of copper and moisten them in very hot and strong vinegar. And put them in a pot leaning on its side, and smear the mouth of the pot with honey and cover it with potsherds, and bury it under the manure of large animals, and let it stand there for thirty-one days. And after these days take the pot out and you will find verdigris, and scrape it with a spatula. And if you want to make more, repeat as directed, and you will have good verdigris.' [1].

*\*in Portuguese Strolovich transliterates as 'toma folhas de cobre muito delgadas e moles'.*

### Reproduction

The surface of a leaf of copper foil was cleaned with sandpaper and immersed in strong, pre-heated at 60–70°C and filtered vinegar, pH ≈ 3, for 10 min.

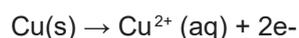
It was then placed inside a pot of clay, sealed (with clay), and the board was coated with honey.

The sealed pot was carefully put inside a larger clay pot, covered with potsherds, and let stand for 31 days buried in horse manure or in sand.

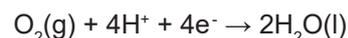
After the 31 days, the pot was carefully opened, and the leaves were found covered with verdigris.

### Rationalisation / Chemical reactions

When copper or copper alloys are exposed to acetic acid solutions (such as vinegar), in a closed vessel, the surface of the metal is corroded, due to the oxidation of copper [2]:



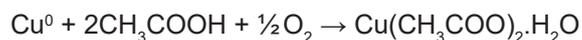
At the same time, in the interface between the metal surface and the acidic solution, the electrons provided by copper oxidation reduce atmospheric oxygen, producing water:



Acetic acid, a weak acid, in solution establishes an acid-base equilibrium:



Therefore, the acetate ions bind to the copper cations, producing insoluble copper acetates.



These copper acetates may differ in their acetate to hydroxide component ratio and degrees of hydration. These variations have impact on the colour, in the sense that they can produce different shades of blue and green [3-7].

In our experimental conditions, only the formation of the neutral copper acetate  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ , was observed.

### Key aspects

**Reaction stoichiometry:** The electrolytic corrosion of the copper leaves occurs in a proportion of one mole of copper per two moles of acetic acid, however we should consider more complex reactions, as discussed above.

**Corrosion of copper leaves:** For the redox reaction of copper it is important to leave the copper foil in contact with air to improve the production of verdigris, as opposed to submerging the copper in the acetic acid solution.

## Missing / Obscure indications

**Amount of vinegar:** The recipe says to 'moisten' the thin leaves of copper foil in 'very hot and strong vinegar'. The moistening suggested in the treatise appears to be insufficient to oxidize the entire surface of the copper foil; it is possible that the information on a vinegar deposit, to be included in the vessel along with the copper, is missing.

**Type of vinegar:** In this recipe the vinegar is described as 'strong', but no other description is given. Strong could mean a high concentration of acetic acid and thus a strong smell and a lower pH. During our experiments, several types were tested, such as commercial white and red vinegars (pH=2.5) and oak-matured homemade vinegars (pH=3). The best results were achieved with a 50-year-old homemade vinegar [3,4].

**Sealing method:** The exposure to high acetic acid concentration in the gas phase is important for the reaction yield. Thus, the sealing of the pot should be very efficient (to concentrate acetic acid in the gas phase), which is not clear on the recipe.

## Comments

**Vinegar** is only introduced for moistening the copper leaves. To improve the reaction yield, vinegar must be available on the bottom of the pot to corrode the copper foil, otherwise only the non-flat areas and the borders and cracks of the copper leaves will accumulate small amounts of vinegar and, therefore, the verdigris will be produced in small restricted areas.

There are other recipes from that period, such as the ones found in treatises like *Mappae Clavicula* or *De diversis artibus*, which suggest the continued exposure of the copper leaves to vinegar vapours. Our experiments suggest that a higher yield is obtained from the continued exposure to vinegar vapours than by moistening or immersion.

**Horse manure:** Animal manure was most likely used to maintain moisture and a certain temperature inside the pot, once its decomposition occurred [8]. This would promote the corrosion of the copper foil. Temperature could be a critical issue in cold climates.

**Honey:** This hygroscopic ingredient may improve the oxidation of the copper foil by increasing the contact area between the metal foil and the acetic acid.

## Verdigris in Portuguese medieval illuminations

Green is an important colour in Portuguese medieval illuminations, particularly a certain deep green named *bottle green* ('verde garrafa' in Portuguese), which is based on synthetic copper proteinate [3,4], Fig. 2. According to some authors [10], copper proteinates may have been formed in the course of time, as a reaction between verdigris and a proteinaceous binder, meaning that this copper proteinate was not intentionally made. In our case studies, considering the consistency of the colour values and the absence of a heterogeneous surface, which could sign the presence of solid state reaction(s), we do not think this to be probable.

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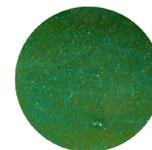
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#### Main collaboration:

Juliana Buse and Catarina Miguel

## Appendix

### Verdigris characterisation: synthesised following 'The book on how to make colours', Chapter 11

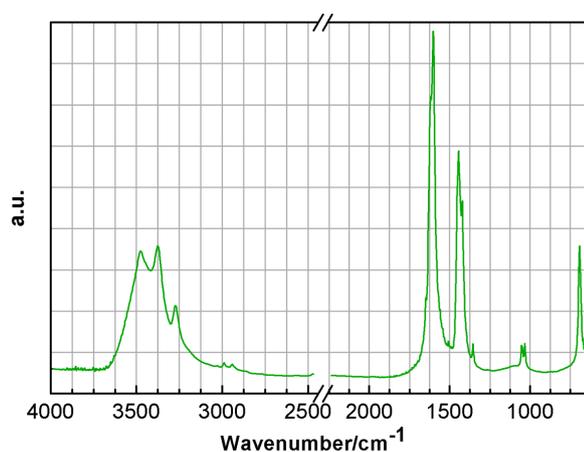


#### Colour

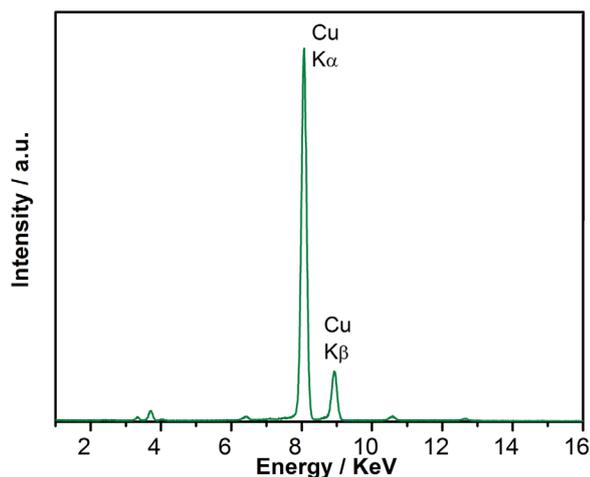
*Table 1* Colour coordinates, Lab\*, for verdigris paint reconstructions using two different binders (arabic gum and parchment glue) applied over filter paper and parchment. Spectroscopic characterisation

Support	Binder	L	a*	b*
Filter paper	Parchment glue	49.10	-64.86	-33.80
	Arabic gum	60.80	-65.28	-33.68
Parchment	Parchment glue	62.40	-20.86	2.06
	Arabic gum	60.80	-20.90	6.42

#### Spectroscopic characterisation



*FTIR spectrum acquired with 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<sup>-1</sup> and 128 scans.*



*EDXRF spectrum ArtTAX spectrometer acquired with an mobile arm with a molybdenum (Mo) anode, Xflash detector refrigerated by the Peltier effect. Experimental parameters: 40 kV of voltage, 300 µA of intensity, for 200 s, under Helium gas flux.*

## CHAPTER 13 Making carmine (lac)

*Para fazeres nobre carmin*



Figure 1 Main steps in the reproduction of the process of making lac.

'In order to make fine carmine, take a large new pot that holds four açumbres of water, and fill it with human urine. And mix it for days, and make it very clear all the while so that it gives off foam. And once it is very clear and skimmed, take a large bowl and place rye-straw over it, and above the straw a linen cloth. And on the cloth place ashes of vine branches, two parts, and a third part quicklime, and place a pot underneath. And throw on the lye the strained urine that you strained through asado [a pot with two handles] and continue straining it until the pot is full of this strained lye, in such a way that there are four açumbres of it there. And place it on the fire until only two fingers of it are left, and on the fire put another pot full of clear urine with the strained lye and heat both. And into the pot of clarified urine with the strained lye toss one pound of lac, and heat it gently, all the while stirring it with a slightly forked stick. And when the lac is melted, strain it with a linen bag, and place a basin underneath; whatever remains in the bag, place it in the pot of strained lye, which you have kept on the fire with gentle heat, until it is melted, stirring with a piece of wood. And then strain it separately with the bag containing the powder. Thus you can make carmine of two kinds, though first you must clarify the urine.' [1,2].

### Reproduction

Take a beaker and fill it with 150 ml of urine and let it stand for several days (pH between 7 and 8). Keep the solution in continuous stirring during a whole day. Remove all the foam and scum formed during that period until it becomes clearer.

Afterwards, the urine is strained in a linen cloth (which can also be substituted by a paper filter) and on top of the filter make a 'bed' of a mixture of quick-

lime and ashes (3 to 5 g, in a 1:2 proportion). Then, the urine is filtered in that bed, at least two times, so that the pH may be above 9. The strained solution is put to stir and heated at around 90°C until it reduces a third of its volume (ca. 50 ml).

During this process, 10g of sticklac are cleaned and finely ground in a mortar with a pestle.

The ground lac is added to the urine solution and left to stir during two hour at 60°C.

After that, the mixture is filtered over a linen cloth into a glass container. The filtered solution is then used to paint.

### Rationalisation / Chemical reactions

Lac is a part of a resinous cocoon secreted by insects on twigs of branches of host trees. The dark red resinous raw material is commonly called sticklac [2,3]. Lac dye, the colouring substance, represents only 10 % of all the resin matter and its main components are laccaic acids A and B; also laccaic acids C, D and E are found in minor quantities [4,5]. When these dyes are removed, the resin gives the well-known shellac, which is a complex mixture of mono- and polyesters of hydroxyl aliphatic and sesquiterpenoid acids [6]. Erythrolaccin, also shown in Fig. 1, contributes to the yellowish orange hue that characterises the resin [5, 6-8].

Laccaic acid A, as the major component in lac dye, is the main responsible for the lac colour (it is also the one that has been most studied over time). This laccaic acid changes its colour from dark pink to dark red, by increasing the pH. According to literature, pKa values for laccaic acid A are 5.6, 7.0 and 9.8 [9,10].

The incorporation of the resin components in the final paint is essential to acquire the glassy appearance seen in Portuguese medieval illuminations (12th-13th c.).

This recipe uses urine as dye extraction solution. Human urine has in its constitution high concentrations of nitrogen (N), from the urea ( $\text{CO}(\text{NH}_2)_2$ ), phosphorous (P), potassium (P), sodium (Na) and chloride (Cl) [11]. The pH values of fresh urine are within the normal physiological range of 5.6 and 6.8 [11,12], which indicates that the extraction solution is not alkaline. However, stale urine may develop higher pH values, due to urea hydrolysis, which may elevate pH values up to 9 [12].

Overall, by adding the quicklime and ashes extracts to the urine, the pH may increase to 9, turning the solution basic. When adding the lac to the extraction solution, the pH decreases to 6-7, making its appearance more reddish than pink.

### Key aspects

**pH control:** There are several factors that will influence the pH along the recipe. Maintaining the extraction solution up to at least neutral conditions is important to guarantee a good lac colour. For instance, using stale urine is imperative to assure a pH ca. 7-8.

**Resin extraction:** It has been observed that heating around 60°C promotes more easily the incorporation of the resin in the final solution (lower than that is more difficult, since it tends only to extract the dye),

as referred in the recipe: 'the lac is melted'. The use of basic extraction solutions (preferably above pH 8) tends to promote better dissolution of the resin. Furthermore, long extraction periods (at least one hour) can also contribute to the dissolution of the shellac constituents.

**Filtration:** The filtration step is also important to assure the neutral to basic extraction. Although the recipe does not give quantities, it refers proportions: 'place ashes of vine branches, two parts, and a third part quicklime' (2:1).

### Missing / Obscure indications

**asado:** This word was only proposed recently by Débora Matos [2], which is associated to a Galician word for a pot with two handles. This type of pot is still found in Portugal, particularly in rural areas. Prior to that, Strolovitch transliterated the Portuguese word 'assado' as 'fried meat' [1]. We believe the recently proposed version is probably more accurate, since we did not find any rational reason for the use of 'fried meat'.

**Rye-straw:** The rye-straw could have been used as a bed just to give additional support to the linen cloth during the filtration.

The other 'pot of strained lye' is normally left out of the recipe, since its purpose is to produce another type of carmine ('make carmine of two kinds'), less concentrated. The instructions suggest putting two equal solutions of urine (previously filtered in the quicklime and ashes bed) in the heat. On the first

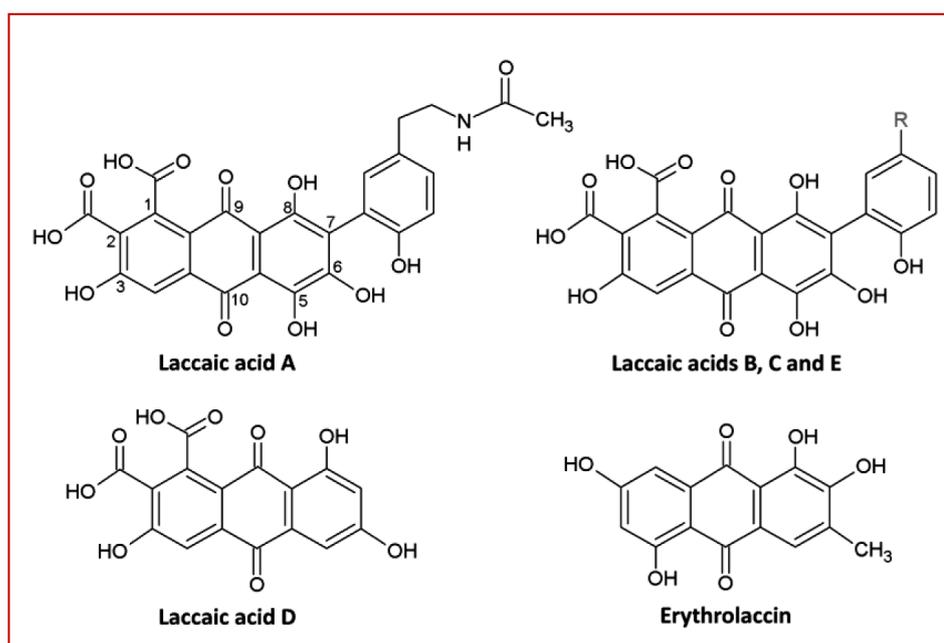


Figure 3 Chemical structures of laccaic acid A, laccaic acids B, C and E (B, R=CH<sub>2</sub>CH<sub>2</sub>OH; C, R=CH<sub>2</sub>CHNH<sub>2</sub>COOH; E, R=CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>), laccaic acid D and erythrolaccin.



Figure 3 Above, De Avibus (Lv.5, f.4) from Lorvão monastery, Legendarium (ALC 419, f.98) from Alcobaca monastery and Hagiographies (20, f.128v) from Santa Cruz monastery; Bellow, several examples of lac paints from the three monasteries.

pot, the lac is added. Then, the second pot, is only used after the other pot with the lac mixture has been filtered. In other words, after straining the first lac solution, the remaining in the bag/filter is added to the second pot ('whatever remains in the bag, place it in the pot of strained lye, which you have kept on the fire with gentle heat') and after melting that second pot is finally filtered. In this manner, new carmine is obtained (with a much less intense colour), as seen in Fig. 4.

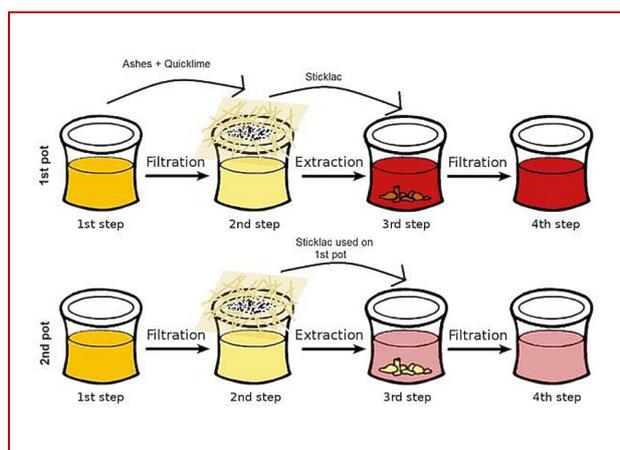


Figure 4 Scheme for the reproduction of the recipe.

## Comments

This recipe allows a satisfactory extraction of the colourant on the first pot; however we still find some dye and most of the resin in the filter at the end. On

the second pot, when using the remains from the first one, the extraction is much less efficient and the final colour is less intense. Therefore, we could be obtaining better yields, but this indication behind the two types of carmine could mean that this was the desired extraction. Whether this was the purpose of this recipe we cannot be certain, but in order to increase the efficiency of the first pot, we could try to increase the pH of the extraction solution (which under the proposed conditions tends to be around 8), increase the temperature (never above 90°C) and leave the sticklac in the solution for a longer period.

The part of the recipe that describes the other pot is actually important since it says from where you should take the lac paint. For a while there was this idea that the final product should be taken from the filter, but by re-utilizing the same bag/filter for another pot/ another carmine suggests that the final product is the filtered solution and not the solid part (which is mostly composed of resin) remained in the linen.

In the infrared analysis the main fingerprint comes from the shellac (the resinous part of the lac) and occasionally, calcium carbonate appears as well as characteristic bands from urea. This confirms at least that the first extraction is effective in extracting a part of the resin.

## Lac dye in Portuguese medieval illuminations

Lac dye has been identified in Portuguese medieval illuminations (12th-13th c.) [13,14]; it was used both

to paint small initials as well as illuminations, displaying in general a good conservation condition.

The dark reds, carmine or pink colours found in the manuscript illuminations were applied as a single colour or as a matiz; the pink colour was admixed with white lead or with white lead and vermilion (found particularly in Alcobaça manuscripts [15]); dark red could be admixed with vermilion (more characteristic in Santa Cruz manuscripts) [16]. All of these paints were applied with a proteinaceous binder, such as parchment glue or egg white [17], which may also have an influence in the glassy appearance. In some samples, the dye is indirectly detected by the shellac resin, particularly by the C-H stretching absorption bands seen in the infrared spectra. The use of chalk or gypsum as fillers was characteristic of Alcobaça, but was also found in some paints from Santa Cruz.

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**Reviewer:** Maria João Melo

## Appendix

Lac dye characterisation: synthesised following  
'The book on how to make colours', Chapter 13

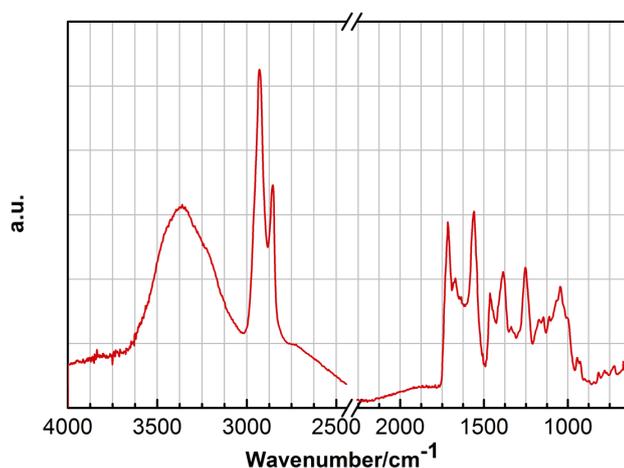


### Colour

*Table 1* Colour coordinates, Lab\*, for lac dye 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	45.66	14.52	4.88
	Arabic gum	42.09	13.97	5.50
Parchment	Parchment glue	26.1	26.7	25.3
	Arabic gum	28.54	13.77	5.74

### Spectroscopic characterisation



*Infrared spectrum acquired with a Nicolet Nexus spectrophotometer coupled to a Continuum microscope with a MCT-A detector. Spectra was obtained in transmission mode, with a resolution of 4 cm<sup>-1</sup> and 128 scans. The dye was previously compressed using a Thermo diamond anvil compression cell.*

## CHAPTER 15 To make vermilion *Para fazeres vermelhom*



Figure 1 Main steps in the making of vermilion.

"To make vermilion, take five pounds of quicksilver, that is mercury, and place it in a bottle or large glazed bowl, and take a pound of very fine virgin sulphur. And pour the powdered sulphur over the quicksilver little by little until it is well incorporated, always stirring it with a dog's foot that has its hair and wool, until the fire turns to ashes. And once the fire has thus died down, place it in two new pots that are made like bottles, broad below and narrow above. And seal them, leaving only a small hole through which the vapor will escape. And place the pots on the fire on their holders and cover them well with clay, and place a bowl over the holes. And when you see the smoke coming out red and not malodorous, place a thin spit in it.

And if anything sticks to the spit, remove the pots from the fire and let it cool. And once it is cool break the pots and you will find the vermilion made. With these measures you will make as much vermilion as you wish: for a *terça* of mercury take five pounds of sulphur, and for five pounds of mercury take one pound of sulphur. And regulate the first in such a way that it does not [10v.] burn, and keep the fire moderate, neither quick nor slow. On this note, if by chance the vermilion burns, break the pots and grind it and incorporate it and mix it with another measure of mercury and sulphur, and place them in other pots and proceed as described. And pay attention to the vapours that escape, thus you will never ruin anything." [1]

### Reproduction

The *olhas* (clay container) were designed, hand-made using white or red clays, and fired as necessary to obtain a ceramic pot. In this reproduction,

we used a white crucible made of two parts: a base where metacinnabar is heated and a cover.

The proportion present in the treatise was followed: 1.047 g of mercury and 0.1674 g of sulphur were weighed and ground in an agate mortar with a pestle.

To improve the incorporation of both compounds, sulphur was slowly added and mixed with mercury, until all were bound and a silver-black-greyish compound was formed. What is observed may be described as in the treatise "until the fire turns to ashes" [1]. This step takes time and patience.

Black mercury sulphide, was then transferred into the base of the clay crucible, which was covered and sealed with fresh clay.

Experiments placing the pot directly into the fire were carried out. When needed, small amounts of water were dropped over the necessary areas to avoid flames or lowering the temperature. For maintaining the embers, combustion air was introduced with the aid of a wooden air blower.

In a successful experiment, after two and a half hours, the pot was taken from the fire and cooled to room temperature. Afterwards, the *olha* was opened and vermilion was found inside its base.

### Rationalisation / Chemical reactions

In the first step, mercury and sulphur are ground to produce metacinnabar, a silver-black compound with a cubic crystal structure, which is the kinetic product of this reaction [2-5], being thermodynamically stable only for high temperatures, above about 370°C. The thermodynamic stable form at room temperature is the hexagonal mercury sulphide (vermilion).

For more details please see [2-11]. In a second step, metacinnabar is heated at 350-370° C, and will rearrange into the hexagonal form that corresponds to the red product, vermillion.

It is important to stress that, for our experimental conditions, the production of red mercury sulphide – vermillion – is a solid-state reaction and not a sublimation process [13, 14]. When sublimation occurs, for temperatures higher than 580° C, a black product, not yet characterized, is formed. This product can be a mixture of meta and hipercinnabar [4].



### Key aspects

**Reaction stoichiometry:** one mole of sulphur reacts with one mole of mercury.

**Mixing mercury with sulphur to produce black mercury sulphide** may be achieved by a thorough grinding, heating or using amalgam. In our reproductions we tested both thorough grinding and amalgam formed by heating sulphur: both worked in the same way, although in the text grinding is described and with very specific details.

**Temperature at which black metacinnabar is converted into red vermillion** is "the crucial" parameter. To transform the black mercury sulphide form ( $\alpha'$ -HgS)

into the red form ( $\alpha$ -HgS), it is necessary to avoid temperatures above about 400-450° C. On the other hand, the higher the temperature the more efficient will be the solid state reaction that enables the conversion of the cubic black form into the red one. To test the influence of temperature control over reaction yield, sand baths were used and temperature was measured over time in the sand. For our experimental conditions, starting with about 0.5 g of black metacinnabar, we found that introducing the pot in the sand bath heat at 285° C for 2h30 and afterwards rising the temperature (heating rate of 15° C/min) until circa 350° C for 2h30 produced the best results.

### Missing / Obscure indications

**Pot design:** There is no precise information about the shape of the *olha*. Strolovitch in his translation refers to it as a vessel "like bottles, broad below and narrow above", [1]. In Spain the term "olla" is currently used to refer to a cooking pot with a lid, traditionally an earthen pot that may be found in many shapes. In this recipe *olha* could stress the fact that the pot was covered.

**Heating temperature and time:** the only information given is "place the pots on the fire" and "keep the fire moderate, neither quick nor slow", [1]. Usually, embers' temperature fall between 620–670° C. We do not know if the pots should be placed directly on the fire neither for how long (a couple of hours? all day?). Where was this fire made? In a special apparatus or just on the ground? How was it maintained and controlled? We infer, from the lack of information, that the experiment time was to be expected more in the 1-2h range than in the 3h-6h.

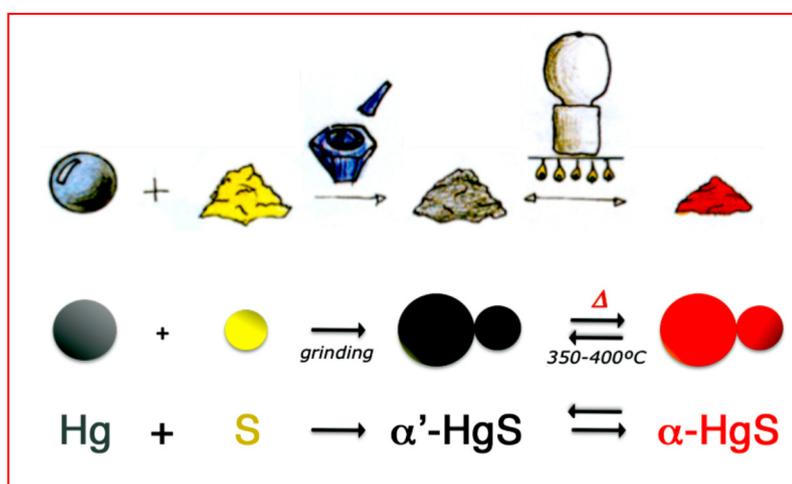


Figure 2 Reaction scheme for vermillion synthesis.



Figure 3 Examples of vermilion on Portuguese medieval illuminations. From left to right: Santa Cruz 20, f.137v: the red is pure vermilion paints and the dark red is a mixture of vermilion with lac dye; Alcobaça 419, f.91v: pure vermilion paint; De Avibus (Lorvão 5), f.25: the vermilion is admixed with the extender calcium carbonate; and Lorvão Apocalypse, f.210: vermilion with red lead.

**Heating time and red smoke:** The information present in the treatise says “and when you see the red smoke coming out red and not malodorous, place a spit in it. If anything sticks to the spit, remove the pots from the fire and let them cool” [1]. However, no red smoke was observed in any of the many experiments conducted. The only smoke observed was black, probably the result of metacinnabar sublimation.

#### Comments

**heating temperature:** The reference of “red smoke” as a signal for the complete transformation of metacinnabar into cinnabar, prompt us to considerer that a sublimation process could be present. In fact this smoke colour was never observed. The only "smoke" we observed was black, and an indication of the formation of a black product due to overheating.

**heating time:** Although there is no specific information about the heating time, it is clear that this reaction takes hours and not days.

**pot design:** The olha's base thickness is essential on allowing a controlled heating rate and on maintaining a constant temperature inside the olha, undoubtedly the two determinant parameters of this recipe.

**the dog's foot:** "always stirring it with a dog's foot that has its hair and wool until the fire turns to ashes" is possibly one of the most precise instruction found in a medieval treatise. Those who have tried to mix sulphur with mercury know how "fugitivas" the small drops of mercury may turn to be. The use of a fluffy surface could help in capturing Hg, facilitating the grinding and reaction of big amounts of Hg and S, as those described in the text. Also, the description "until the fire turns to ashes" conveying a beautiful im-

age it depicts accurately what is observed; indeed, during the grinding, the yellow sulphur and the bright mercury are transformed into a greyish colour that may be described as "ash colour".

#### Vermilion in Portuguese medieval illuminations

Vermilion red is an important colour in Portuguese Medieval manuscripts; it was used both to paint the rubricae and in the illuminations, displaying a very good conservation condition. Vermilion as a proteinaceous paint was applied as a pure pigment or mixed with red lead or/and calcium carbonate and white lead. The later compounds were added as extenders as they did not affect the final colour. In the Lorvão collection, we found pure vermilion in the lettering and mixtures of vermilion with variable percentages of red lead (from 5% up to 40% wt) or other additives in big size illuminations. To produce dark reds, it was mixed with lac dye, as found in Santa Cruz 20.

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**Main collaboration:** Catarina Miguel.

**Reviewer:** Maria João Melo

## Appendix

Vermilion characterisation: synthesised following  
"The book on how to make colours", chapter 15

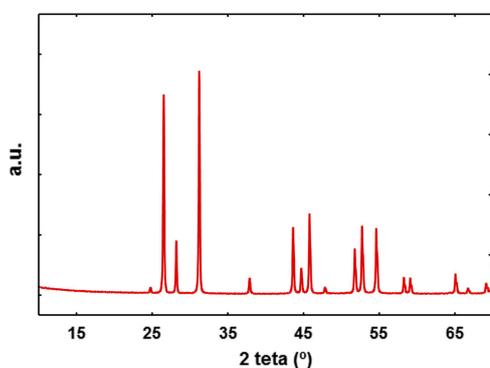


### Colour

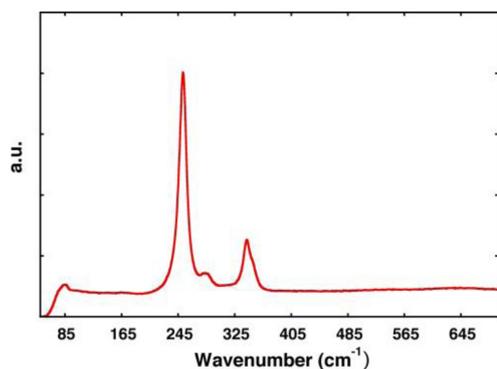
*Table 1* Colour coordinates, Lab\*, for vermilion paint reconstructions using two different binders (arabic gum and parchment glue) applied over filter paper and parchment.

Support	Binder	L	a*	b*
Filter paper	Parchment glue	49.72	36.97	19.96
	Arabic gum	49.64	38.30	22.68
Parchment	Parchment glue	46.64	36.18	26.30
	Arabic gum	46.56	37.24	27.77

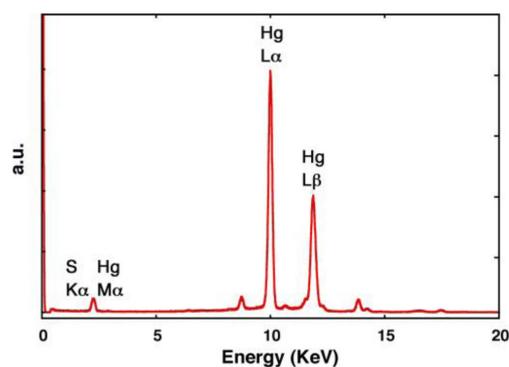
### Spectroscopic characterisation



*XRD diffractogram* acquired with a Philips X'Pert diffractometer using monochromatised CuK $\alpha$  radiation in the 10° < 2 $\theta$  < 70° range with a step width of 0.03° and a constant counting time of 1s per step.



*Raman spectrum* acquired with a Labram 300 Jobin Yvon spectrometer. Laser excitation, 632.8nm; 100x objective ULWD; laser power 1.7mW (characteristic bands at 253, 285 and 343 cm $^{-1}$ )



*EDXRF spectrum* ArtTAX spectrometer of Intax GmbH, with a molybdenum (Mo) anode and Xflash detector. Experimental parameters: 40 kV of voltage, 300  $\mu$ A of intensity, for 200 s, under Helium gas flux.

## 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 egg-white, 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 100ml 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 2.0g 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 photo-oxidised 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 ( $\text{CO}(\text{NH}_2)_2$ ), 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 ( $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ), a source for aluminium ions ( $\text{Al}^{3+}$ ). 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, 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  $\text{CO}_2$  release. This  $\text{CO}_2$  release may be explained by the acid-base equation established by  $\text{CO}_3^{2-}$  (see further ahead) [2b]. The solution turned to an orange/brown colour, getting redder with time.

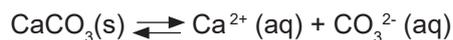
After the three days, the extracting solution with urine and alum presented a pH around 4.5. Urine (pH 7) proved to be ineffective at keeping a neutral pH of extraction.

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.  $\text{CO}_2$

release and chalk's buffering effect may be explained by the acid-base equation established by  $\text{CO}_3^{2-}$  [2b]:



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  $\text{CO}_3^{2-}$  in the form of  $\text{CO}_2$  and the simultaneous presence of  $\text{SO}_4^{2-}$  ions from alum and  $\text{Ca}^{2+}$  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).

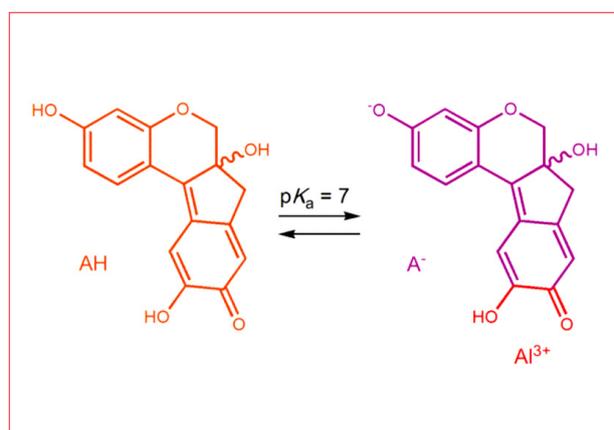
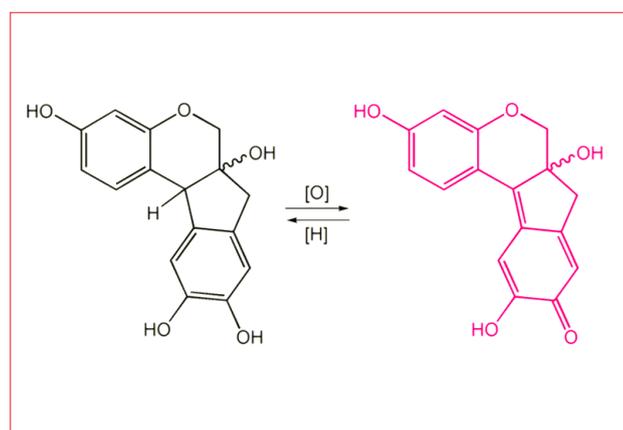


Figure 2 Brazilin (reduced form) and brazilein (oxidised form) left. Acid-base equilibrium for brazilein, right.

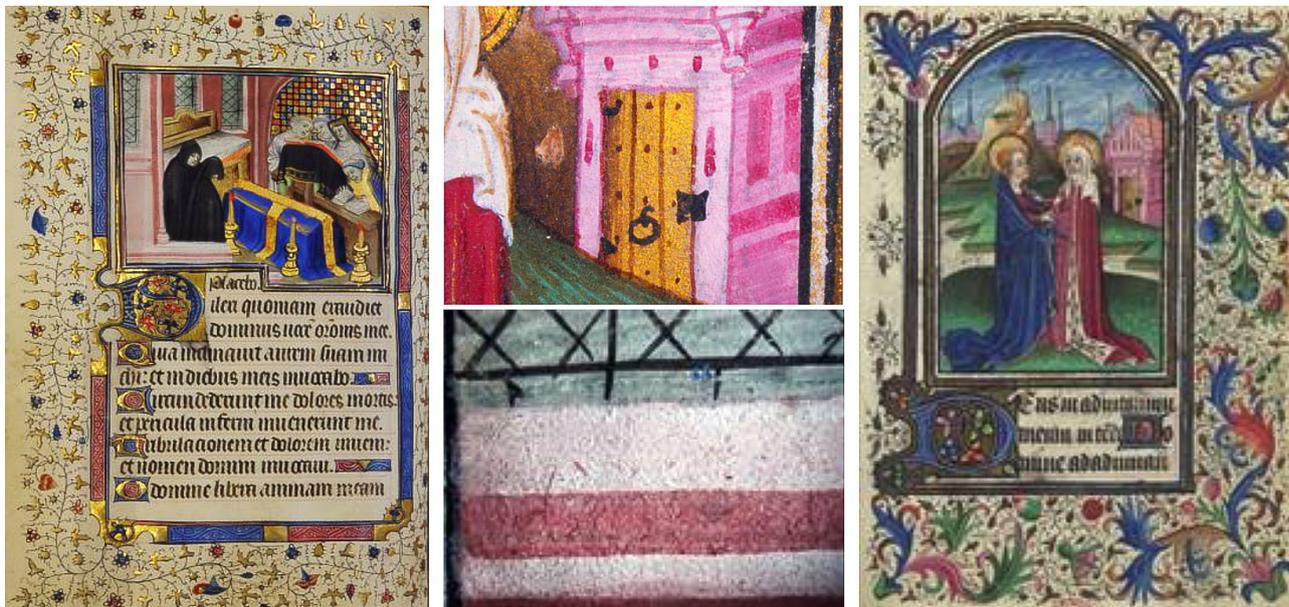


Figure 3 Examples of brazilwood in several Books of Hours. From left to right, Ms.22, f.76 (PNM); IL.15, f.26 (BNP); with their respective details in the middle.

**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 pig-

ment. 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 13<sup>th</sup>–14<sup>th</sup> 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 15<sup>th</sup> 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 16<sup>th</sup> century (ANTT-DGARQ), which was most likely produced in Goa [7].

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**Main collaboration:** Tatiana Vitorino

**Reviewer:** Maria João Melo

## Appendix

**Brazilwood lake pigment characterisation: synthesised following 'The book on how to make colours', chapter 27.**

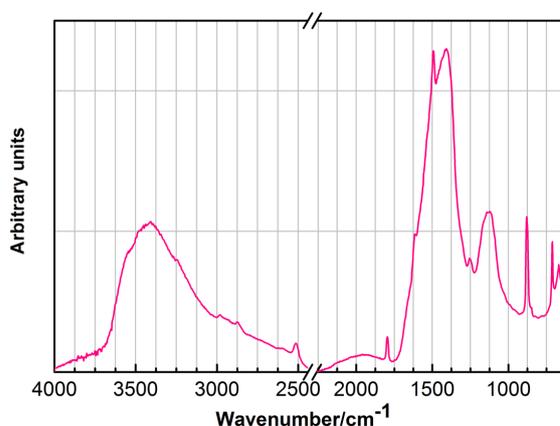


### Colour

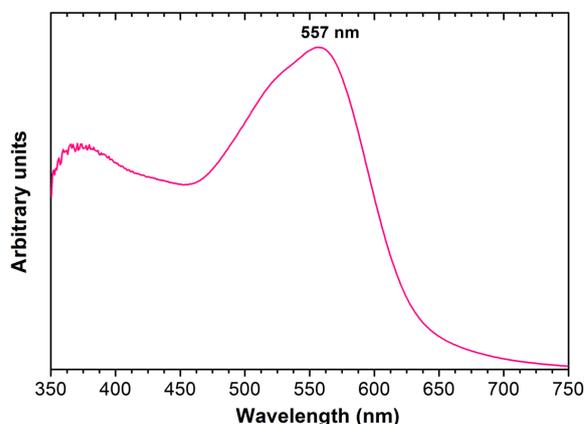
*Table 1 Colour coordinates, Lab\*, for brazilwood paint reconstructions using two different binders (arabic gum and parchment glue) applied over filter paper and parchment.*

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

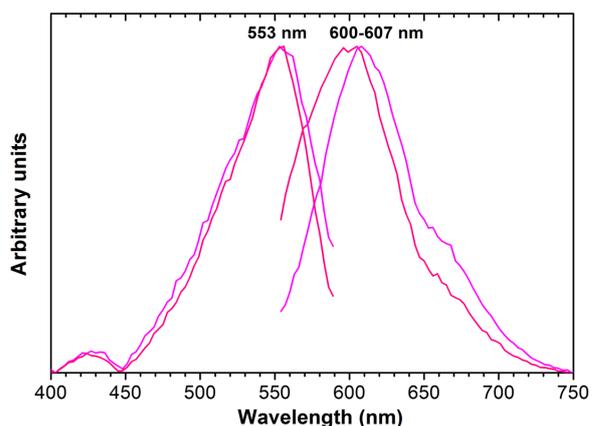
### Spectroscopic characterisation



**Infrared** spectrum acquired with a Nicolet Nexus spectrophotometer coupled to a Continuum microscope with a MCT-A detector. Spectra were obtained in transmission mode, with a resolution of 4 cm<sup>-1</sup> 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 hyphenated 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 μm spot (50x objective) with the following slits set: emission = 3 / 3 / 3 mm; excitation = 5 / 3 / 0.8 mm.

## CHAPTER 40 Making glue from parchment

*Se quixeres fazer cola*



Figure 1 Main steps in the making of parchment glue.

'If you wish to make glue, take two pieces of parchment and wash them very well, and then place them in a new [old] pot, and heat them vigorously until they are well boiled. And once the first water has disappeared, add more water into it, and as soon as you wish to try [it], take a little of it and place it in your palm. And place one hand with the other, and if your hands grip, it must be that your glue is well made.' [1].

### Reproduction

A 9x9 cm square of parchment are washed with water. Afterwards, it is cut into small pieces (0.5 x 0.5 cm).

The small pieces of parchment are then placed on a beaker, covered with water (c.a. 50 ml), and heated at ca. 80°C. For this, the beaker is covered and coated with aluminium foil to promote a homogeneous heating.

After the water begins to boil, the glass container is uncovered to allow evaporation of the water and then more water is added, as suggested in the recipe, to optimise the collagen extraction. Once again it is covered and after boiling, uncovered to concentrate the glue. At this point, the glue consistency is tested as described in the recipe by emerging a stainless steel spatula in the solution and then touching the surface with the fingers to see if it grips. To finish, the pieces of parchment are removed and parchment glue is decanted into a glass container. The glue should be kept at lower temperatures (*i.e.* in a refrigerator). And whenever needed, it should be gently heated (40-50°C) so that it will become liquid again and ready to use as a binder media.

### Rationalisation / Chemical reactions

Parchment is made from animal skins, mainly from calf, sheep or goat [2]. Collagen is the main fibrous protein in the dermis of the animal skin. When partially hydrolysed, it gives gelatine and the adhesive quality to the skin glue [3].

Three-protein chains that are helically wind to each other, in a triple helix, compose collagen. These chains are made by repeated units of amino acids that are strongly linked between them by hydrogen bridges. These structures provide stability and rigidity to the matrix, like a rope; juxtaposed, they form microfibrils, that group into one fibril. These, in turn, gather into bundles or lamellae generating collagen fibres. Thus, the fibres are organised in a two-dimensional network, randomly oriented, which confer tensile strength in all directions. It is through this complex network of microfibrils, fibrils and collagen fibres of the skin matrix that the parchment is sustained [3-7].

However, when heated, these chains start to unfold as consequence of the collagen denaturation; chain scission is also promoted by heating. The shorter chain proteins, after cooling, begin re-linking between them, forming new hydrogen bridges that will compose a new two-dimensional composition, amorphous – the gelatine – with the ability to be well dispersed in aqueous solutions [3-4, 7].

### Key aspects

**Heating temperature** usually temperatures around 70-80°C are adequate to extract collagen from parchment. To promote chain scission and gelatine formation, the water boiling temperature worked well in our reproductions.

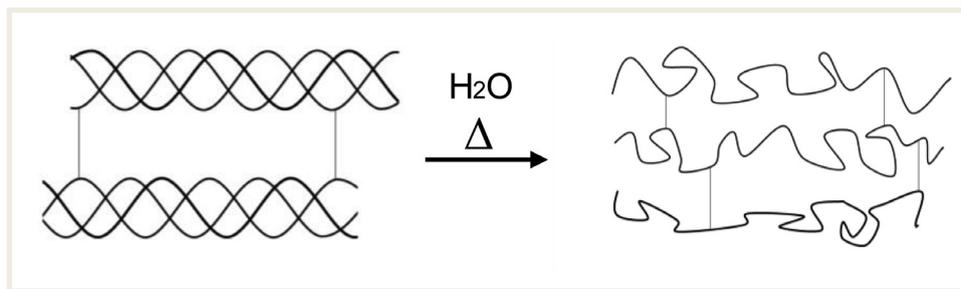


Figure 2 Reaction scheme for collagen denaturation.

### Missing / Obscure indications

The point at which the heating can be stopped is not evident on the recipe (it only refers to keep it until 'your hands grip'). However, this is an important information since this provides a direct control on the production of a 'strong glue', meaning a well-concentrated collagen-based glue.

### Comments

This recipe can be also found in Cennino Cennini's treatise. There are no major differences between them, although in *Il libro dell'arte* the descriptions are more detailed, such as, in leaving the parchment soaking a whole day, after boiling; reducing the boiling water up to 1/3 or using the glue for 'gessoing panels or ancones' [8].

### Parchment glue in Portuguese medieval illuminations

Our research has found that the main binder used in Portuguese illuminated manuscripts was a proteinaceous one. This includes parchment glue and/or egg white, which have very similar fingerprints in the infrared analysis [9].

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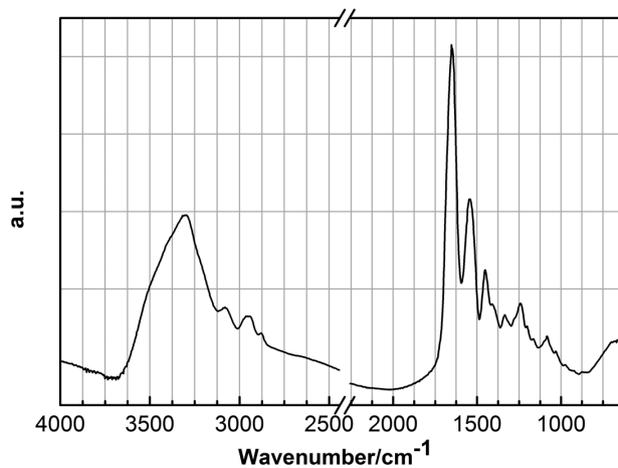
D. Strolovitch. 2005. *Old Portuguese in Hebrew script: convention, contact, and convivência*, 116-184. PhD Dissertation, Cornell University.

**Main collaboration:** Rita Castro and Catarina Miguel

## Appendix

Parchment glue characterisation: synthesised following 'The book on how to make colours', chapter 40.

### 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<sup>-1</sup> and 128 scans. The dry binder was previously compressed using a Thermo diamond anvil compression cell.*

## 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

5.0g 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.

0.5g 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,  $(\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O})$ , a source for aluminium ions ( $\text{Al}^{3+}$ ), 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 13<sup>th</sup>-14<sup>th</sup> century. It was admixed with lead white for lighter tones, and shaded with a proteinaceous binder [6].

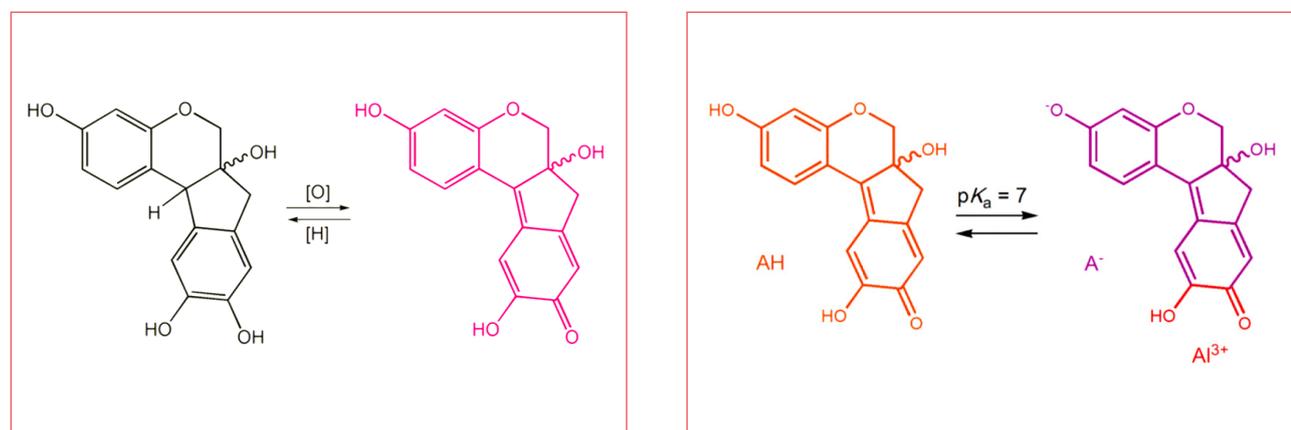


Figure 2 Brazilin (reduced form) and brazilein (oxidised form) left. Acid-base equilibrium for brazilein, right.

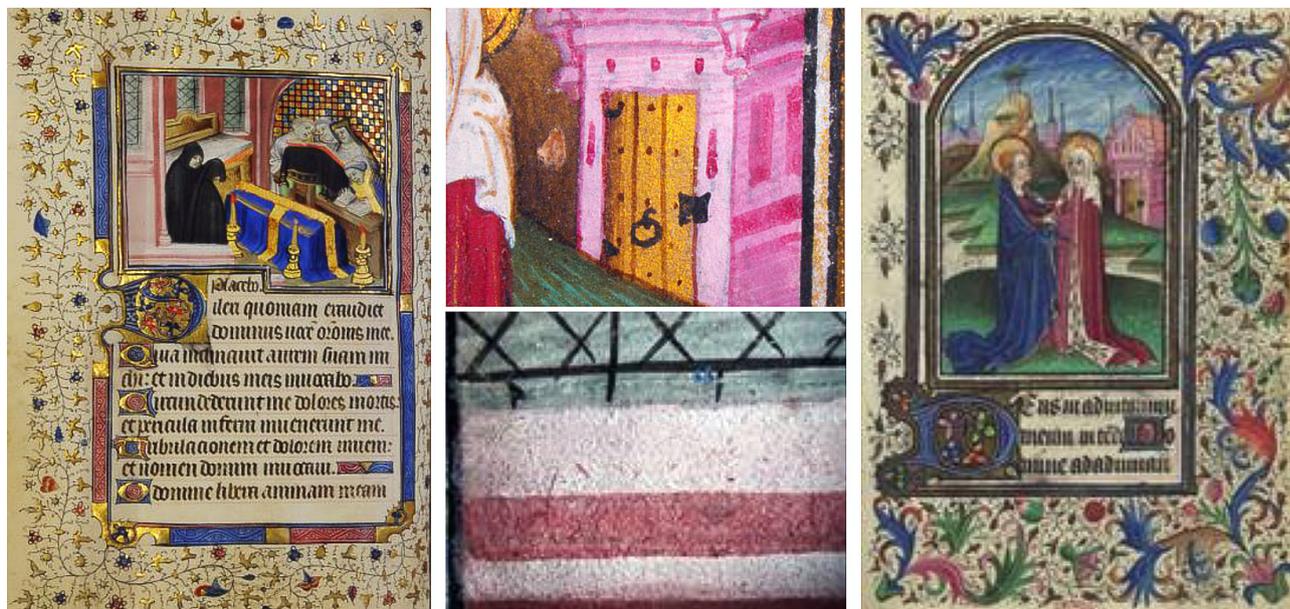


Figure 3 Examples of brazilwood in several Books of Hours. From left to right, Ms. 22, f. 76 (PNM); IL. 15, f. 26 (BNP); with their respective details in the middle.

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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**Reviewer:** Maria João Melo

## Appendix

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

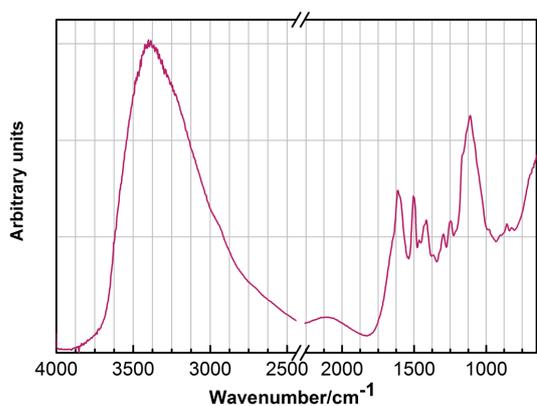


### Colour

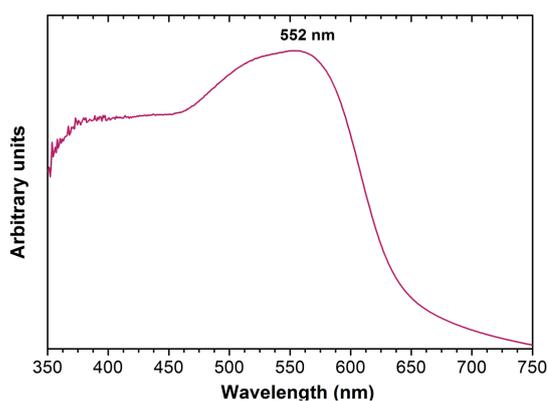
*Table 1* Colour coordinates, Lab\*, for brazilwood paint reconstructions using two different binders (arabic gum and parchment glue) applied over filter paper and parchment.

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

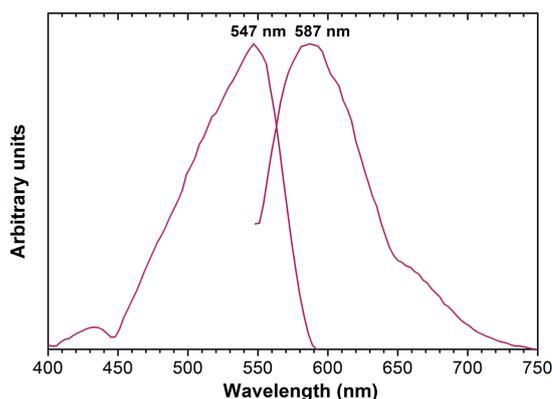
### Spectroscopic characterisation



*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<sup>-1</sup> 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 hyphenated 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.

## Appendix 1

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## Appendix 2

### Conversion table for weights and measures

<b>Unit</b>	<b>Equivalent to</b>
1 açumbre	≈ 2 litres
1 ounce	28.35 g
parts (half, two, etc)	both weight and volume were tested
1 pennyweight	1.55 g
1 pound	453,59 g
<i>terça</i>	one third

## Editorial information (ficha técnica)

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<b>Photographs of manuscript illuminations</b>	Ana Lemos, Catarina Miguel, Rita Araújo, Rita Castro
<b>Graphic Design</b>	Nuno Gonçalves
<b>Acknowledgments</b>	Mark Clarke Pedro Redol Nabil Ali Isabella Whitworth Jo Kirby Maria Adelaide Miranda Rita Araújo Luís U. Afonso Débora Matos Ana Lemos

This critical edition was financially supported by FCT-MCTES within the framework of the projects POCI/EAT/33782/2000, PTDC/EAT/65445/2006 and PTDC/EAT-EAT/104930/2008; and from the Associated Laboratory for Sustainable Chemistry—Clean Processes and Technologies—LAQV, which is financed by national funds from FCT/MEC (UID/QUI/50006/2015) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER-007265).